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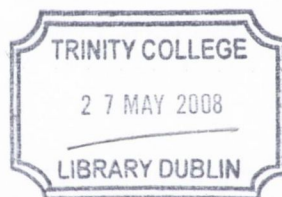
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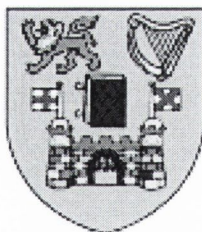


**The Frequency and Field Dependence of Magnetic Colloidal
Suspensions.**

**by
Colm mac Oireachtaigh**

**A thesis submitted for the degree of
Doctor of Philosophy**

November 2007



**Department of Electronics and Electrical Engineering
University of Dublin-Trinity College**

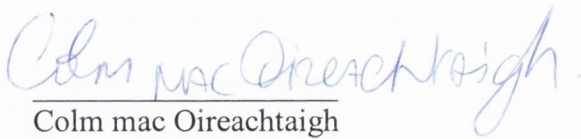
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Summary

This thesis is a study of the dynamic magnetisation of various magnetic fluids, commonly known as ferrofluids. The fluids contain either magnetic nanoparticles, or magnetic microspheres. The method used to study the magnetization is the frequency and field dependent complex susceptibility, $\chi(\omega, H)$. Experimental data of $\chi(\omega, H)$ is obtained using impedance measurement techniques. The slit toroid technique is used for measurement at frequencies below 10 MHz, whilst the transmission line technique is used for measuring at frequencies in excess of this. The impedance measurements are made by using a suitable impedance or network analyser, and are then inserted into a computer program which evaluates the susceptibility.

As predicted by theory, the experimental results reveal the presence of relaxation and resonance processes within the ferrofluids, whereby the magnetic moments rotate into, or precess about, the field direction. They may also switch direction within the particle itself. The effects on the fluids, of cyclic strong polarising fields are revealed to be negligible and the fluids are deemed to be isotropic, i.e. their susceptibility is independent of the direction of the applied polarising field.

The Néel relaxation of nanoparticles, and the chaining of microspheres is believed to be responsible for the observed increase in the $\chi''(\omega, H)$ and $\chi'(\omega, H)$ respectively, of a suspension of magnetic microspheres containing maghemite nanoparticles. These results do not concur with the accepted theory for the field dependence of magnetic fluids.

The equations proposed by Dejardin are shown (i) to be suitable for describing the nonlinear susceptibility of a ferrofluid under the influence of a strong alternating magnetic field and (ii) to be suitable for describing the losses induced by the nonlinear magnetization in the ferrofluid.

At high frequencies in excess of 10 MHz, the relevant theory is used to perform fits to the susceptibility data, allowing important material parameters to be easily evaluated. The inaccuracies of the short circuited transmission line technique are highlighted and it is demonstrated how improved results may be obtained by means of combining data obtained from open and short circuited measurements.

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Dublin, November 2007

Colm mac Oireachtaigh

To my Mother, Father, and family.

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List of Symbols

A	area of a current loop, m^2 first bimodal particle fraction
A_c	coaxial line parameter
a	acceleration, ms^{-2}
a_n	polynomial coefficients
B	magnetic flux density, T second bimodal particle fraction
C	capacitance, F capacitance per unit length, F
C_{sample}	capacitance of sample, F
D	diffusion coefficient, Hz
d	cell depth, sample depth, mm
E	electric field, Vm^{-1}
E_0	magnitude of electric field E , Vm^{-1}
e	magnitude of charge on an electron, C
F	Force, N
f	frequency, Hz
f_{max}	frequency at which maximum value of χ'' occurs, Hz
f_{min}	frequency at which minimum value of $\Delta\chi''$ occurs, Hz
f_{max1}	f_{max} of first bimodal particle fraction, Hz
f_{max2}	f_{max} of second bimodal particle fraction, Hz
f_{maxA}	f_{max} of first bimodal particle fraction, Hz
f_{maxB}	f_{max} of second bimodal particle fraction, Hz
f_{res}	resonance frequency, Hz
g	Landé splitting factor
H	magnetic field, Am^{-1}
H_0	magnitude of the magnetic field, Am^{-1}
H_A	equivalent anisotropy field, Am^{-1}
H_c	coercive field strength, Am^{-1}
H_d	demagnetising field, Am^{-1}
H_{in}	internal magnetic field, Am^{-1}

H_S	static magnetic field, Am^{-1}
h	Plank's constant, Js
h'	rotary mobility factor, $\text{m}^2\text{s}^{-1}\text{N}^{-1}$
h_a	alternating magnetic field, Am^{-1}
I	current, A
I_{in}	input current, A
I_p	moment of inertia of a particle, kgm^2
i	imaginary number, $\sqrt{-1}$
J	angular momentum, $\text{kg m}^2\text{s}^{-1}$
J_d	drift current, A
J_{diff}	diffusion current, A
j	quantum mechanical spin number
K	anisotropy constant, Jm^{-3}
k_B	Boltzmann's constant, JK^{-1}
L	Langevin function
	inductance, H
	length, m
L_1	length of slit, m
L_2	circumference of toroid
L_0	inductance of empty inductor, H
L_{full}	inductance of toroid full of ferrofluid, H
L_{empty}	inductance of empty toroid, H
L_{sample}	inductance of sample material, H
l	length, m
M	magnetisation, T
$M_{ }$	parallel magnetisation
$M_{\perp}$	transverse magnetisation
M_r	remanent magnetisation, T
M_{sat}	saturation magnetisation, T
m	magnetic moment, Wbm
m_0	z component of the magnetic moment
m_{av}	average magnetic moment, Wbm
m_{chain}	magnetic moment of a chain of microspheres, Wbm
m_e	mass of an electron, kg

m_{sp}	magnetic moment of an individual microsphere, Wbm
N	number of atoms per unit volume / particle number density number of inductor turns
N_d	demagnetising factor
P	power, W
P_n	Legendre polynomials
$P(\omega)$	electric polarisation, FVm ⁻²
R	resistance, Ω
R_{empty}	resistance of empty toroid, Ω
R_{full}	resistance of toroid full of ferrofluid, Ω
R_{sample}	resistance of sample material, Ω
R_w	wire resistance, Ω
R_x	unknown resistance, Ω
r	radius, m
r_i	inner conductor radius of coaxial line, m
r_o	outer conductor radius of coaxial line, m
S	reflection coefficient surface, m ²
T	torque, Nm temperature, °K
$\tan\delta$	loss factor
t	time, s
U	energy, J
U_A	anisotropy energy of a particle, J
U_d	demagnetising energy, J
U_{heat}	heat rate energy density in the period of one cycle, Jm ⁻³
U_{mag}	magnetic energy, J
V	potential / voltage, V
$V(r)$	potential, V
V_e	e.m.f, V
V_{in}	input voltage, V
V_x	unknown voltage
v	velocity, m/s
v_m	magnetic volume, m ³

W	realisation of the random variable describing the trajectory of a Brownian particle
X	reactance, Ω
X_x	unknown reactance, Ω
x	length, m displacement, m
Z	impedance, Ω
Z_0	characteristic impedance, Ω
Z_1	impedance of sample material, Ω
Z_e	impedance of empty inductor, Ω
Z_f	impedance of inductor full of ferrofluid, Ω
Z_{in}	input impedance, Ω
Z_{inoc}	open circuited input impedance, Ω
Z_{insc}	short circuited input impedance, Ω
Z_x	unknown impedance, Ω

Greek symbols

α	Cole-Cole parameter damping parameter angle, rad
α_0	attenuation factor, Npm^{-1}
α_1	Cole-Cole parameter for linear susceptibility Cole-Cole parameter for first bimodal particle fraction
α_2	Cole-Cole parameter for nonlinear susceptibility Cole-Cole parameter for second bimodal particle fraction
β	Cole-Davidson distribution parameter, Nakagami distribution parameter
β_0	phase coefficient, rad
χ	susceptibility, dimensionless
$\chi(\omega)$	frequency dependent complex susceptibility
$\chi_1(\omega)$	first harmonic of the frequency dependent complex susceptibility
$\chi_3(\omega)$	third harmonic of the frequency dependent complex susceptibility
$\chi(\omega, H)$	frequency and field dependent complex susceptibility
$\chi'(\omega)$	real component of complex susceptibility
$\chi''(\omega)$	imaginary component of complex susceptibility
$\Delta\chi(\omega)$	nonlinear increment of the susceptibility
$\Delta\chi_1(\omega)$	nonlinear increment of the first harmonic of susceptibility
$\Delta\chi_3(\omega)$	nonlinear increment of the third harmonic of susceptibility
χ_0	zero or static susceptibility
$\chi_{0,1}$	zero or static susceptibility in linear region of magnetisation
$\chi_{0,2}$	zero or static susceptibility in nonlinear region of magnetisation
$\Delta\chi_0$	nonlinear increment of the static susceptibility
χ_∞	susceptibility at very high frequencies
$\chi_{\infty,1}$	linear susceptibility at very high frequencies
$\chi_{\infty,2}$	nonlinear susceptibility at very high frequencies

$\chi_{lin}(\omega)$	frequency dependent complex susceptibility in the linear region of magnetisation
χ_e	electric susceptibility
δ	Dirac delta function
δW	differential magnetic work, Nm ⁻¹
$\Delta \tan \delta$	nonlinear increment of loss factor
ΔU_{heat}	nonlinear increment of heat rate energy density in the period of one cycle, Jm ⁻³
ϵ	permittivity, Fm ⁻¹
ϵ_0	permittivity of free space, Fm ⁻¹
ϵ_1	absolute permittivity of sample material
ϵ_∞	high frequency permittivity
ϵ'	real component of complex permittivity
ϵ''	imaginary component of complex permittivity
ϵ_r	relative permittivity, Fm ⁻¹
ϵ_s	static permittivity, Fm ⁻¹
ϕ, Φ_B	magnetic flux, A/m
γ	gyromagnetic ratio, mA ⁻¹ s ⁻¹
γ_0	propagation constant propagation constant of sample material
γ_1	propagation constant of section of transmission line filled with sample ratio of electric energy to thermal energy ratio of magnetic energy to thermal energy
γ_g	length ratio
η_h	hydrodynamic viscosity, Nsm ⁻²
η_m	magnetic viscosity of a particle, Nsm ⁻²
λ	wavelength, m
μ	permeability, Hm ⁻¹
μ_0	permeability of free space, Hm ⁻¹
μ_1	absolute permeability of sample material, Hm ⁻¹
μ_∞	high frequency permeability
μ'	real component of complex permeability

μ''	imaginary component of complex permeability
μ_B	Bohr magneton, Wbm
μ_e	electric dipole moment, Cm
μ_{eff}	effective permeability, Hm^{-1}
μ_{pdf}	statistical mean
μ_r	relative permeability
μ_s	static permeability
σ	ratio of anisotropy energy to thermal energy standard deviation
τ	relaxation time, s
τ_0	precessional decay time / Néel prefactor, s
τ_1	linear region relaxation time, s first bimodal relaxation time, s
τ_2	nonlinear region relaxation time, s second bimodal relaxation time, s Coffeys second relaxation time, s
$\tau_{\perp}$	transverse time constant, s
$\tau_{\parallel}$	parallel time constant, s
τ'_d	Internal diffusion time, s
τ_B	Brownian relaxation time, s
τ_D	Debye relaxation time, s
τ_{eff}	effective relaxation time, s
τ_n	Néel relaxation time, s
Ω	angle, rad
ω	angular frequency, rads^{-1}
ω_0	angular frequency of free precession, rads^{-1}
ω_{pre}	angular frequency of free precession without damping, rads^{-1}
ω_{res}	angular frequency of resonance, rads^{-1}
ζ	drag coefficient, Nsm
ζ_m	ratio of magnetic field energy to thermal energy
∇	gradient operator
∂	partial derivative

Physical Constants

c	speed of light in a vacuum	$299.7925 \times 10^8 \text{ ms}^{-1}$
e	magnitude of charge on an electron	$1.6021892 \times 10^{-19} \text{ C}$
h	Plank's constant	$6.626176 \times 10^{-34} \text{ Js}$
k_B	Boltzmann's constant	$1.380662 \times 10^{-23} \text{ JK}^{-1}$
μ_B	Bohr magneton	$1.1654118 \times 10^{-29} \text{ Wbm}$
m_e	electron rest mass	$9.109534 \times 10^{-31} \text{ kg}$
ϵ_0	permittivity of free space	$8.854187818 \times 10^{-12} \text{ Fm}^{-1}$
μ_0	permeability of free space	$4\pi \times 10^{-7} \text{ Hm}^{-1}$

Introduction

This thesis is a study of the dynamic properties of colloidal suspensions of magnetic nanoparticles, commonly known as ferrofluids. The particles are suspended in a carrier liquid, which is usually water or oil based, and are coated in a surfactant to prevent aggregation. The particles tend to range in diameter from 4-25 nm, are considered to be of single domain, and exhibit a spontaneous magnetisation at room temperature. Each particle possesses a vector magnetic moment, m . The focus of this thesis is on the behaviour of the particles under the influence of applied magnetic fields, both static and dynamic. The particles can respond to an applied field by bulk rotation of the entire particle within the carrier liquid. During the course of this action, the magnetic moment vector is considered to be fixed with respect to the particle axis. This is known as the Brownian mechanism. Another mechanism is possible, whereby the magnetic moments can switch direction within the particles. This action is limited to the smaller particles, which have enough thermal energy to switch direction. It is known as the Néel mechanism. In reality, a ferrofluid contains a distribution of different particle sizes, and hence it is possible for some particles to experience the Brownian mechanism, and others the Néel.

Ferrofluids have found many applications to date, and offer exciting possibilities for future research, especially in the biomedical area. In electrical engineering ferrofluids are in common use providing enhancements in the operation of devices with magnetic components such as electromagnets, transformers, and loudspeakers. Magnetic nano and micro particles are commonly used in the information storage industry in hard disk drives, magnetic tapes, and magnetic random access memory (MRAM) amongst others. In medicine, ferrofluids have been employed as devices able to selectively separate biological entities, as drug targeting and delivery agents where drug coated nanoparticles are magnetically guided to target areas within the body, and have also been proposed as hyperthermic agents, whereby a ferrofluid is injected into the body and stimulated to generate heat at a specific site [1].

It is possible to study the behaviour of ferrofluids by measuring the complex field and frequency dependent susceptibility, $\chi(\omega, H)$. $\chi(\omega, H)$ gives a measure of the ferrofluids response to an applied magnetic field, H . The frequency and

amplitude of H can be varied so that the frequency and field response of the fluid can be analysed. The Brownian and Néel mechanisms mentioned previously, are known as relaxation mechanisms, and each have a characteristic relaxation time. These effects tend to occur in the low frequency region below 10 MHz. Above 10 MHz, in the radio frequency and microwave regions, it is possible for the magnetic moment to precess about an applied field. Over the course of many precessions the moment is seen to resonate. The measurement of $\chi(\omega, H)$ enables one to obtain important information on properties such as particle size, relaxation times and also the mechanism by which the particles magnetic moment rotates. Chapter 2 contains a theoretical study of such relaxation and resonance mechanisms. Equations are derived for describing $\chi(\omega, H)$ under the influence of static and alternating magnetic fields. This chapter builds on the basic theory of bulk magnetic materials given in chapter 1 to describe the theory underlying the magnetic effects observable in magnetic nanoparticles and ferrofluids.

The measurements performed in this thesis are based on impedance measurement concepts. In the low frequency region where relaxation effects dominate, the slit toroid technique [2] is used to generate the complex susceptibility data. At higher frequencies, measurements are performed using the transmission line technique, which is based on the work of Roberts and von Hippel [3]. The expressions necessary to generate $\chi(\omega, H)$ are derived and given in chapter 3. The full derivation of the slit toroid technique is given in appendix A.

Chapter 4 contains the experimental results obtained from the impedance measurements. The results are explained and analysed using the applicable theory given in the preceding chapters. Measurements were performed on a variety of ferrofluids in both frequency ranges, by both techniques. The low frequency study focuses on the application of cycled large polarising fields, and whether their application has any lasting effect on the fluid. Measurements are also performed on a suspension of magnetic microspheres. These measurements mark the first measurements of $\chi(\omega, H)$ ever performed on microspheres of this type and revealed some unusual effects. These effects are explained in terms of the inner relaxation mechanisms of the microspheres and of the action of the spheres themselves in suspension.

In the high frequency region, the accuracy of the equations given in chapter 3 for the transmission line technique is analysed. A comparison is given between the

susceptibility as measured by the short circuited technique, and the susceptibility as measured by the combined open and short circuited technique. Finally, using the relevant theoretical equations, the material parameters of the measured fluids are analysed using the Cole-Cole plotting format.

Chapter 5 extends the theory of the nonlinear relaxation of a dielectric under the influence of a strong alternating field to the case of a ferrofluid. This is done using the equations of Coffey and Paranjape [4] and Dejardin [5,6] adapted for the magnetic case. Several fits of the experimental data to the theoretical models are performed. The fits obtained support the validity of the model used. The analysis is further extended to the loss processes in the fluid, where the frequency dependent loss factor, $\tan\delta$, and heat losses, U_{heat} , are analysed in terms of the losses generated by the nonlinear magnetisation.

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Chapter One: Properties of Bulk Magnetic Materials

1.1. The Origin of Magnetism

All materials are to an extent, magnetic. This is due to the electronic nature of magnetism, where magnetic effects arise due to the movement of electrical charge. Since all matter contains moving electrical charge, in the form of electrons orbiting nuclei or protons and neutrons with orbital motion inside the nuclei, we can say that every material can respond to a magnetic field in one way or another. However there is an essential difference between magnetism and electricity, whereby in magnetism it is impossible for positive and negative poles to exist independently, in contrast to the case of electricity. This is a direct consequence of the fact that magnetic fields are generated by the movement of electrical charge.

In reality, with the exception of a special group of materials, the magnetic response of the majority of materials is very weak, and we tend to discount their effects. These special materials are called the ferromagnets and their effect is a thousand to a million times greater than the normal weak effect.

The main source of magnetism arises from either the orbital or spin motions of electrons or a combination of these. An applied magnetic field will exert a force on the moving charges in a material altering their movement. If a material is repelled by a region of strong magnetic field, it is said to exhibit diamagnetism, whilst if it is attracted to a region of strong magnetic field it can be said to exhibit paramagnetism. Paramagnetism and diamagnetism account for the weak magnetic effects in the majority of materials. A brief explanation of the above effects follows.

In many substances the atoms have no permanent magnetic moments. The electron spins and orbital motions all balance out completely, so that each atom has no overall or average magnetic moment. Turning on an external magnetic field in the vicinity of the atom, small currents are generated inside the atom by induction. Lenz's law states that these currents oppose the external magnetic field. Therefore the induced magnetic moments are orientated opposite to the external magnetic field, resulting in the mechanism of diamagnetism. It should be noted that the diamagnetic effect is present in all materials even when other magnetic mechanisms are operating.

On the other hand, there are materials which do have a net or permanent magnetic moment. In this case the electron spins and orbits do have a net circulating current that is nonzero, and hence it may be possible to align the individual atomic magnetic

moments. Again, upon applying an external magnetic field the moments attempt to line up with the external field, and the induced magnetism has the effect of enhancing the magnetic field. This is the underlying mechanism of paramagnetism. This mechanism is usually fairly weak as thermal motions tend to act against the alignment of moments.

As stated previously, there is a very strong magnetic effect called ferromagnetism. Iron, Nickel and Cobalt are common elements that exhibit ferromagnetic effects. In ferromagnetism, all the atomic moments tend to align up and lock together, leading to a very strong net effect. To explain this effect, quantum mechanics must be used, and this will be explained later in the chapter.

1.2. Atomic magnetic moments and angular momentum

To characterise the magnetic response of a material it is necessary to define its magnetic moment, and hence its magnetisation. Consider the simplest magnetic circuit, the current loop, which can also describe accurately the effect of orbiting electrical charge. Any current loop can produce a magnetic field at large distance relative to the size of the loop itself. The strength of the magnetic field produced by the loop is proportional to its area, and the current flowing in the loop. The magnetic moment, m , arising from a current loop is given by

$$m = \mu_0 I A \quad (1.2.1)$$

where $\mu_0 = 4\pi \times 10^{-7}$ H/m is the permeability of free space, I is the current and A is the area of the loop. The magnetic moment is directed normal to the plane of the loop and it has units of Wbm.

Consider now an electron orbiting a nucleus on a circular path of radius, r , like the one shown in figure 1.1. The magnetic moment of the orbiting electron is proportional to the current times the area of the orbit. The current is defined as the charge per unit time passing any point on the orbit, that is the charge, $-e$, times the frequency of rotation, f . The frequency is the velocity, v , divided by the circumference of the orbit.

Now, $I = -e \times f$ and $f = v/2\pi r$, so that $I = -ev/2\pi r$. The area of the orbit is πr^2 so that the magnetic moment is

$$m = -\mu_0 \frac{evr}{2}. \quad (1.2.2)$$

An orbiting electron will also possess an angular momentum. The angular momentum is denoted by J . The magnitude of the angular momentum is the mass of the electron times the velocity times the radius, and its direction is perpendicular to the plane of the orbit as shown in figure 1.1.

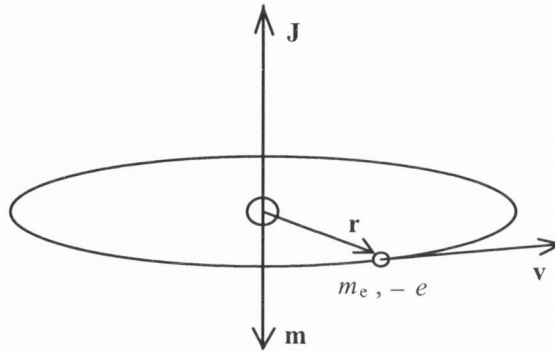


Figure 1.1: An electron orbiting a nucleus with angular momentum, J and velocity, v producing a magnetic moment in the opposite direction to J .

$$J = m_e v r . \quad (1.2.3)$$

It is now desirable to obtain a relationship between the angular momentum, J , and the magnetic moment, m . Combining equations (1.2.2) and (1.2.3) gives

$$m = -\frac{\mu_0 e}{2m_e} J \text{ (electron orbit)} \quad (1.2.4)$$

Note from equation (1.2.4) that the magnetic moment is directed opposite to the angular momentum. This is the case for particles with a negative charge only. The opposite is the case for protons, where the magnetic moment would be directed along the same direction as the angular momentum, due to the positive charge of a proton. Also, from equation (1.2.4), notice that the relationship between magnetic moment and angular momentum is independent of both the velocity, and the radius of the orbit. This relationship holds true in both the classical and quantum mechanical sense. However the magnetism due to the orbital motion is not the only mechanism present. The electron also has a spin rotation about its own axis, and hence has an extra angular momentum and magnetic moment.

Quantum mechanics states that the ratio of m to J for the electron spin is twice as large as that for the electron orbital motion i.e.

$$m = -\frac{\mu_0 e}{m_e} J \text{ (electron spin).} \quad (1.2.5)$$

Naturally in atoms, there are many electrons, each generating their own spin and orbital magnetic moments. The total atomic magnetic moment will be the vector sum of all the electron spin and orbital magnetic moments. The resultant magnetic moment is in a direction opposite to the angular momentum. The ratio of the two is not explicitly $\mu_0 e/m_e$ or $\mu_0 e/2m_e$ but somewhere in between the two values, due to the mixture in the contributions of spin and orbital motions.

In general equation (1.2.4) can be rewritten as

$$m = -g \frac{\mu_0 e}{2m_e} J, \quad (1.2.6)$$

where g is a dimensionless number known as the Landé splitting factor which has a value between one and two. When the magnetic moment is due entirely to electron spin, $g = 2$, and $g = 1$ when the magnetic moment is due to orbital motion alone. Using quantum mechanics it is possible to predict the value of g for any particular atomic state.

1.3. The quantum mechanical description of angular momentum

In quantum mechanics a system can only exist in a certain number of energy states, i.e. the system is quantised. If the system in question is large, there will be a correspondingly large amount of possible energy states. If the system is small, the opposite is true. In classical mechanics it is possible to describe the state of a system by the direction of its angular momentum, however in quantum mechanics a different convention is used. The state of the system can be described by giving the component of the angular momentum along some direction, for example, the z direction. Classically the z component of the angular momentum, J , could take on any value from $+J$ to $-J$. Quantum mechanically due to its quantized nature, the z component of the angular momentum can only have certain discrete values. The z component of the angular momentum of any given system, in our case an atom or an electron, with a given energy, can take on one of the following values

$$\begin{aligned}
J_z &= j\hbar \\
&(j-1)\hbar \\
&(j-2)\hbar \\
&\vdots \\
&\vdots \\
&-(j-2)\hbar \\
&-(j-1)\hbar \\
&-j\hbar,
\end{aligned} \tag{1.3.1}$$

where j is known as the ‘spin’ of the system, and $\hbar = h/2\pi$ where h is Planck’s constant. The largest z component is $j\hbar$ and the smallest $-j\hbar$. The values in (1.3.1) above are valid for the angular momentum along any axis, not just the z axis, for a given spin. Generally the spin, j , is either an integer or a half integer. The difference between the maximum and minimum value of j must however be an integer. There are $(2j + 1)$ possible states for a given j .

Recalling equation (1.2.6) where the magnetic moment of an atomic system was written in terms of its angular momentum, it is possible to derive a term to describe the magnetic energy of atoms. Any magnet placed in an external magnetic field will possess an extra magnetic energy that will depend on the component of its magnetic moment which is directed along the external magnetic field.

The magnetic energy U_{mag} can be written as

$$U_{\text{mag}} = -\mathbf{m} \cdot \mathbf{H}. \tag{1.3.2}$$

Choosing the z axis along H ,

$$U_{\text{mag}} = -m_z \cdot H. \tag{1.3.3}$$

Combining equations (1.2.6) and (1.3.2) gives

$$U_{\text{mag}} = g(\mu_0 e / 2m_e) J_z H, \tag{1.3.4}$$

where J_z can take the values $j\hbar, (j-1)\hbar, \dots, -(j-1)\hbar, -j\hbar$.

It can be concluded from equation (1.3.4) above that the magnetic energy of an atomic system can take on certain discrete values only. Equation (1.3.4) can be simplified further by introducing the concept of the Bohr magneton, μ_B , where

$$\mu_B = \mu_0 e \hbar / 2m_e, \tag{1.3.5}$$

and

$$U_{\text{mag}} = g\mu_B H(J_z / \hbar), \quad (1.3.6)$$

where J_z can take on the values $j, (j-1), \dots, -(j-1), -j$. From equation (1.3.6) it can be concluded that the application of an external magnetic field to an atomic system results in a change of the energy of that system that is proportional to the field, H , and to the z component of the atomic angular momentum, J_z .

The energy of an atomic system is effectively split into $(2j + 1)$ different energy levels by the application of a magnetic field. Taking the case of the electron whose spin number is $j = \frac{1}{2}$, gives $(2 * (\frac{1}{2}) + 1) = 2$ possible energy states in the presence of a field, H . For an electron at rest, the Landé factor, $g = 2$ giving $U_{\text{mag}} = \pm \mu_B H$.

1.4. Precession of Magnetic Moments

If an atomic magnetic moment, m , is suspended freely in a uniform magnetic field of strength H , it will feel a torque, T , equal to $m \times H$, which tries to align it with the field direction. However, as discussed previously, the atomic moment has angular momentum, J , so it will behave like a gyroscope, and precess about H . This is shown classically below. Taking Newton's third law for rotational motion:

$$\text{Rate of change of angular momentum} = \text{Torque}. \quad (1.4.1)$$

The equation of motion for an electron with angular momentum J and magnetic moment m in a magnetic field H is

$$\frac{dJ}{dt} = m \times H. \quad (1.4.2)$$

The relationship between magnetic moment and angular momentum given by equation (1.2.6), can be rewritten in a less cumbersome form by letting

$-g(\mu_0 e / 2m_e) = \gamma$, where γ is the gyromagnetic ratio i.e.: the ratio of magnetic moment to angular momentum.

We now obtain the relationship

$$m = \gamma J. \quad (1.4.3)$$

Equation (1.4.3) can now be used to eliminate the J term in (1.4.2), giving

$$\frac{dm}{dt} = \gamma(m \times H). \quad (1.4.4)$$

(i, j, k) are used as unit vectors which define a right handed Cartesian axis system. Let H lie along the z axis, with magnitude H_0 (figure 1.2) so that $H = H_0 k$.

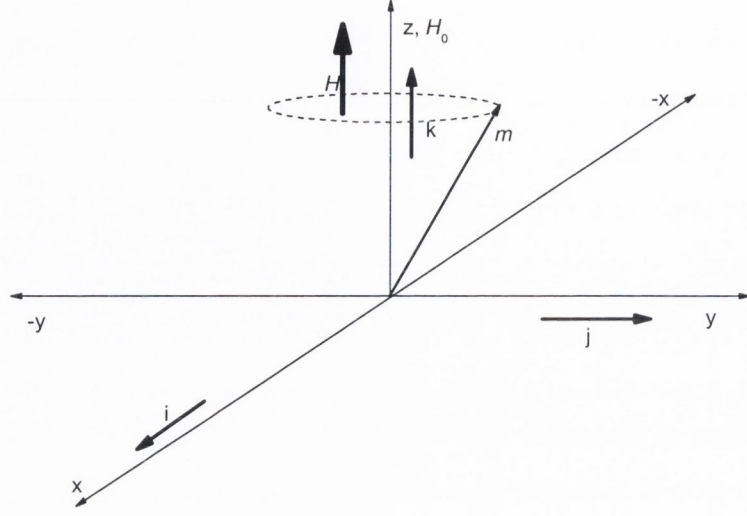


Figure 1.2: Precession of a magnetic moment about an applied magnetic field H (Cartesian coordinate system).

The cross product in equation (1.4.4) reduces to

$$m \times H = H_0(m_x j - m_y i) \quad (1.4.5)$$

where m_x and m_y are the components of the magnetic moment along the x and y axes respectively. Using the above result and rewriting (1.4.4) gives

$$\frac{dm_x}{dt} + \frac{dm_y}{dt} + \frac{dm_z}{dt} = \gamma H_0 (m_x j - m_y i). \quad (1.4.6)$$

Equating the vector components on each side of equation (1.4.6) leads to

$$\frac{dm_x}{dt} = -\gamma H_0 m_y; \quad \frac{dm_y}{dt} = \gamma H_0 m_x; \quad \frac{dm_z}{dt} = 0 \quad (1.4.7)$$

whose solutions are $m_x = \cos(\omega_0 t) \quad m_y = \sin(\omega_0 t); \quad m_z = \text{constant}, \quad (1.4.8)$

where $\omega_0 = \gamma H_0$.

The motion described above is of a precession about the z axis with angular frequency ω_0 . It is called Larmor precession, and the characteristic frequency of Larmor precession can be defined as $f_{pre} = \omega_0 / 2\pi$. The torque due to the magnetic field will not cause the magnetic moment to align with it, instead it causes the magnetic moment (and with it the angular momentum) to precess about an axis

parallel to the applied field. The above case neglects the effect of damping. Should damping be present, the precession of the moment will decay with some time constant, until the magnetic moment is aligned along the magnetic field.

Section 1.3 discussed the notion of the splitting of the energy of an atomic system into $(2j + 1)$ different energy levels when in the presence of a magnetic field. It turns out that it is possible to cause a transition between different energy levels by applying an additional small alternating magnetic field H_1 ($H_1 \ll H_0$) rotating about the z axis with angular frequency ω as illustrated in figure 1.3.

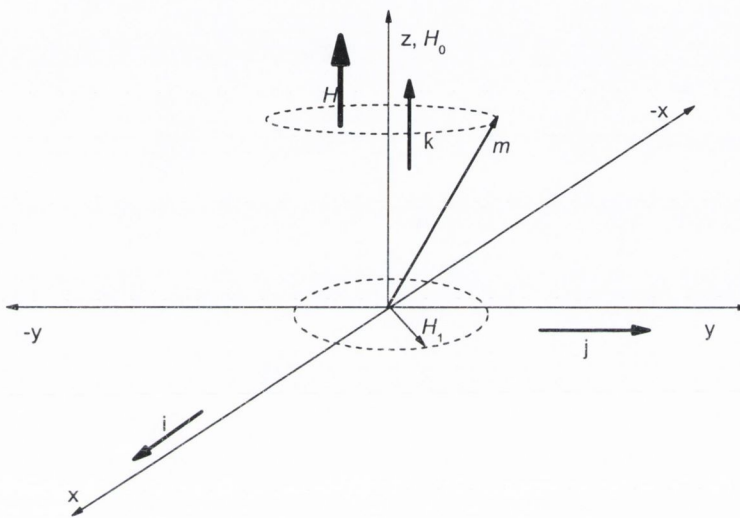


Figure 1.3: Precession of a magnetic moment about an applied magnetic field H_0 . The application of a smaller a.c. field H_1 can cause an interaction between it and the magnetic moment.

When an atom has two levels which differ in energy by an amount ΔU , it can make a transition from the upper to the lower level or vice versa by emitting or absorbing a light quantum of frequency ω . A similar process can happen to atoms in a magnetic field. The absorption of microwave energy of the correct frequency can cause the atoms to jump to a different energy state. If the applied microwave energy, in our case the a.c. field H_1 , is not at the correct frequency, the probability of a transition is very low. It happens that the correct frequency of transition is that of equation (1.4.8), the Larmor angular frequency. Over the course of many Larmor precessions, the magnetic moment will be seen to spiral down until its projection on $-z$ has the same value as it had originally on $+z$. It will then oscillate between these two extreme values so long as H_1 is still operating with angular frequency ω_0 . This

process is known as magnetic resonance. However this is not a continuous process as the downward spiral would suggest but a regular transition to a different energy level as the precessing magnetic moment absorbs energy from the alternating magnetic field during the course of each cycle.

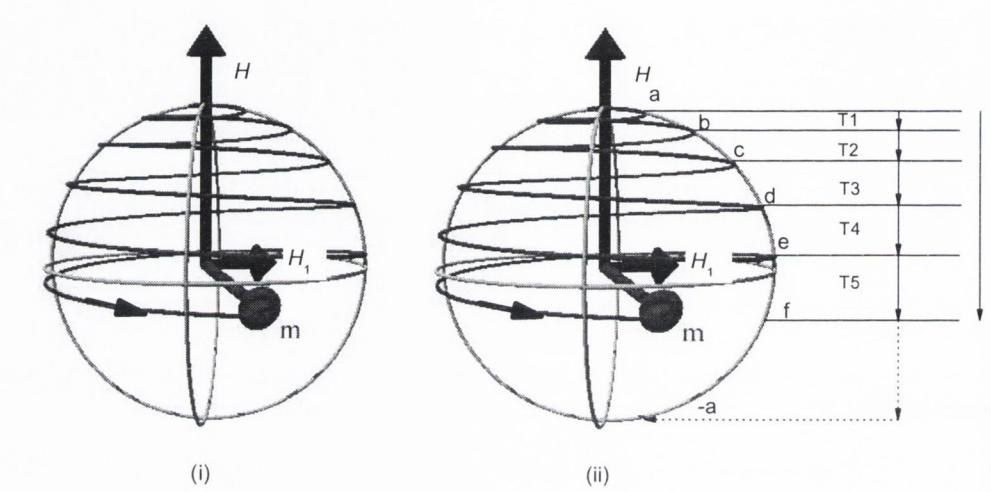


Figure 1.4: (i) Transitions of a magnetic moment precessing about a static field H and a smaller alternating field H_1 . The magnetic moment is seen to spiral down until it reaches its mirror image on the z axis. (ii) The regular transitions (T1-T5) of the magnetic moment from point a down to its projection point $-a$.

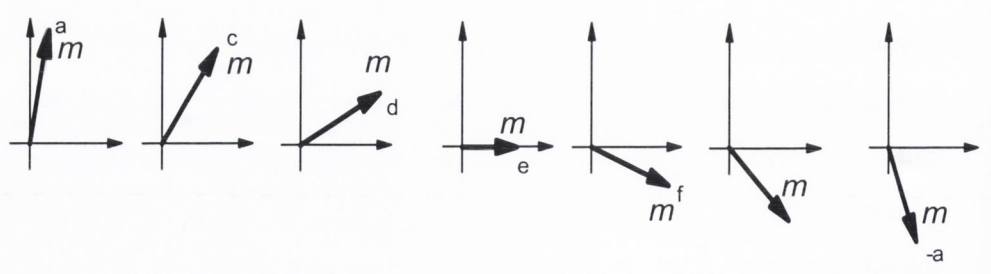


Figure 1.5: Side view of the magnetic moment transitions seen in figures 1.4 (i) and (ii) at the points a, c, d, e, f , and finally $-a$, the projection of a on the $-z$ axis .

Figure 1.4 (ii) shows the analogy between the classical spiralling motion of the magnetic moment, and the quantized transitions between different energy states starting at point a and undergoing various transitions T1-T5-TN and eventually reaching the projection of a on the $-z$ axis. Figure 1.5 takes a side view looking at the $x - z$ plane and shows the transitions of the magnetic moment through different energy levels as it absorbs energy from the applied microwave magnetic field H_1 .

1.5. Diamagnetism

A material is said to be diamagnetic if it is repelled from a region of strong magnetic field. Diamagnetic materials possess no net magnetic moment. However when placed in a magnetic field, the orbital motion of the electrons change and thereby contribute to a change in the overall magnetic moment. Once a magnetic field has been applied the change in electron velocity can be worked out and from there the change in magnetic moment. Recalling the treatment of the magnetic moment and the electron orbit as a current loop, the magnetic moment, $m = -e\mathbf{r}v/2$, where $-e$ is the charge on the electron, and r is the radius of the circular current loop. Switching on a magnetic field causes a change in the magnetic flux of the electron orbit leading to the generation of an e.m.f., V_e . This leads to an electric field, E , given by

$$E = -\frac{V_e}{L} \frac{d\phi}{dt} = -\frac{1}{L} \frac{d(BA)}{dt} = -\frac{\pi r^2}{2\pi r} \frac{d(B)}{dt}, \quad (1.5.1)$$

with the area of the loop, $A = \pi r^2$, and the length of the electron orbit, $L = 2\pi r$. giving

$$E = -\frac{r}{2} \frac{d(B)}{dt} \quad (1.5.2)$$

From Newton's second law of motion $F = ma$ and hence the acceleration,

$$a = F/m. \quad (1.5.3)$$

The force on the electron, F is equal to the electric field strength, E , times the charge on the electron, e giving $F = -Ee$. Substituting into equation (1.5.3) gives $a = -Ee/m_e$, where m_e is the mass of the electron.

$$\frac{dv}{dt} = a = -\frac{Ee}{m_e} = -\frac{re}{2m_e} \frac{dB}{dt}. \quad (1.5.4)$$

Knowing $B = \mu_0 H$ equation (1.5.4) becomes

$$\frac{dv}{dt} = \frac{\mu_0 r e}{2m_e} \frac{dH}{dt}. \quad (1.5.5)$$

Integrating both sides from v_1 to v_2 and from zero field to an arbitrary field strength H gives

$$\int_{v_1}^{v_2} dv = \left(\frac{\mu_0 r e}{2m_e} \right) \int_0^H dH \Rightarrow v_2 - v_1 = \left(\frac{\mu_0 r e}{2m_e} \right) H. \quad (1.5.6)$$

Recalling $m = -evr/2$, the change in magnetic moment arising from (1.5.6) is

$$\Delta m = \frac{-er}{2} (v_2 - v_1) = -\frac{\mu_0 e^2 r^2 H}{4m_e}. \quad (1.5.7)$$

The minus sign signals that the added moment is opposite to the magnetic field and is the characteristic of diamagnetism. For the above result to tally with quantum theory, it must be modified slightly. One cannot say the exact location of an electron in an atom at any specific time, (due to the uncertainty principle), it is only possible to give the probability that it will be at some position. To account for this, the average radius, r_{av} , is introduced. Keeping to the convention of H directed along the z axis, then r has only x and y components and $r^2 = x^2 + y^2$. Assuming the atoms are spherically symmetric, then the average value of r^2 is $2/3$ the average of the square of the true radial distance from the centre of the atom. Equation (1.5.7) can then be written as

$$\Delta m = -\frac{\mu_0 e^2 r_{av}^2 H}{4m_e} * \frac{2}{3} = -\frac{\mu_0 e^2 r_{av}^2 H}{6m_e}. \quad (1.5.8)$$

Equation (1.5.8) represents the induced moment for just one electron, the net induced moment per atom is found by summing over all the electrons in that atom.

1.6. Paramagnetism

Paramagnetic materials have permanent magnetic moments. The permanent moments arise when the atoms have unfilled electron shells. An unfilled electron shell will have an odd number of electrons, leading to unpaired electrons which will contribute an orbital and spin magnetic moment. Ordinarily, and in the case of the

formation of compounds, all electrons are paired and their spin and orbital contributions cancel out leading to zero net magnetic moment. The transition group of elements all have a net magnetic moment due to an unfilled inner electron shell.

Consider an assembly of paramagnetic atoms such as those in figure 1.6. When there is no magnetic field applied, the atoms are in constant random motion due to thermal agitation and consequently their moments point in random directions leading to zero net moment and magnetisation. However when a magnetic field is applied, it acts upon the atomic moments tending to align some of them towards the field. There are now more moments lying in or near the direction of the field than there are pointing away from it, leading to an overall magnetisation in the direction of the applied field. The magnetisation M of a material is defined as the net magnetic moment per unit volume or the vector sum of all atomic magnetic moments per unit volume. M usually has the unit of Tesla (T).

If there are N atoms per unit volume and the average magnetic moment in the direction of the applied field is m_{av} then M can be written as the sum of all average moments in the unit volume of material, i.e.

$$M = Nm_{av} \quad (1.6.1)$$

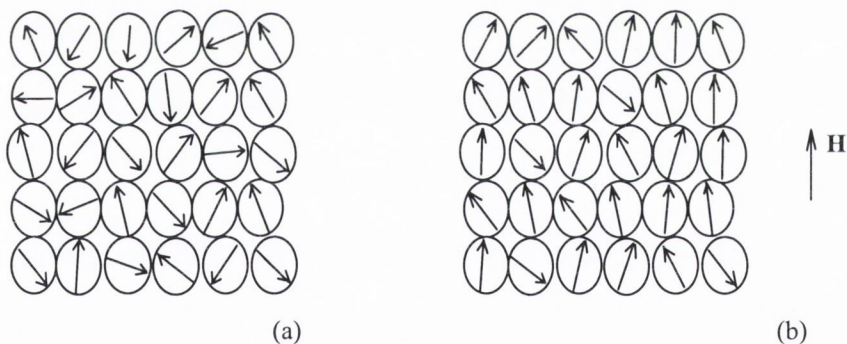


Figure 1.6(a): No applied field, the atomic moments point in random directions cancelling each other out and resulting in zero net magnetisation. **(b)** Applying a magnetic field causes the moments to align themselves in the direction of the field leading to a net magnetisation.

1.6.1. Classical Treatment of Paramagnetism

The classical treatment of paramagnetism assumes that each atom has a magnetic moment m , which has a constant magnitude but is free to point in any direction. In an applied field H , the magnetic moment makes an angle ϑ with the field so that the magnetic energy, $U_{mag} = -\mu_0 m \cdot H = -\mu_0 m H \cos \vartheta$.

The magnetic energy is minimised when the moment points along the field direction ($\vartheta = 0$). Due to thermal agitation most moments will generally not align directly with the field but will instead make an angle with it. Smaller angles are more favourable in the context of minimisation of energy. Using Boltzmann statistics, the relative probability of having any angle is $\exp(-U/k_B T)$, so that angles near zero (low energy) are more probable than those near π (higher energy). For an isotropic material (zero applied field) the number of moments lying between the angles ϑ and $\vartheta + d\vartheta$ is dn which will be proportional to the surface area dA (Figure 1.7).

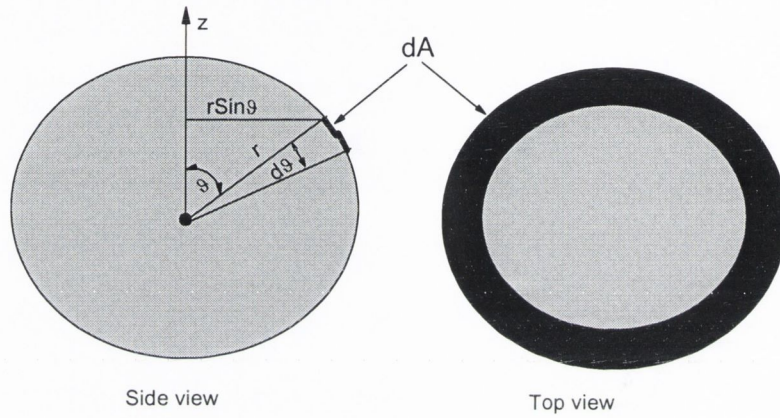


Figure 1.7: Side and top view of sphere used to define the distribution of magnetic moments of an assembly of paramagnetic atoms.

From figure (1.7), dA is given by its length, $2\pi r \sin \vartheta$, times its width, $r d\vartheta$, where $r d\vartheta$ is the area of an arc, so that

$$dA = 2\pi r^2 \sin \vartheta d\vartheta \quad (1.6.1.1)$$

and

$$dn = C 2\pi r^2 \sin \vartheta d\vartheta \quad (1.6.1.2)$$

where C is a normalising constant which gives the total amount of moments per unit area. Incorporating the probability of occupation of any given state with an applied field gives

$$dn = C 2\pi r^2 \sin \vartheta d\vartheta \exp\left(\frac{\mu_0 m H \cos \vartheta}{k_B T}\right). \quad (1.6.1.3)$$

Integrating (1.6.1.3) over the entire range of possible directions gives the resultant total number of moments per unit volume N .

$$N = 2\pi C \int_0^\pi \sin \vartheta \exp\left(\frac{\mu_0 m H \cos \vartheta}{k_B T}\right) d\vartheta \quad (1.6.1.4)$$

giving

$$C = \frac{N}{2\pi \int_0^\pi \sin \vartheta \exp\left(\frac{\mu_0 m H \cos \vartheta}{k_B T}\right) d\vartheta}. \quad (1.6.1.5)$$

The magnetisation is then given by

$$M = \int_0^N m \cos \vartheta dn = \frac{Nm \int_0^\pi \cos \vartheta \sin \vartheta \exp\left(\frac{\mu_0 m H \cos \vartheta}{k_B T}\right) d\vartheta}{\int_0^\pi \sin \vartheta \exp\left(\frac{\mu_0 m H \cos \vartheta}{k_B T}\right) d\vartheta}. \quad (1.6.1.6)$$

Letting $x = \cos \vartheta$ and $dx = -\sin \vartheta d\vartheta$ and integrating gives

$$M = Nm \left[\coth\left(\frac{\mu_0 m H}{k_B T}\right) - \frac{k_B T}{\mu_0 m H} \right] \quad (1.6.1.7)$$

which may also be written as

$$M = NmL\left(\frac{\mu_0 m H}{k_B T}\right) = NmL(x). \quad (1.6.1.8)$$

This is the Langevin equation for the magnetisation of a paramagnet where $L(x)$ is the Langevin function. The Langevin equation will become very important in subsequent chapters where the magnetisation of a magnetic fluid is described. The Langevin function can be expressed as an infinite power series in $\mu_0 m H / k_B T$. In most cases $\mu_0 m H / k_B T \ll 1$ so that the expression for M can be estimated by the first term in the power series

$$M = N \frac{\mu_0 m^2 H}{k_B T}. \quad (1.6.1.9)$$

The ratio of M to H is defined as the susceptibility and is commonly written using the symbol χ with

$$\chi = \frac{M}{\mu_0 H}. \quad (1.6.1.10)$$

1.6.2. Quantum Mechanical Treatment of Paramagnetism

Section 1.3 discussed the magnetic energy U_{mag} and arrived at equation 1.3.4 for the magnetic energy with,

$$U_{mag} = g \left(\frac{\mu_0 e}{2m_e} \right) J_z H,$$

where J_z can take the values $j\hbar, (j-1)\hbar, \dots, -j\hbar$. Take the case of an atom with spin $\frac{1}{2}$. In the absence of a magnetic field the atom has a certain energy, but with the application of a magnetic field the atom can have two possible energies, one for each value of J_z . For $J_z = +\frac{1}{2}$ the energy is changed by the magnetic field by the amount

$$\Delta U = +g \left(\frac{\mu_0 e \hbar}{2m_e} \right) \frac{1}{2} H. \quad (1.6.2.1)$$

For $J_z = -\frac{1}{2}$ the energy is changed by the amount

$$\Delta U = -g \left(\frac{\mu_0 e \hbar}{2m_e} \right) \frac{1}{2} H. \quad (1.6.2.2)$$

Letting the z component of the magnetic moment equal to m_0 ,

$$m_0 = \frac{1}{2} g \left(\frac{\mu_0 e \hbar}{2m_e} \right) \quad \text{and} \quad \Delta U = \pm m_0 H. \quad (1.6.2.3)$$

where $-m_0$ is the z component of the magnetic moment in the up-spin case, and $+m_0$ is the z component of the magnetic moment in the down-spin case. Statistical mechanics states that the probability that an atom occupies a certain state is proportional to

$$\exp^{-(\text{energy of that state})/kT} \quad (1.6.2.4)$$

With no magnetic field applied, the up-spin and the down-spin states have the same energy. With a field present the states have different energies and the probabilities are proportional to $\exp^{-(\Delta U/kT)}$.

The number of atoms per unit volume with spin-up is

$$N_{up} = N_1 \exp(-m_0 H / k_B T), \quad (1.6.2.5)$$

whilst the number with spin-down is

$$N_{down} = N_1 \exp(m_0 H / k_B T). \quad (1.6.2.6)$$

N_1 is given by

$$N_1 = \frac{N}{\exp(m_0 H / k_B T) + \exp(-m_0 H / k_B T)}, \quad (1.6.2.7)$$

where

$$N = N_{up} + N_{down}.$$

Considering only the average magnetic moment along the z axis, the atoms with spin-up and spin-down, will have moments of $-m_0$ and $+m_0$ respectively, so that the average moment can be defined as

$$m_{av} = \frac{N_{up}(-m_0) + N_{down}(+m_0)}{N}. \quad (1.6.2.8)$$

From equation (1.6.1) we know that $M = N m_{av}$ and hence we can substitute in equations (1.6.2.6-1.6.2.8) to obtain a value for the net magnetisation, M

$$M = N m_0 \frac{\exp(m_0 H / k_B T) - \exp(-m_0 H / k_B T)}{\exp(m_0 H / k_B T) + \exp(-m_0 H / k_B T)}. \quad (1.6.2.9)$$

This is the quantum mechanical formula for the magnetisation of a paramagnetic material for atoms with spin, $j = 1/2$. Utilising the hyperbolic tangent function, it is possible to rewrite equation (1.6.2.9) in a neater form with,

$$M = N m_0 \tanh\left(\frac{m_0 H}{k_B T}\right), \quad (1.6.2.10)$$

and the hyperbolic tangent function

$$\tanh z = \frac{\exp(+z) - \exp(-z)}{\exp(+z) + \exp(-z)}. \quad (1.6.2.11)$$

At very high values of H , the hyperbolic tangent approaches one, and M approaches the limiting value of $N m_0$, which means that at high fields the magnetisation reaches a saturation level past which it can no longer increase. This is because at high fields the magnetic moments are all aligned completely along the applied field and can no

longer respond to an increase in H . Equation (1.6.2.10) can be simplified further subject to the condition that the ratio $m_0 H / k_B T$ is small, which is usually the case under normal conditions. Equation (1.6.2.10) can now be rewritten as

$$M = \frac{N m_0^2 H}{k_B T}, \quad \text{for } m_0 H / k_B T \ll 1. \quad (1.6.2.12)$$

Comparing equation (1.6.2.12) to that of the classical theory it is clear that they are similar save for the absence of a factor of a third in equation (1.6.2.12). This can be remedied by drawing a comparison between the moment, m_0 , used above in the quantum mechanical formula and that of the moment, m , used in the classical theory. In classical theory, the quantity that appeared was the square of the vector magnetic moment, $m^2 = m \cdot m$. This can be written as

$$m \cdot m = \left(g \frac{\mu_0 e}{2 m_e} \right)^2 J \cdot J. \quad (1.6.2.13)$$

In quantum mechanics it is usually possible to calculate $J \cdot J$ by replacing it by $j(j+1)\hbar^2$. For the above calculation $j = 1/2$ so that,

$$m \cdot m = \left(g \frac{\mu_0 e}{2 m_e} \right)^2 \frac{3 \hbar^2}{4}. \quad (1.6.2.14)$$

In terms of equation (1.6.2.3)

$$m \cdot m = 3 m_0^2. \quad (1.6.2.15)$$

Substituting (1.6.2.15) for m^2 in the classical formula reproduces the correct quantum mechanical formula given in equation (1.6.2.12).

1.7. Ferromagnetism

Like paramagnets, ferromagnets are materials that have permanent magnetic moments, however unlike paramagnets, the net effect of these moments is very large, many many times greater than paramagnets or diamagnets. The induced magnetic fields produced by diamagnets or paramagnets are usually so small as to be neglected. However, this is not the case with ferromagnets, where the application of a small magnetic field can induce a huge magnetic moment, very much greater than the original applied field. The question is, why are the magnetic moments so strong in ferromagnets, but not in paramagnets?

As in the case of paramagnets the theory of ferromagnetism supposes that its magnetisation arises from the spin of an electron. From previous sections the following is known:

That the electron has spin of $\frac{1}{2}$ and carries one Bohr magneton of moment

$$m = \pm g\mu_B j.$$

That the spin of the electron can be either 'up' or 'down'.

That the moment of an 'up' electron is negative and the moment of a 'down' electron is positive.

That m is directed opposite to the spin j .

It is also known, as before, that the magnetic energy of an electron placed in a magnetic field is $U_{mag} = -\mu_0 m.H$. However the energy of a spinning electron also depends on neighbouring alignments of electrons. In a ferromagnetic material, if the moment of an atom is 'up', there is a very strong likelihood that the moment of a neighbouring moment will also be 'up'. This is what makes the ferromagnets so strongly magnetic, all their spins want to line up parallel to each other.

To find out why this happens, the following is considered. The Pauli exclusion principle states that two electrons cannot occupy the same quantum mechanical state. That is to say that, two electrons cannot occupy the exact same location in space *and* have the same spin orientation. This means that for two electrons to have the same spin, they must be located some distance from each other, or, for two electrons to occupy the same point in space, they must have opposite spins. In a chemical bond, which is a region in space where electrons tend to concentrate, if one electron needs to be placed on top of another, then the two electrons must have opposite spin so as not to violate the exclusion principle.

For this reason, two electrons with parallel spins close to each other, will have a far greater energy than two electrons with opposite spins close to each other. It can be said that there is some apparent force trying to turn the adjacent spins over. Sometimes this is called the exchange force. So what has been said above is that the exclusion principle causes adjacent electrons to have opposite spins. This is actually the physical mechanism that causes the lack of magnetism in most materials. The opposite spinning electrons cancel each other out, leading to zero net magnetic moment in the absence of an applied field.

To explain the ferromagnetic effect it is necessary to look further into the electronic configuration of the material. The unpaired electrons that contribute to magnetism are located in the inner shells of the atom. Orbiting around the outside of these 'magnetic electrons' are the conduction electrons in the valence shell of the atom. It is believed that due to the exclusion principle, the magnetic electrons in the inner shells tend to make the conduction electrons have the opposite spin. It is convenient to think of these conduction electrons as the 'middlemen' of ferromagnetism. Because they are free to move about, the conduction electrons can come into contact with the magnetic electrons of neighbouring atoms, in turn, causing the neighbouring magnetic atoms to have the opposite spin to the conduction electrons. Now, due to the exclusion principle, there is a double interaction, between neighbouring magnetic electrons, with the conduction electrons as the 'middlemen'. This leads to neighbouring magnetic electrons having parallel spins, and hence the creation of large net magnetic moments. It should be noted that the conduction electrons need only have a slight prejudice to have an opposite spin to the original magnetic electrons, which is just enough to cause neighbouring electrons to have the same spins. Therefore in ferromagnets, it is energetically favourable to have parallel spins.

This parallel alignment of spins does not take place throughout the bulk of the material, but only in small regions known as domains. Weiss [1, 2] first suggested the existence of domains in ferromagnetic materials. In these domains, large numbers of atomic moments, typically between 10^{12} and 10^{18} , are aligned parallel so that the magnetisation within the domain is almost saturated. The direction of alignment differs from domain to domain, so that throughout the bulk of the material, the domains cancel each other out leading to zero net magnetisation.

The cancellation of domains is the reason that some samples of iron are in an unmagnetised state.

However, the question remains, as to why do the domains not align as one single domain. Why do they point in different directions? The answer provided by Landau and Lifschitz [3] is that domains are a consequence of energy minimisation. A single large magnetic domain has associated with it a large magnetostatic energy. The break up of the single large domain into a multi domain material reduces the magnetostatic energy. An example of this process is shown in figure 1.8 which shows the formation of domains.

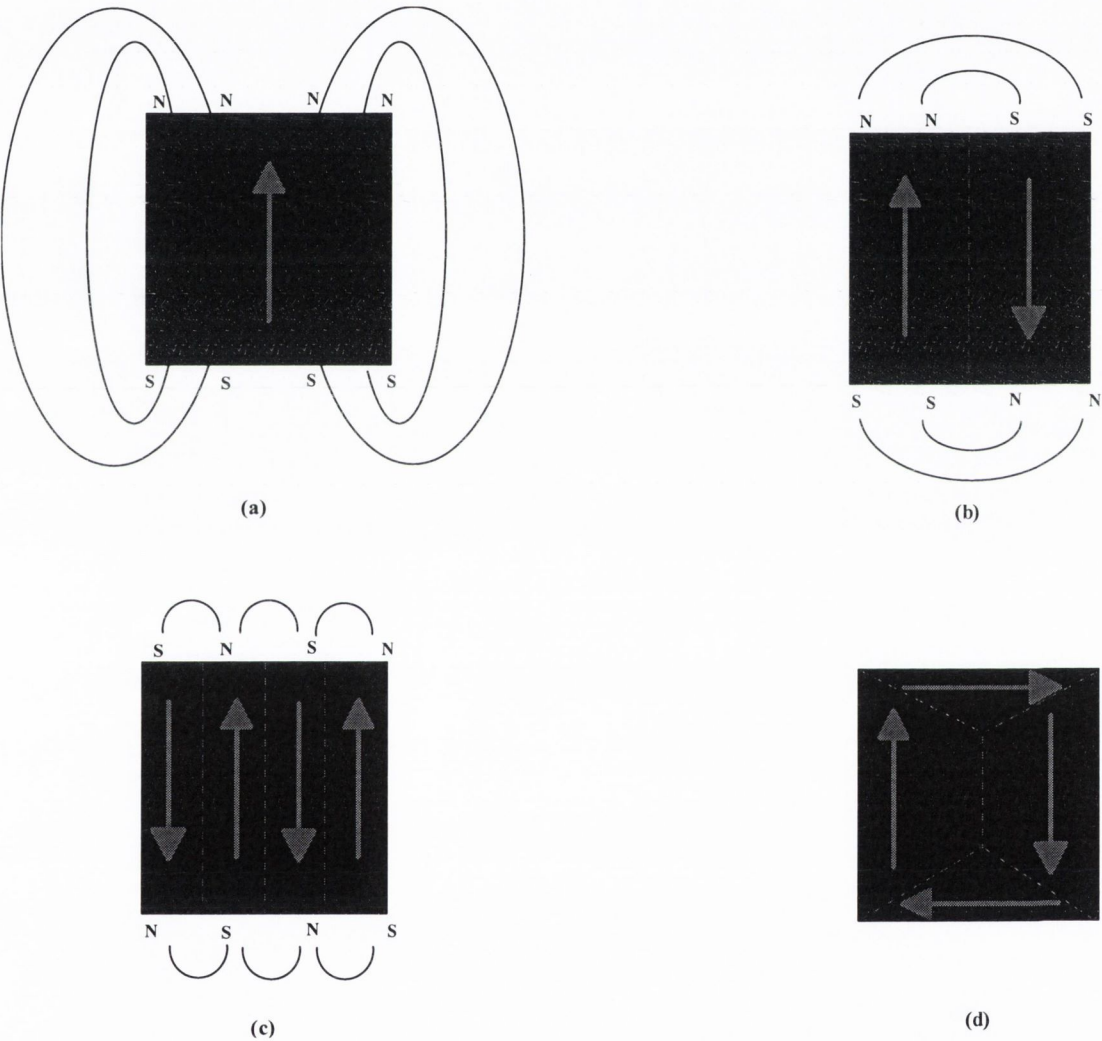


Figure 1.8: Domain formation in a single crystal of iron[4].

Figure 1.8 (a) shows a single domain ferromagnetic specimen. It is spontaneously magnetised all in one direction, the ‘up’ direction. This configuration has a considerable external magnetic field as shown by its field lines. This external

magnetic field will have a lot of energy. To reduce this energy, the external field must extend over less volume. This can be achieved if one side of the specimen is magnetized 'up', and the other is magnetised in the opposite direction, 'down' (figure 1.8 (b)). The region between two domains (the dotted lines in figure 1.8) is called the domain wall. In the region of the domain wall there are 'up' spinning electrons adjacent to 'down' spinning electrons. However in ferromagnetic materials energy is reduced if electrons are parallel rather than opposite. So in the domain wall there is now an extra energy term, which is called the domain wall energy. Splitting of a specimen into domains continues until the energy needed to create one domain wall is as great as the energy reduction in the magnetic field outside the specimen. It should be noted that it is possible for the specimen to be split down into domains such that there is no external field present, as shown in figure 1.8 (d) where two triangular regions are magnetised in opposition sideways.

It has been stated above that in domain walls 'up' spinning electrons are present adjacent to 'down' spinning electrons. This would suggest that there are electrons spinning exactly opposite to one another at the boundary between two domains. In reality there is a more gradual transition between spinning electrons at the domain wall as shown in figure 1.9.

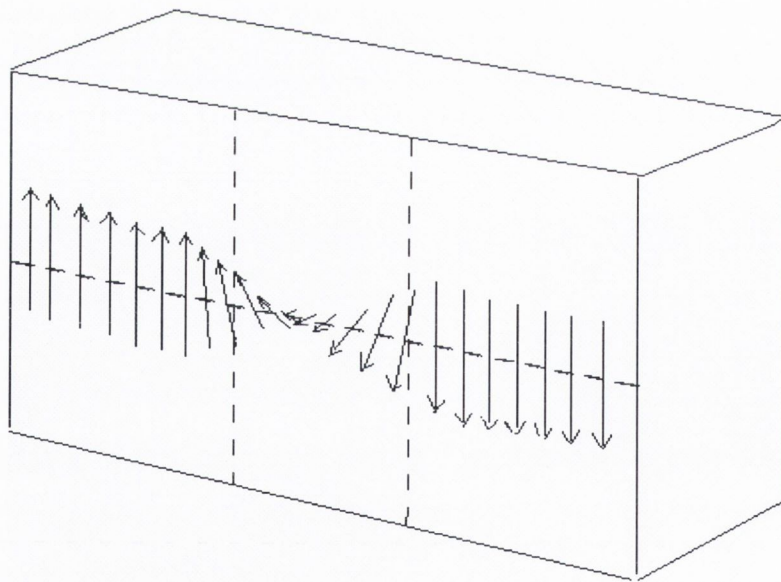


Figure 1.9: Alignment of magnetic moments within a 180° domain wall. The domain wall is contained inside the dotted lines, bounded on either side by an 'up' spinning and a 'down' spinning region.

In figure 1.9 above, consider the application of a weak magnetic field orientated in the 'down' direction. The moments in the 'up' direction are held strongly in place by

their mutual interaction through the exchange field, and consequently they will not change direction to align with the applied field. Inside the domain wall the direction of the moments is defined by a fine balance between the exchange energy and the anisotropy energy which, due to energy minimisation, strives to align the moment along some crystallographic axis. The exchange energy tends to thicken the domain walls as it favours parallel alignments of spins, whilst the anisotropy energy tends to make the walls thinner since the anisotropy energy is lowest when all spins are aligned along a favourable crystalline axis. The applied field can disrupt this energy balance, turning the moments into the field direction as the field increases. The domain wall is seen to ‘grow’ into the field direction, effectively moving to the left in figure 1.9.

Possessing the above information it is now possible to consider the process of magnetisation in a ferromagnetic material in the context of the magnetisation curve and domain alignment and growth. When a magnetic field is applied to a demagnetised ferromagnetic material, the changes in magnetisation M with applied field can be plotted on the $M-H$ plane, generating the initial magnetisation curve for the material. At low fields the favourably aligned domains grow in the direction of the applied field due to domain wall growth as discussed above. This preferential growth is to the detriment of unfavourably aligned domains with respect to the applied field, which shrink. This process is shown in figure 1.10 (b) and is reversible. At higher field strengths the atomic magnetic moments within unfavourably aligned domains overcome the anisotropy energy binding them to a certain crystallographic easy axis, and rotate from their original magnetisation direction to another easy axis direction closer to the applied field. This process is known as domain rotation, is irreversible and is shown in figure 1.10 (c). At higher fields still, the magnetic moments, which now lie along the easy axis close to the field direction, are rotated gradually into the field direction as the applied field is increased (figure 1.10 (d)). This process is reversible and is known as coherent rotation. The result of these processes is a single domain sample.

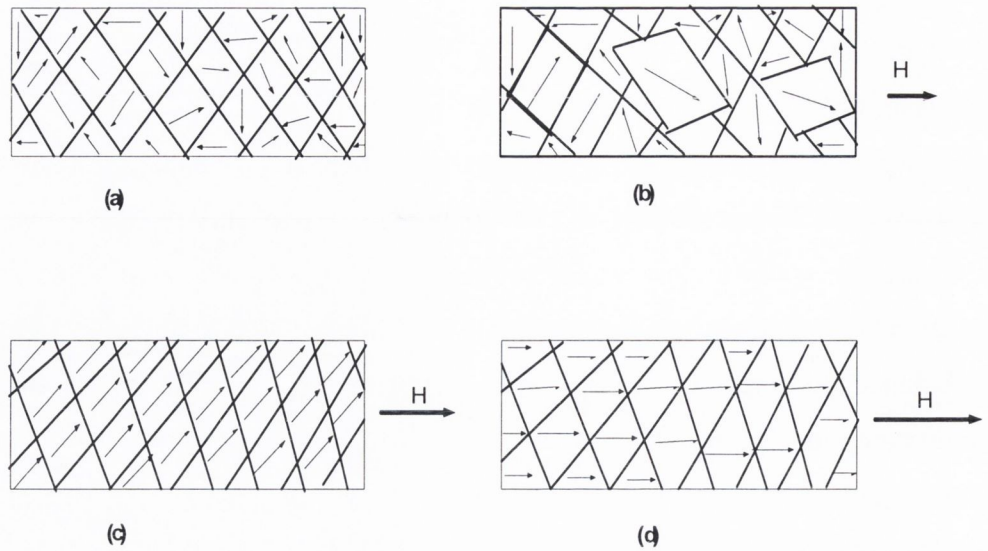


Figure 1.10: Domain processes which occur as a material is magnetised to saturation from the unmagnetised state (a). After application of a small magnetic field, domain growth occurs leading to the partially magnetised state (b). With moderate field strengths domain rotation occurs (c), and finally with increasing field all domains coherently rotate into the field direction.

Having considered the case of a single crystal of magnetic material containing few or many domains, we must now turn to the case of a polycrystalline material. Iron is one such material, with many crystals with their crystalline axes pointing in many different directions. When a small field is applied to a piece of polycrystalline material as before, the domain walls begin to move and the domains with favourable direction of easy magnetisation with respect to the applied field grow in the direction of the field. So long as the applied field remains small, this growth is reversible, and the magnetisation will return to zero upon removal of the applied field. This corresponds to the section marked 'arev' in figure 1.11. When the field increases to larger values, the magnetisation continues to increase. However at these stronger fields the domain walls get 'stuck' on dislocations, imperfections and impurities within the crystal structure. There is then some interaction energy between the domain wall and these dislocations, impurities or imperfections. The domain wall remains 'stuck' at these locations until it has gained enough energy from the increasing applied field to suddenly snap past these impediments. Because of these effects the second part of the magnetisation is irreversible and leads to an energy

loss. This is marked as ‘a-irrev’ on figure 1.11. This energy loss is the cause of the ‘hysteresis’ effect.

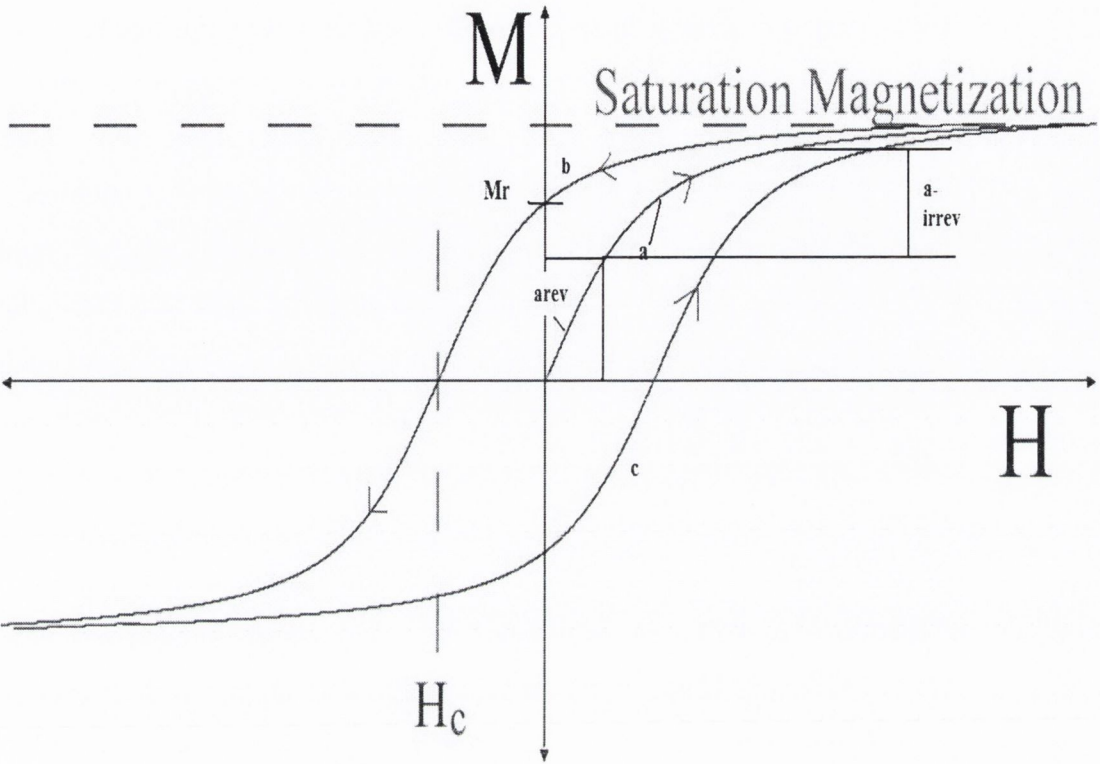


Figure 1.11: Typical magnetisation and hysteresis curves for a ferromagnetic material.

Finally at higher fields still, when all the domain walls have moved and each crystal is magnetised in its best direction, there are still a small number of crystals which do not align with the field. It will take a large amount of energy to slowly rotate these crystals around in the field direction, and so the magnetisation rises slowly but smoothly for very high fields until it reaches the saturation magnetisation, M_{sat} , where all crystals are aligned with the applied field. Once saturation has been reached it is of interest to know what happens when the applied field is decreased. Because of the nonlinearity and irreversibility of the magnetisation process, the demagnetisation curve does not follow the same path as the magnetisation. It typically follows some path such as that of ‘b’ in figure 1.11. When the field is switched off, the magnetisation does not return to zero. Some magnetisation remains. This is termed the remnant magnetisation, M_r . To return the magnetisation to zero it is necessary to apply a field in the opposite direction (or reverse the direction of the current generating H). The value of the reverse field needed to return the

magnetisation to zero is known as the coercive field, H_c . H_c will differ from material to material depending on its method of manufacturing. Continuing to reverse the field along 'b', leads to saturation in the negative direction. Increasing the applied field once more, the magnetisation follows the path 'c' back thorough zero and up to positive saturation once more. The loop 'abc' formed by this action is known as the hysteresis loop. The hysteresis is in effect a form of magnetic memory, where the magnetic material retains a portion or memory of its previously applied magnetic state or applied field. Due to this property ferromagnetic materials with wide hysteresis loops have found applications as permanent magnets and memory elements. However, the wider the hysteresis loop, the larger the energy losses in the material. For applications which require low energy or power losses such as power transformers, a narrower, 'softer' hysteresis loop is required. Such materials are deemed magnetically 'soft' as their magnetisation is easily varied by applied fields, and their coercivity is very small. Traditionally the coercivity is used to distinguish between hard and soft magnetic materials. Soft materials have a coercivity of less than 1000 A/m, whilst hard materials have a coercivity of greater than 10,000 A/m.

The magnetisation of a ferromagnetic material is therefore very complicated and can only be accurately described by the loop generated by an experimental variation of M with H . It cannot be described by a relatively simple expression as that described by the Langevin equation for the magnetisation of a paramagnet. Paramagnets do not exhibit this hysteresis behaviour and this fact is used to define the concept of superparamagnetism which is the mechanism of magnetisation of magnetic nanoparticles which are the constituents of magnetic fluids, to be described in subsequent chapters.

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Chapter Two: Theory of Magnetic Nanoparticles and Ferrofluids.

2.1. Introduction

In this chapter the theory of the magnetic nanoparticles which are the constituents of magnetic fluids or ferrofluids, is presented. Ferrofluids are stable colloidal suspensions of single domain [1] magnetic nanoparticles dispersed in a suitable non magnetic carrier liquid. Each particle possesses a magnetic moment and a spontaneous magnetisation at room temperature. Each particle consists of a magnetic core of ferromagnetic or ferrimagnetic material of type $m\text{-Fe}_2\text{O}_4$, where m is a metal from the transition group of elements such as Iron (Fe), Cobalt (Co), Manganese (Mn), Zinc (Zn) or Nickel (Ni). Hence the ferrofluid may have magnetic constituents such as magnetite (Fe_3O_4), maghemite (Fe_2O_4), cobalt ferrite ($\text{Co}_x\text{Fe}_{1-x}\text{O}_4$), manganese or zinc ferrite ($\text{Mn}_x\text{Fe}_{1-x}\text{O}_4$, $\text{Zn}_x\text{Fe}_{1-x}\text{O}_4$) where x is ≤ 1 . It is also possible for the fluid to consist of materials such as nickel zinc ferrite ($\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$) or cobalt zinc ferrite ($\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$), where x is as before. The particles tend to be spherical with radii of between 2 – 10 nm.

The main carrier liquids tend to be water, mineral oil, kerosene, isoparaffin or some other liquid hydrocarbon. Each carrier has its own advantages and disadvantages. Water based ferrofluids for example, tend to aggregate easily but are biocompatible whilst oil based ferrofluids tend to be more aggregation resistant but are also non biocompatible and sometimes highly flammable. The particles are coated by a surfactant to resist the strong dipole-dipole particle interaction which tends to aggregate the particles. However, the surfactant is not always successful in preventing particle agglomeration, especially in highly concentrated liquids, and it is possible for aggregates to form with arbitrary spherical shapes or as chains. The mean size of aggregates tend to be anywhere from 30 – 200 nm in diameter.

In the absence of an applied field the magnetic moments of the nanoparticles that form the ferrofluid point in random directions due to thermal agitation and hence there is no overall magnetisation present in the ferrofluid. The application of an applied field causes the magnetic moments to rotate in response to the field by aligning with it and hence an overall magnetisation is developed in the ferrofluid.

There are two mechanisms by which the magnetic moments in ferrofluids can rotate in response to an applied field. For the treatment of each such mechanism it is supposed that the other mechanism is 'blocked' or prevented from operating.

The first mechanism, where the magnetic moment is locked rigidly within the particle axis (magnetic moment is blocked), occurs by physical rotation of the entire nanoparticle within the carrier liquid. This is termed the Brownian mechanism [2]. The second mechanism occurs when the magnetic moment switches direction within the magnetic nanoparticle. This is termed the Néel mechanism [3]. When considering the Néel mechanism it is assumed that the nanoparticles are mechanically frozen in space so that the Brownian mechanism does not take place. Under certain circumstances both mechanisms can operate.

The magnetisation resulting from the application of a field to a ferrofluid is similar to that of paramagnets, i.e. as described by the Langevin function with no Hysteresis. However the magnetic moments of the nanoparticles in ferrofluids are a few orders of magnitude greater than those of paramagnetic atoms because each nanoparticle can contain hundreds of thousands to millions of atoms ferromagnetically coupled together. Hence the magnetisation strength of a typical ferrofluid will be a few orders of magnitude greater than an ordinary paramagnetic substance. The term commonly used to describe the behaviour of ferrofluids is *superparamagnetism* [4,5]. This term describes the paramagnetic behaviour of ferrofluids, such as the Langevin characteristic of the magnetisation curve, and also the relatively large magnetisation by comparison to paramagnets. Superparamagnetism is described in detail in section 2.6 and 2.6.2. The concept of relaxation is also discussed in the context of superparamagnetism in section 2.6.1. When a magnetic field is applied to a ferrofluid sample the magnetic moments of the individual nanoparticles align with the applied field. When this field is removed the magnetic moments revert to their original chaotic state. One can say that the magnetisation 'relaxes' back to its equilibrium state or value. The relaxation can take place via either Brownian or Néel mechanisms or a combination of both. Each relaxation mechanism has a characteristic relaxation time. The relaxation times depend on a number of factors such as particle size, carrier liquid viscosity, and the composition and magnetic properties of the materials themselves. The information gleaned from the relaxation processes can be used to study and evaluate the magnetic properties of ferrofluids.

Section 2.4 and 2.5 deal with the complex magnetic susceptibility, $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ which is a method of viewing the response of the materials magnetisation to an applied field in the frequency domain. $\chi(\omega)$ is linked to the relaxation of the magnetisation in the time domain via the Fourier transform. $\chi(\omega)$ is also frequency dependent and can be split into real (reversible) and imaginary (loss) components.

Ferromagnetic resonance, which was introduced in chapter one, can take place in magnetic nanoparticles and ferrofluids. The resonance arises from the precession of magnetic moments about the total magnetic field which the moments experience. The total magnetic field experienced by the moments usually consists of an applied static field and an equivalent internal anisotropy field. The phenomenon of ferromagnetic resonance is indicated by the real component of $\chi(\omega)$ going negative and an absorption peak in the imaginary component of the magnetic susceptibility. Ferromagnetic resonance usually occurs in the microwave range. Magnetite based ferrofluids tend to exhibit a resonance at around 1 GHz, whilst cobalt or cobalt ferrite ferrofluid resonate at somewhere nearer 6 GHz. The theory of ferromagnetic resonance in ferrofluids is dealt with in section 2.7.

2.2 Single Domain Particles

As discussed in chapter 1, bulk ferromagnetic materials consist of magnetic domains in which all the atomic magnetic moments are aligned in the same direction due to quantum mechanical exchange forces. Therefore each magnetic domain is spontaneously magnetised in a given direction. The size of the domains is determined by the condition that the total free energy of the specimen should be minimised. Magnetic anisotropy impedes the formation of domain walls because the magnetic moment prefers to align along some crystallographic axis. This is in opposition to the exchange energy which tends to make domain walls larger because of the favourable alignment of parallel magnetic spins. A balance is struck between the competing forces at a critical domain size where the free energy is minimised. Because of this it is reasonable to assume that below a certain critical size, a ferromagnetic material will consist of a single magnetic domain. Frenkel and Dorfman [6] were the first to predict the existence of single domain particles. Raihker and Shliomis [7] calculated the critical size for a single domain particle of a ferromagnetic material to have a diameter of 30 nm. Anisotropy energy differs between different materials. Materials

with higher anisotropy energy will have larger critical diameters. For example, cobalt has larger anisotropy energy than magnetite, making it harder for domains to form. Aharoni and Shtrikman [8] calculated a critical diameter of 60 nm for cobalt nanoparticles. This would compare with the 30 nm critical size which is applicable to magnetite. A single domain particle is characterised by its saturation magnetisation, M_{sat} . The saturation magnetisation is the vector sum of all the atomic magnetic moments, m , over the volume of one domain (called the magnetic volume, v_m), so that

$$M_{sat} = m / v_m. \quad (2.2.1)$$

The single domain particles retain their spontaneous magnetisation at all temperatures below the Curie temperature which is the temperature at which all ferromagnetic materials become paramagnetic. Naturally the value of the Curie temperature differs from material to material. At absolute zero, the single domain is magnetised to saturation with perfect alignment of all atomic moments. At room temperature there is some thermal agitation which attempts to disorientate the moments so that they are no longer aligned. However the thermal agitation is weak in comparison to the exchange forces that align the atomic moments and as a result the spontaneous magnetisation of the domain is only slightly below the saturation value.

2.3 Anisotropy

The magnetisation vector within a single domain particle tends to align itself in certain preferential directions, giving rise to the phenomenon of anisotropy. There are two main types of anisotropy which will be discussed in this section. Namely crystalline anisotropy and shape anisotropy. The crystalline anisotropy arises from the spin orbit coupling of the electrons in a ferromagnetic crystal. The electron spins contribute mostly to the magnetism, whilst the electron orbits participate in bonding. Effectively the interaction of electron spins and orbits couples the atomic moment to the underlying crystalline lattice or structure. Hence the atomic moment prefers to lie along preferred or easy directions within the crystal. Shape anisotropy arises as the name would suggest, from the shape of the particle and is associated with the demagnetising fields within the particle. A third anisotropy mechanism also operates,

and that is the surface anisotropy. This only becomes important when the size of the nanoparticle is reduced such that the magnetic contributions from the surface of the particle become greater than those from the bulk of the particle. As stated previously in chapter one, ferromagnetism is a cooperative phenomenon, where the exchange interaction causes ferromagnetic coupling between adjacent atoms. For nanoparticles below a certain size range ($\sim d = 5\text{nm}$) the spontaneous magnetisation of the nanoparticle will decrease because there is a deficiency of neighbouring atoms at the surface site to ferromagnetically couple together.

All ferromagnetic materials are to some degree anisotropic. However some such as cobalt possess far greater anisotropy constants than that of magnetite or the ferrites.

2.3.1. Crystalline Anisotropy

The simplest form of anisotropy is that of uniaxial anisotropy in which the magnetic moment or magnetisation vector favours either of two opposite directions within the particle. These opposite directions form the easy axis. The energy of the particle depends partly on the direction of the magnetisation relative to the easy axis (figure 2.1). This energy is referred to as the anisotropy energy.

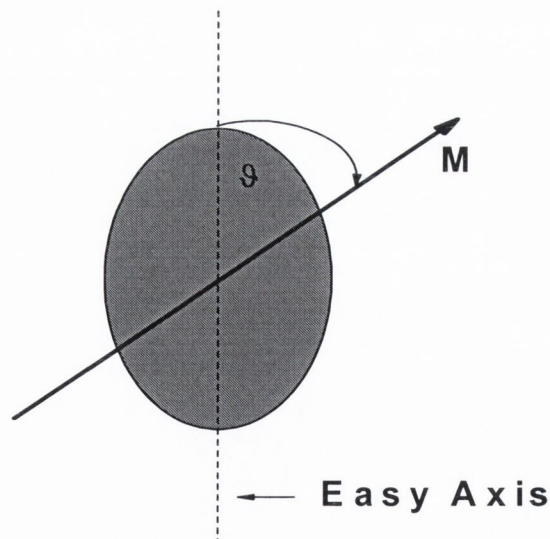


Figure 2.1: Ellipsoidal particle with uniaxial anisotropy.

For a uniaxial crystal, the major term in the anisotropy energy can be written as

$$U_A = K v_m \sin^2(\vartheta), \quad (2.3.1.1)$$

where ϑ is the angle between the magnetisation vector (or the magnetic moment) and the easy axis, K is the anisotropy constant also known as the anisotropy energy density and v_m is the particle volume. The lowest energy is attained when M lies along the easy axis, i.e. where $\vartheta = 0$ or π (figure 2.2). The maximum energy is at $\vartheta = \pi/2$. This acts as a potential barrier which the magnetic moment must surmount to jump to the other energy state at $\vartheta = 0$ or π .

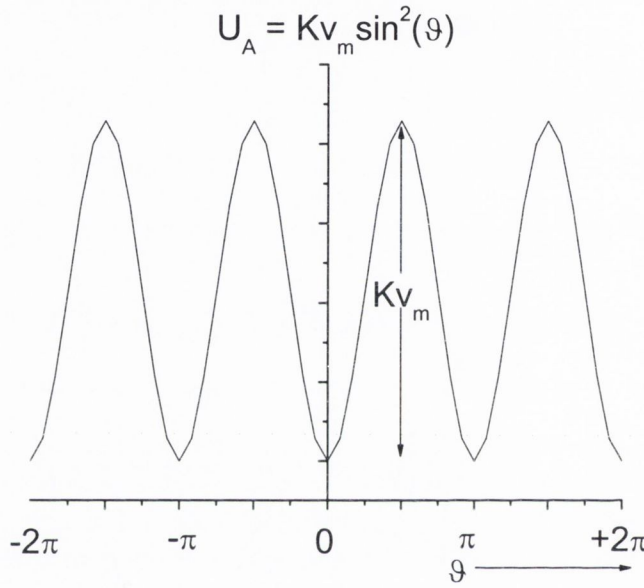


Figure 2.2: Anisotropy energy, H_A as a function of ϑ . Minima occur in the anisotropy energy at $\vartheta = 0$ and $\vartheta = \pm\pi$ and multiples of π . The maximum value of U_A occurs at multiples of $\pm \pi/2$ and this equals the barrier height Kv_m .

It is convenient to consider the effect of the anisotropy energy in terms of an equivalent internal magnetic field. The equivalent field is known as the anisotropy field, H_A (A/m). The torque exerted on the magnetic moment by the equivalent anisotropy field is defined as being equal to the torque exerted by the anisotropy energy i.e.

$$m \times H_A = \frac{\partial U_A}{\partial \vartheta}. \quad (2.3.1.2)$$

Knowing that $m = M_{sat} v_m$, equation (2.3.1.2) can be written as

$$M_{sat} v_m H_A \sin \vartheta = \frac{\partial U_A}{\partial \vartheta}. \quad (2.3.1.3)$$

Differentiating U_A in equation (2.3.1.1) with respect to ϑ gives

$$\frac{\partial U_A}{\partial \vartheta} = 2Kv_m \sin \vartheta \cos \vartheta. \quad (2.3.1.4)$$

Equating (2.3.1.3) and (2.3.1.4) gives

$$H_A = \frac{2K}{M_{sat}} \cos \vartheta. \quad (2.3.1.5)$$

From equation (2.3.1.5) above it can be noted that the equivalent anisotropy field is directly dependent on the anisotropy constant and on the angle that the magnetisation vector makes with the easy axis. Equation (2.3.1.5) represents the equivalent anisotropy field for a uniaxial particle and when the magnetic moment vector is pointing at an angle relative to the direction of H_A it will experience a torque which tries to align it with this field. When the anisotropy energy is large the magnetic moment will be closely aligned near to the easy axis or along it so that the angle ϑ becomes small and in the limit as $\vartheta \rightarrow 0$ then $\cos \vartheta \rightarrow 1$ so that equation (2.3.1.5) becomes

$$H_A = \frac{2K}{M_{sat}}, \text{ for small } \vartheta. \quad (2.3.1.6)$$

Equation (2.3.1.6) gives the maximum value of the magnetic field required to rotate the magnetic moment from one easy direction to the other, and this maximum gives the coercivity. Returning to the concept of the anisotropy energy barrier the parameter σ can be defined as the ratio of anisotropy energy to thermal energy

i.e.
$$\sigma = Kv_m / k_B T. \quad (2.3.1.7)$$

If the term Kv_m is large in comparison to the thermal energy then the magnetic moment will have difficulty overcoming the energy barrier and the moment can be considered to be stuck in a potential well. This leads to the magnetic moment being ‘blocked’. If enough thermal energy or heat is added to the system the term $k_B T$ becomes comparable to the anisotropy energy allowing the moment to jump over the potential barrier to another potential well. This process is shown in figures 2.3 (a) and (b). This process will become more important in subsequent sections of this chapter when superparamagnetism is discussed. The action of the magnetic moment switching between energy wells is the basis of the Néel relaxation mechanism.

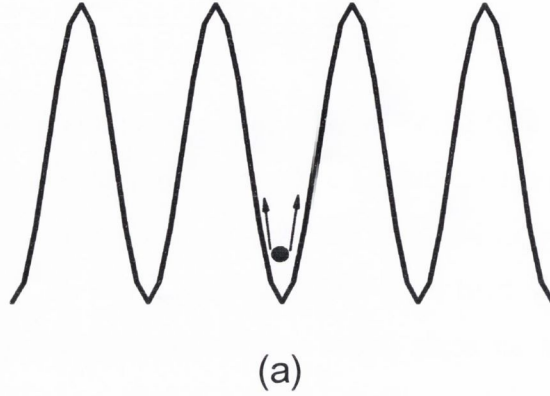


Figure 2.3 (a): Magnetic moment trapped in a potential well. The anisotropy energy barrier is large in comparison with the thermal energy. A large energy barrier can be a result of a high anisotropy constant or a large particle size. The magnetic moment is considered ‘blocked’ and does not possess enough energy to surmount the energy barrier.

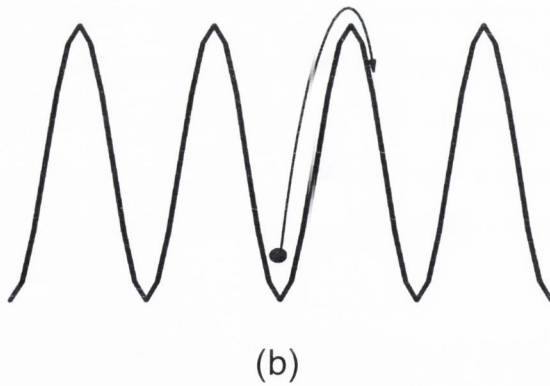


Figure 2.3 (b): If enough added thermal energy is added to the system, the thermal energy term, $k_B T$, becomes comparable to the anisotropy energy term. The magnetic moment now has enough energy to surmount the energy barrier and move to the next state of lowest potential. In actual fact the magnetic moment switches rapidly between the two energy wells.

Cubic anisotropy appears in cubic crystals where the following equation can be used as a first approximation for the anisotropy energy.

$$U_A = K_1 v_m (\cos^2 \vartheta_1 \cos^2 \vartheta_2 + \cos^2 \vartheta_2 \cos^2 \vartheta_3 + \cos^2 \vartheta_3 \cos^2 \vartheta_1), \quad (2.3.1.8)$$

where $\vartheta_1, \vartheta_2, \vartheta_3$ are the angles which the magnetisation vector makes relative to the three crystal axes.

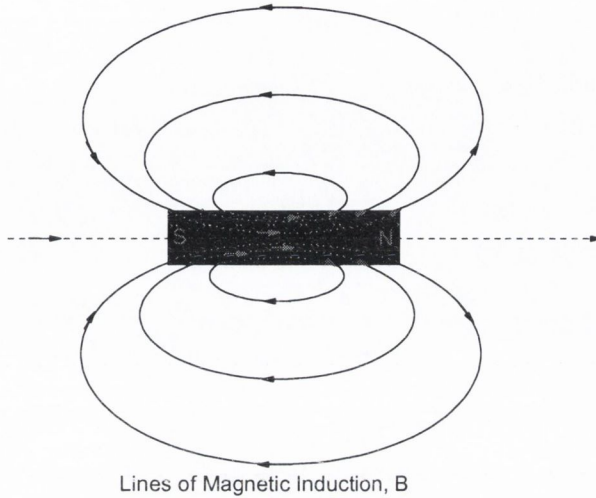


Figure 2.4: Lines of magnetic induction inside (Dashed lines) and outside (Solid black lines) a ferromagnetic bar magnet. Outside the magnet the lines of induction point from north to south. However inside the material the lines are orientated south to north due to the magnetisation of the ferromagnet.

2.3.2. Shape Anisotropy

Any non spherical particle shape will give rise to shape anisotropy. The shape anisotropy arises from the demagnetising fields within a particle. A magnetic material of finite length inside a magnetic field will have ‘magnetic poles’ near its ends which gives rise to another magnetic field opposing the applied field. This opposing field is the demagnetisation field and its strength depends on the geometry and magnetisation of the material. Consider the lines of magnetic induction of the bar magnet in figure (2.4). The magnetisation inside the ferromagnetic material, points from the South Pole to the North Pole. On the other hand the magnetic induction (B) or the magnetic field (H) outside the material points from the North Pole to the South Pole. In light of the fact that the magnetisation, M , and the magnetic field, H , point in different directions inside a magnetic material of finite length, it is possible to define a demagnetising field, H_d , which is present whenever magnetic poles are created

inside a material. The demagnetising field is proportional to the sample geometry and the magnetisation with

$$H_d = N_d M, \quad (2.3.2.1)$$

where N_d is a demagnetising factor which is calculated from the sample geometry.

For a finite length magnetic sample placed in a magnetic field a correction for the demagnetising field should be taken into account when calculating the true internal magnetic field in the material, i.e.

$$H_{in} = H - N_d M. \quad (2.3.2.2)$$

In ferrofluids the magnetic nanoparticles appear as a distribution of spheroidal shapes. The distribution of particle shapes can be well estimated by the normal or log-normal distributions, so that the majority of particles have spherical shapes while a minority have prolate or oblate ellipsoidal or long needle shapes. Spherical particles will have equal demagnetising factor in the x, y, and z directions, whilst an infinite cylinder magnetised longitudinally will have equal demagnetising factors in two directions but will have zero demagnetising factors in the other direction. The effect this has on shape anisotropy is shown in the following equations. Consider the prolate ellipsoid shown in figure (2.5). If the demagnetising factors are N_a and N_b in the direction of the major axis and in any direction perpendicular to the major axis respectively, then the demagnetising energy is

$$U_d = \frac{1}{2\mu_0} M_{sat}^2 v_m (N_a \cos^2 \vartheta + N_b \sin^2 \vartheta).$$

(2.3.2.3)

Differentiating with respect to ϑ gives after some manipulation

$$\frac{\partial U_d}{\partial \vartheta} = \frac{1}{\mu_0} M_{sat}^2 v_m (N_b - N_a) \sin \vartheta \cos \vartheta \quad (2.3.2.4)$$

equating with an equivalent magnetic field as before gives

$$H_A = \frac{1}{\mu_0} M_{sat} (N_b - N_a) \cos \vartheta. \quad (2.3.2.5)$$

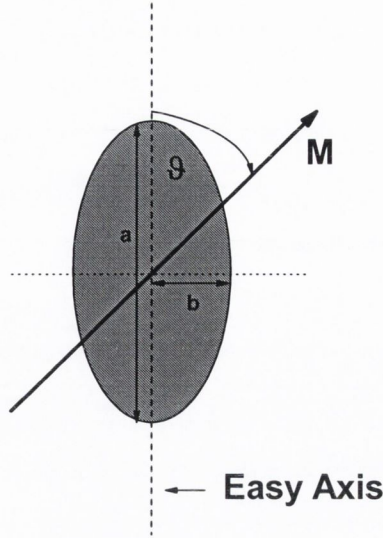


Figure 2.5: Prolate ellipsoid with shape anisotropy, with major axis along a , and minor axis along b .

For a general ellipsoid the demagnetising factors N_a, N_b, N_c , along the three principle axes are related by the expression $N_a + N_b + N_c = 1$. As previously stated spherical particles possess equal demagnetising factors along all three axes with $N_a = N_b = N_c = 1/3$. Therefore it is clear from equation (2.3.2.5) that spheres have no shape anisotropy. The maximum value of equation (2.3.2.5) is defined as the coercivity with

$$H_c = \frac{1}{\mu_0} M_{sat} (N_b - N_a). \quad (2.3.2.6)$$

For the infinite cylinder magnetised longitudinally $N_b = N_c = 1/2$ and $N_a = 0$, which results in a coercivity of $M_{sat} / 2\mu_0$. The infinite cylinder therefore possesses a large shape anisotropy. Because of the distribution of particle sizes in the ferrofluid the particles have a range of shape anisotropies from none at all to those of the infinite cylinder.

2.4. Theory of Debye Relaxation

In this section the basic theory of magnetic relaxation will be introduced. Relaxation can be explained in the following context. Upon the application of a magnetic field to a ferrofluid sample, the magnetic moments of the individual magnetic nanoparticles align themselves along the applied field direction. Thus it can

be said that the ferrofluid is magnetised (or polarised) along the applied field. If the applied field is then removed, the particles must return to their original, unmagnetised state. This is the phenomenon of relaxation. The time it takes for the relaxation to occur depends on a number of factors such as the particle size, anisotropy, and carrier fluid viscosity. In the following treatment of Debye relaxation the Brownian motion of the individual nanoparticles in their carrier fluid is considered. This theory was constructed by Debye [9,10] originally for the case of polar liquids, by modifying Einstein's theory [11,12,13] of translational Brownian motion.

The result of Einstein's theory can also be arrived at by a method first used by Langevin [12]. Langevin's treatment of Brownian motion is considered more straight forward and easier to understand than that of Einstein because it deals directly with the time evolution of the *random variable* describing the process of Brownian motion rather than the time evolution of the underlying *probability distribution* describing the motion. For completeness both methods of describing the translational Brownian motion will be presented here, starting with the theory of Einstein. However, only the solution to the Langevin equation will be presented.

Einstein theorised that a particle in a fluid without friction, which undergoes collisions with other molecules, should experience a change in its velocity. However, if the fluid possesses a large viscosity, then the change in velocity of the particle is quickly dampened, and the overall result is that the particle experiences a change in displacement. Thus, Einstein theorised that the net effect of collisions is that the particle experiences random jumps in position rather than velocity. Supposing that each jump in position was small, he constructed a partial differential equation for the probability distribution of the displacement in one dimension [13]. This type of equation has become known as the *Fokker – Planck equation*. From the solution of the Fokker-Planck equation, he was able to show that the mean square displacement of a Brownian particle should increase with time. It is possible to derive a specialised form of the Fokker-Planck equation, known as the Smoluchowski equation.

Suppose there are W Brownian particles, or W realisations of the random variable describing the trajectory of a Brownian particle, suspended in a liquid per unit volume between r and $r + dr$ at a time t . It is also supposed that these particles are subject to an external force which is the negative gradient of a potential $V(r)$ such that

$$F = -\nabla V(r). \quad (2.4.1)$$

Considering a volume v , in the liquid bounded by a closed surface S , let us calculate the drift current of particles crossing S due to the force F . Using Gauss's divergence theorem it is possible to arrive at the continuity equation

$$\frac{\partial W}{\partial t} + \nabla \bullet J_d = 0, \quad (2.4.2)$$

where J_d is the drift current.

The drift current can also be written as the product of W and the drift velocity of a particle moving in the liquid, v , so that

$$J_d = W v. \quad (2.4.3)$$

The force, F , acting on the particle can also be expressed as the product of the drift velocity, v , and the drag coefficient of a particle, ζ , giving

$$F = \zeta v. \quad (2.4.4)$$

Combining equations (2.4.1), (2.4.3) and (2.4.4) leads to an expression for the drift current with

$$J_d = -\frac{W}{\zeta} \nabla V \quad (2.4.5)$$

The above analysis neglects the effect of the Brownian movement due to the thermal agitation of the particles. To take this into account it is necessary to include a diffusive term in the expression for the total current, so that $J_{total} = J_d + J_{diff}$. An expression for J_{diff} can be written with

$$J_{diff} = -D \nabla W, \quad (2.4.6)$$

where D is the diffusion coefficient.

The continuity equation can then be written as

$$\frac{\partial W}{\partial t} = \nabla \bullet \left(D \nabla W + \frac{W}{\zeta} \nabla V \right), \quad (2.4.7)$$

which is a specialised form of the Fokker-Planck equation called the *Smoluchowski equation*. Einstein solved the above equation for both the translational case and this

solution can be extended to the rotational case about the diameter of a particle. He obtained the mean square translational displacement of a particle to be $\langle \Delta x^2 \rangle = 2D\tau$, and the mean square rotational displacement to be $\langle \Delta \theta^2 \rangle = 2D\tau$, where D is the diffusion coefficient and is found to be equal to $k_B T / \zeta$ where $\zeta = 6\pi\eta_h r_p$ for the translational case and $\zeta = 8\pi\eta_h r_p^3$ for the rotational case of a sphere rotating about a fixed axis in a viscous liquid. η_h and r_p are the hydrodynamic viscosity and particle radius, respectively. The above results for the diffusion coefficient and the mean square displacement are difficult to arrive at. The much more convenient formulation of the Langevin equation according to Newton's laws of motion will now be used to treat the problem of Brownian motion.

To begin his formulation Langevin wrote down the equation of motion of the Brownian particle according to Newton's second law of motion under the assumption that the Brownian particle experiences two forces which are:

- (i): A viscous drag $-\zeta \dot{x}(t)$ which represents a dynamical friction experienced by the particle. x is the displacement and ζ is the coefficient of friction.
- (ii): A white noise force $F(t)$ which is due to the impacts of the molecules of the liquid on the particle.

Thus the equation of motion according to Newton's second law is

$$m \frac{d^2 x}{dt^2} = -\zeta \frac{dx(t)}{dt} + F(t). \quad (2.4.8)$$

Equation (2.4.8) can also be written as

$$m \ddot{x} = -\zeta \dot{x} + F(t). \quad (2.4.9)$$

The frictional term

$$\zeta \dot{x}(t)$$

is assumed to be governed by Stokes' law which states that the frictional force decelerating a spherical particle of radius, r , and mass, m , is given by

$$\zeta \dot{x} = 6\pi\eta_h r_p \dot{x} \quad (2.4.10)$$

The following assumptions are made for the fluctuating part, $F(t)$.

- (i): That $F(t)$ is statistically independent of x .

(ii): That $F(t)$ varies extremely rapidly compared with the variations of $x(t)$. (i.e. $F(t)$ is a white noise driving force). This would imply that each collision is almost instantaneous.

It is also assumed that the average

$$\overline{F(t)} = 0, \quad (2.4.11)$$

holds because $F(t)$ is so irregular. The overbar in the above equation denotes the statistical average over an ensemble of particles. This rapid variation can be expressed by [12]

$$\overline{F(t)F(t')} = 2\zeta k_B T \delta(t - t') \quad (2.4.12)$$

where δ is the Dirac delta function, t and t' are distinct times and $2\zeta k_B T$ is the spectral density. Following this, Langevin derived a formula for the mean square displacement of the Brownian particle (translational case). He started by multiplying across equation (2.4.9) by $x(t)$ yielding

$$m \ddot{x} x = -\zeta \dot{x} x + F(t)x. \quad (2.4.13)$$

Noting that

$$\dot{x} x = \frac{1}{2} \frac{d}{dt} x^2$$

and

$$\ddot{x} x = \frac{1}{2} \frac{d}{dt} \left(\frac{d(x^2)}{dt} \right) - \dot{x}^2,$$

equation (2.4.13) rewritten as

$$\frac{m}{2} \frac{d}{dt} \left(\frac{d(x^2)}{dt} \right) - m \dot{x}^2 = -\frac{\zeta}{2} \frac{d(x^2)}{dt} + F(t)x. \quad (2.4.14)$$

However equation (2.4.14) only refers to a single Brownian particle. To take account for the realistic case where there are many millions of Brownian particles present, it is necessary to average over a large number of particles which all start with the same velocity so that,

$$\frac{m}{2} \frac{d}{dt} \left(\frac{d(\overline{x^2})}{dt} \right) - m \overline{\dot{x}^2} = -\frac{\zeta}{2} \frac{d(\overline{x^2})}{dt} + \overline{F(t)x}. \quad (2.4.15)$$

It is now possible to assume that the term containing the average of $F(t)$ and x vanishes because of the irregular variations of $F(t)$. Another way of stating this is to say that the random force and the displacement x are completely uncorrelated. When

the velocity process reaches its equilibrium value, the Maxwellian distribution holds so that the mean kinetic energy of the Brownian particle reaches a value

$$\frac{1}{2}m\overline{\dot{x}^2} = \frac{1}{2}k_B T, \quad (2.4.16)$$

where T is the absolute temperature and k_B is the Boltzmann constant. Substituting equation (2.4.16) into equation (2.4.15) and taking into account the uncorrelation of $F(t)$ with x , equation (2.4.15) becomes

$$\frac{m}{2} \frac{d}{dt} \left(\frac{d\overline{x^2}}{dt} \right) + \frac{\zeta}{2} \frac{d\overline{x^2}}{dt} = k_B T. \quad (2.4.17)$$

Using the change of variable

$$u = \frac{d\overline{x^2}}{dt}, \quad (2.4.18)$$

equation (2.4.17) then reads as

$$\frac{m}{2} \frac{du}{dt} + \frac{\zeta}{2} u = k_B T, \quad (2.4.19)$$

which has a solution

$$u = \frac{2k_B T}{\zeta} + C e^{-a}, \quad a = \frac{t\zeta}{m}, \quad (2.4.20)$$

where C is a constant of integration. The exponential term in equation (2.4.20) may be neglected if t is very large in comparison to ζ/m , so that

$$u = \frac{d\overline{x^2}}{dt} = \frac{2k_B T}{\zeta}. \quad (2.4.21)$$

It should be noted that omitting the exponential terms in (2.4.20) is tantamount to ignoring the effect of the inertia of the Brownian particle. Integrating equation (2.4.21) from $t = 0$ to $t = t$ gives

$$\overline{x^2} - \overline{x_0^2} = \frac{2k_B T t}{\zeta}. \quad (2.4.22)$$

The initial conditions require that x_0 is zero at $t = 0$ and because x is small it is possible to write $(\Delta x)^2$ instead of $\overline{x^2}$.

Finally, an equation for the mean square translational displacement of a Brownian particle can be written as

$$\overline{(\Delta x^2)} = \frac{2k_B T}{\zeta} t. \quad (2.4.23)$$

Equation (2.4.22) is the same as the equation for the mean square displacement as derived by Einstein. For the translational case, the drag coefficient, $\zeta = 6\pi\eta_h r_p$.

Langevin's treatment of the mean square displacement in the translational case can easily be extended to the case of rotational motion. The same procedure is followed as for the translational case except that now a single polar angle of a particle of mass, m , having moment of inertia, I_p , is considered so that the Langevin equation according to Newton's second law of rotational motion can be constructed giving,

$$I_p \frac{d^2 \vartheta}{dt^2} = -\zeta \frac{d\vartheta(t)}{dt} + F(t). \quad (2.4.24)$$

Maintaining the same assumptions with regard to the fluctuating force $F(t)$, its time average and its autocorrelation function, and following the steps taken between equation (2.4.13) and (2.4.21), an expression for the mean square rotational displacement of a Brownian particle is given as

$$\overline{(\Delta \vartheta^2)} = \frac{2k_B T}{\zeta} t. \quad (2.4.25)$$

In this case the drag coefficient is for the case of a sphere rotating about a fixed axis in a viscous liquid so that $\zeta = 8\pi\eta_h r_p^3$.

The Debye theory of dielectric relaxation has its starting point in the Fokker Planck equation for the rotational Brownian motion of a sphere in space. The inertia of the sphere is neglected. It is possible to arrive at an equation to describe this process by replacing the Cartesian coordinates of equation (2.4.7) by the corresponding spherical polar coordinates for the rotational case.

As in equation (2.4.3) the current density in the absence of thermal agitation is the drift current J_d where

$$J_d = Wv,$$

$$\text{with} \quad v = \dot{u} = \frac{du}{dt}, \quad (2.4.26)$$

$$\text{so that} \quad J_d = W du/dt, \quad (2.4.27)$$

and $W(\vartheta, \varphi, t)$ is the density of electric dipole moment orientations on a sphere of unit radius. The unit vector $\hat{u}$ is orientated with polar angle ϑ and azimuth φ , with $u_x = \sin \vartheta \cos \varphi$, $u_y = \sin \vartheta \sin \varphi$, and $u_z = \cos \vartheta$. Consider an externally applied electric field $E(t)$ which, as with the external force of equation (2.4.1), is the negative potential of a scalar potential V such that

$$E(t) = -\nabla V = -\frac{\partial V}{\partial \vartheta} e_\vartheta - \frac{1}{\sin \vartheta} \frac{\partial V}{\partial \varphi} e_\varphi, \quad (2.4.28)$$

where e_ϑ and e_φ are unit vectors in the direction of increasing ϑ and φ .

Rewriting equation (2.4.4) as

$$E(t) = \zeta v = \zeta du/dt \quad (2.4.29)$$

and inserting equation (2.4.29) into (2.4.3) gives

$$J_d = W(\varphi, \vartheta) E(t)/\zeta, \quad (2.4.30)$$

which can be written using equation (2.4.28) as

$$J_d = \frac{-1}{\zeta} \left\{ \frac{\partial V}{\partial \vartheta} e_\vartheta + \frac{1}{\sin \vartheta} \frac{\partial V}{\partial \varphi} e_\varphi \right\} W(\vartheta, \varphi). \quad (2.4.31)$$

Once more it becomes necessary to take account of the effects of thermal agitation so that we introduce a diffusion current, J_{diff} , so that as with equation (2.4.6),

$$J_{diff} = -D \nabla W, \quad (2.4.32)$$

where D is the diffusion coefficient. The effect of J_{diff} is to make the density of dipole moment orientations more uniform.

In polar coordinates equation (2.4.32) becomes

$$J_{diff} = -D \left(\frac{\partial W}{\partial \vartheta} + \frac{\partial W}{\partial \varphi} \right). \quad (2.4.33)$$

The components of the total current density, $J_{tot} = J_d + J_{diff}$, can be written in terms of their components along ϑ , and φ as

$$J_\vartheta = - \left\{ \frac{W}{\zeta} \frac{\partial V}{\partial \vartheta} e_\vartheta + D \frac{\partial W}{\partial \vartheta} \right\}, \quad (2.4.34)$$

and

$$J_\varphi = - \left\{ \frac{W}{\zeta \sin \vartheta} \frac{\partial V}{\partial \varphi} + \frac{D}{\sin \vartheta} \frac{\partial W}{\partial \varphi} \right\}. \quad (2.4.35)$$

The continuity equation is as equation (2.4.2) with the divergence of the current density,

$$\nabla \bullet J = \frac{1}{\sin \vartheta} \left\{ \frac{\partial}{\partial \vartheta} (J_\vartheta \sin \vartheta) + \frac{\partial J_\varphi}{\partial \varphi} \right\}, \quad (2.4.36)$$

so that the Fokker Planck equation in spherical coordinates can be written down with

$$\begin{aligned} \frac{\partial W}{\partial t} = D \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial W}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 W}{\partial \varphi^2} \right] + \\ \frac{1}{\zeta} \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta W \frac{\partial V}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial}{\partial \varphi} \left(W \frac{\partial V}{\partial \varphi} \right) \right]. \end{aligned} \quad (2.4.37)$$

In statistical equilibrium, W must reduce to the Maxwell-Boltzmann distribution which is

$$W_0 = A \exp \left\{ \frac{-V(\vartheta, \varphi)}{k_B T} \right\}. \quad (2.4.38)$$

Substituting equation (2.4.38) into equation (2.4.37) yields after some manipulation the diffusion coefficient which is as before, with $D = k_B T / \zeta$.

The Debye relaxation time τ_d can now be defined so that

$$\tau_d = \zeta / 2k_B T. \quad (2.4.39)$$

Equation (2.4.37) can now be rewritten as

$$\begin{aligned} 2\tau_d \frac{\partial W}{\partial t} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial W}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 W}{\partial \varphi^2} + \\ \frac{1}{k_B T} \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta W \frac{\partial V}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial}{\partial \varphi} \left(W \frac{\partial V}{\partial \varphi} \right) \right]. \end{aligned} \quad (2.4.40)$$

Debye adapted the above equation to the case of a uniform applied electric field E along the z axis with $V(\vartheta, \varphi) = V(\vartheta) = -\mu_e E \cos \vartheta$, where μ_e is an electric dipole moment.

Equation (2.4.40) becomes

$$\frac{\partial W(\vartheta, t)}{\partial t} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \left(\frac{k_B T}{\zeta} \frac{\partial W(\vartheta, t)}{\partial \vartheta} + \frac{\mu_e E}{\zeta} \sin \vartheta W(\vartheta, t) \right) \right] \quad (2.4.41)$$

which is the original equation obtained by Debye [10]. This is simply the original Smoluchowski equation (equation (2.4.7)) written in polar coordinates. The general solution to equation (2.4.41) is given by the Legendre polynomials [16] such that

$$W(\vartheta, t) = \sum_{n=0}^{\infty} a_n(t) P_n(\cos \vartheta), (n = 0, 1, 2, \dots), \quad (2.4.42)$$

where P_n are the Legendre Polynomials and the $a_n(t)$ are functions to be determined. Generally speaking for the case of dielectric relaxation (and of course magnetic relaxation), only the linear approximation to the solution to equation (2.4.41) is considered. Thus for the case when a steady field is suddenly switched off at time $t = 0$ (after-effect solution) it can be assumed that W has the form

$$W(\vartheta, t) = A \left(1 + \frac{\mu_e E_0}{k_B T} g(t) \cos \vartheta \right), \quad (2.4.43)$$

where $E = E_0$. Substituting equation (2.4.43) into equation (2.4.41) yields

$$W(\vartheta, t) = A \left(1 + \frac{\mu_e E_0}{k_B T} \exp \left(\frac{-2k_B T}{\zeta} t \right) \cos \vartheta \right), \quad (2.4.44)$$

whilst the mean dipole moment is given as

$$\mu_e \langle \cos \vartheta \rangle = \mu_e \frac{\int_0^{2\pi} \int_0^\pi W(\vartheta, t) \cos \vartheta \sin \vartheta d\vartheta d\varphi}{\int_0^{2\pi} \int_0^\pi W \sin \vartheta d\vartheta d\varphi} = \frac{\mu_e E_0}{3k_B T} \exp \left\{ \frac{-2k_B T}{\zeta} t \right\}. \quad (2.4.45)$$

A similar equation for the case of the mean dipole moment under the action of an alternating electric field may be derived, so that $E = E_0 e^{i\omega t}$.

The mean dipole moment is then given as

$$\mu_e \langle \cos \vartheta \rangle = \frac{\mu_e^2}{3k_B T} \frac{E_0}{1 + \omega^2 \tau_d^2} [(\cos \omega \tau_d + \omega \tau_d \sin \omega \tau_d) + i(\sin \omega \tau_d - \omega \tau_d \cos \omega \tau_d)]. \quad (2.4.46)$$

It is possible to extract the alternating field in the above equation and rewrite so that

$$\mu_e \langle \cos \vartheta \rangle = \frac{\mu_e^2}{3k_B T} \frac{1 - i\omega \tau_d}{1 + \omega^2 \tau_d^2} E_0 \exp \{i\omega t\}. \quad (2.4.47)$$

This is the mean dipole moment for a single Brownian particle. For a realistic system account must be taken for an extremely large number of particles, say N per unit volume. Multiplying equation (2.4.47) across by N gives the polarisation of a polar liquid with

$$P(\omega) = P'(\omega) - iP''(\omega) = N\mu_e \langle \cos \vartheta \rangle = \frac{N\mu_e^2}{3k_B T} \frac{1 - i\omega\tau_d}{1 + \omega^2\tau_d^2} E_0 \exp\{i\omega t\}. \quad (2.4.48)$$

From equations (2.4.46) and (2.4.48) we notice a difference in phase between $N\mu_e \langle \cos \vartheta \rangle$ and the alternating field. The imaginary or quadrature component of the polarisation lags the applied field by $\pi/2$ radians and is denoted by $P''(\omega)$, whilst the real component of the polarisation, $P'(\omega)$ is in phase with the applied field.

It is possible to define the electric susceptibility, which is the amount of polarisation induced by an applied field, by dividing across equation (2.4.48) by the electric field, giving

$$\chi_e(\omega) = \chi_e'(\omega) - i\chi_e''(\omega) = \frac{P(\omega)}{\varepsilon_0 E_0 \exp\{i\omega t\}} = \frac{N\mu_e^2}{3\varepsilon_0 k_B T} \frac{1 - i\omega\tau_d}{1 + \omega^2\tau_d^2} = \frac{N\mu_e^2}{3\varepsilon_0 k_B T} \frac{1}{1 + (i\omega\tau_d)},$$

where ε_0 is the permittivity of free space. (2.4.49)

The relative complex electric permittivity can also be defined as

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \chi_e(\omega) + 1 = \chi_e'(\omega) + 1 - i\chi_e''(\omega), \quad (2.4.50)$$

with

$$\varepsilon'(\omega) = \chi_e'(\omega) + 1, \quad \varepsilon''(\omega) = \chi_e''(\omega). \quad (2.4.51)$$

Thus the complex permittivity can be written in terms of the Debye dielectric with

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \frac{N\mu_e^2}{3\varepsilon_0 k_B T} \frac{1}{1 + (i\omega\tau_d)} + 1, \quad (2.4.52)$$

where

$$\varepsilon'(\omega) = \frac{N\mu_e^2}{3\varepsilon_0 k_B T} \frac{1}{1 + \omega^2\tau_d^2} + 1, \quad \varepsilon''(\omega) = \frac{N\mu_e^2}{3\varepsilon_0 k_B T} \frac{\omega\tau_d}{1 + \omega^2\tau_d^2}. \quad (2.4.53)$$

Equation (2.4.52) is the Debye equation defining the spectrum of dielectric permittivity. It describes what is known as anomalous dispersion, and is effectively the frequency response of the dielectric material. This is shown in figure 2.6.

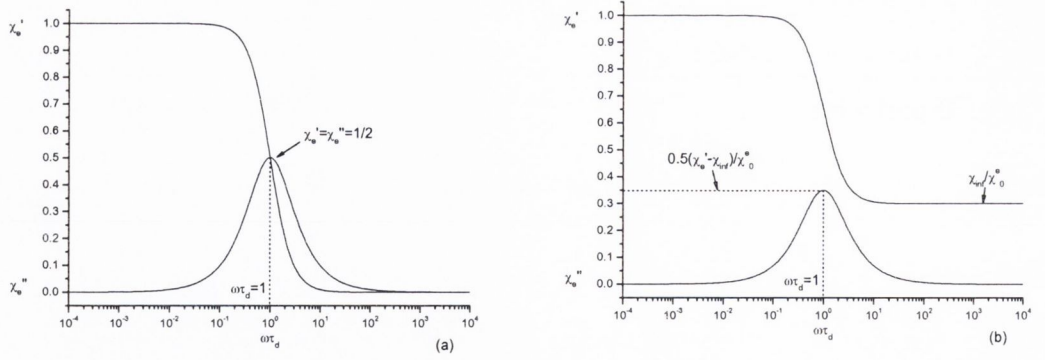


Figure 2.6 (a), (b): Debye type profile of the complex electric susceptibility showing real and imaginary components as a function of angular frequency ω . Plot (a) represents the Debye equation with $\chi_0 = 1$, and $\chi_\infty = 0$. The maximum of the imaginary part of the susceptibility occurs at $\omega\tau_d = 1$. Plot (a) is for the purely theoretical case of a single particle size, in reality a single particle size is rare, and a distribution of particle sizes is observed leading to a flattening in the susceptibility profile. Plot (b) accounts for the high frequency behaviour of the dielectric with the term χ_∞ . In this case $\chi_\infty = 0.3$.

At low frequencies the dipole moments are able to respond to the applied alternating electric field so that the polarisation (and the susceptibility) is in phase with the applied field. This leads to a large real component of susceptibility (χ_e') and a small or zero imaginary component (χ_e''). As the frequency increases the polarisation begins to lag the applied field, which leads to a decrease in χ_e' and an increase in χ_e'' . χ_e'' is at a maximum when the polarisation is completely out of phase with the applied field. As the frequency increases further both χ_e' and χ_e'' are unable to respond to the field and fall to zero. This type of response is known as a Debye type response and it can accurately describe the behaviour of a dielectric system at low frequencies.

At zero frequency or as close to zero as is realisable the static permittivity can be written as

$$\varepsilon(\omega \rightarrow 0) = \varepsilon_s = \frac{N\mu_e^2}{3\varepsilon_0 k_B T} + 1 \Rightarrow \chi_{e,0} = \frac{N\mu_e^2}{3\varepsilon_0 k_B T}. \quad (2.4.54)$$

In the derivation of equations (2.4.49) and (2.4.52) the effect of inertia on the system of dipoles was ignored. Because of this the derived equations are invalid for short observation times i.e. where the frequency is high, commonly in the MHz region and beyond. It takes time, τ_d , for the dipoles to reach equilibrium. If the observation time (or the period of the alternating electric field) is shorter than τ_d , then

the dipoles cannot follow the change in field. So now the Debye equation cannot accurately predict the high frequency behaviour of the system. To counteract this it is necessary to introduce a high frequency term, χ_∞^e . It is now possible to write down a corrected version of the Debye equation for the complex electric susceptibility with,

$$\chi_e(\omega) = \chi_e'(\omega) - i\chi_e''(\omega) = (\chi_0^e - \chi_\infty^e) \frac{1 - i\omega\tau_d}{1 + \omega^2\tau_d^2} + \chi_\infty^e, \quad (2.4.55)$$

where
$$\chi_0^e = \frac{N\mu_e^2}{3\varepsilon_0 k_B T} \quad (2.4.56)$$

is the static electric susceptibility.

2.5. Brownian Complex Susceptibility and Relaxation

In the preceding section an equation for the Debye-type complex electric permittivity and susceptibility has been derived, along with an expression for the Debye relaxation time. The same theory may be used to describe the magnetic case by changing the electric terms to their corresponding magnetic terms. In doing so, it is necessary to assume that the magnetic particle behaves as a rigid body meaning that the Néel relaxation mechanism is blocked, so that we only consider the Brownian relaxation.

By application of an alternating magnetic field,

$$h_a(t) = H_0 \exp\{i\omega t\}, \quad (2.5.1)$$

the magnetisation will be in accordance with 2.4.48

$$M(\omega) = M'(\omega) - iM''(\omega) = Nm \langle \cos \vartheta \rangle = \frac{Nm^2}{3k_B T} \frac{1 - i\omega\tau_B}{1 + \omega^2\tau_B^2} H_0 \exp\{i\omega t\}. \quad (2.5.2)$$

In equation (2.5.2) the symbol of electric dipole moment has changed to that of the magnetic moment, m , whilst the Debye relaxation time τ_d has changed to the Brownian relaxation time, τ_B where

$$\tau_B = \frac{\zeta}{2k_B T} = \frac{8\pi\eta_h r_p^3}{2k_B T} = \frac{4\pi\eta_h r_p^3}{k_B T} = \frac{3\eta_h v_p}{k_B T}, \quad (2.5.3)$$

where r_p , η_h are as before and v_p is the volume of a particle.

In magnetism, the equivalent quantity to the complex electric susceptibility is the complex magnetic susceptibility which can be written as

$$\chi(\omega) = \frac{dM(\omega)}{dh_a} = \chi'(\omega) - i\chi''(\omega) = \frac{(\chi_0 - \chi_{\text{inf}})}{1 + i\omega\tau_B} + \chi_{\infty}, \quad (2.5.4)$$

where

$$\chi'(\omega) = \frac{(\chi_0 - \chi_{\text{inf}})}{1 + \omega^2\tau_B^2} + \chi_{\text{inf}}, \quad \chi''(\omega) = \frac{(\chi_0 - \chi_{\text{inf}})\omega\tau_B}{1 + \omega^2\tau_B^2}, \quad (2.5.5)$$

with the static susceptibility

$$\chi_0 = \frac{dM(\omega \rightarrow 0)}{dh_a} = \frac{Nm^2}{3\mu_0 k_B T}. \quad (2.5.6)$$

In the above equation μ_0 is the free space permeability, which corresponds to the free space permittivity, ϵ_0 , of the dielectric case. The complex susceptibility is a measure of the frequency response of the magnetisation of a material to an applied alternating field.

The equivalent to the complex permittivity is the complex permeability, $\mu(\omega)$, given by

$$\mu(\omega) = \mu'(\omega) - i\mu''(\omega) = (\mu_s - \mu_{\infty}) \frac{1 - i\omega\tau_B}{1 + \omega^2\tau_B^2} + \mu_{\infty} = \frac{(\mu_s - \mu_{\infty})}{1 + (i\omega\tau_B)} + \mu_{\infty}, \quad (2.5.7)$$

where

$$\mu'(\omega) = \frac{(\mu_s - \mu_{\infty})}{1 + \omega^2\tau_B^2} + \mu_{\infty}, \quad \mu''(\omega) = \frac{(\mu_s - \mu_{\infty})\omega\tau_B}{1 + \omega^2\tau_B^2}, \quad (2.5.8)$$

with the static value of permeability

$$\mu_s = \frac{Nm^2}{3\mu_0 k_B T} + 1. \quad (2.5.9)$$

The profile of the above equations in the frequency domain is identical to those of figure (2.6) (a) and (b). However these graphs and equations describe the monodisperse case, where a single size species of magnetic nanoparticles is present in the ferrofluid. In reality this is not the case. Account must be taken of the polydispersity of the ferrofluid sample by including a distribution function in the equation for the susceptibility. A ferrofluid will generally contain a large number of particle sizes distributed about a mean, along with a far smaller number of oddly shaped particles and particles of extreme sizes. For this reason the normal and log normal distributions are commonly used to account for polydispersity and usually

give excellent results. It is also possible to apply other distribution functions such as the Nakagami or Frohlich distributions. The effect of a distribution function with increasing standard deviation, σ , is to broaden the susceptibility profile, so that the real component of susceptibility tends to decrease at a slower rate, and the magnitude of the imaginary component decreases.

To calculate the distributed susceptibility it is necessary to integrate over all particle sizes and probabilities of a particular particle size, to obtain

$$\chi(\omega) = \frac{\int_{r_{\min}}^{r_{\max}} \chi(\omega, r_p) P(r_p) dr_p}{\int_{r_{\min}}^{r_{\max}} P(r_p) dr_p}, \quad (2.5.10)$$

where $r_{\max}$ and $r_{\min}$ are the maximum and the minimum particle radii, respectively. For typical magnetic nanoparticles, these values are $r_{\max} = 10$ nm, and $r_{\min} = 1$ nm. Various different values of the standard deviation of the normal distribution are shown in figure 2.7 (a).

It is also possible to take account of particle size distribution using the modified Debye equation of Cole and Cole [15]. This equation is given by

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \frac{\chi_0 - \chi_\infty}{1 + (i\omega\tau_d)^{1-\alpha}} + \chi_\infty, \quad (2.5.11)$$

where α is the Cole-Cole parameter and it is possible to regard it as a distribution of relaxation times. Cole and Cole were concerned initially with the dielectric case, but it is possible, as before, to modify equation (2.5.11) to the magnetic case by letting $\tau_d = \tau_B$, and by using the static magnetic susceptibility, as in equation 2.5.12 below.

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \frac{\chi_0 - \chi_\infty}{1 + (i\omega\tau_B)^{1-\alpha}} + \chi_\infty, \quad (2.5.12)$$

α can take any value between zero and one. For $\alpha = 0$, equation (2.5.12) returns to the monodisperse case of equation (2.5.4). For the extreme value of $\alpha = 1$, the exponent $(1-\alpha)$ becomes equal to zero and the graph of the susceptibility becomes a straight line. This is never the case as it refers to an infinite distribution of particle sizes. A value of $\alpha = 0.5$ would correspond to a reasonably large distribution of particle radii, and from equation (2.5.3), relaxation times. Figure 2.7 (b) shows the effect of different value of α on the susceptibility spectrum.

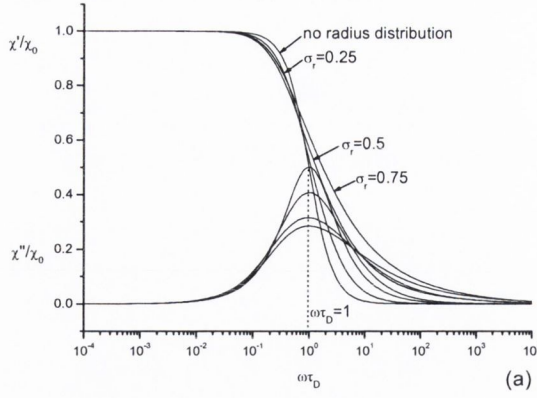


Figure 2.7 (a): Shows the effect of the normal distribution of the radius r_p on the complex susceptibility. With increasing σ the real component of susceptibility decreases slower, and the maximum of the imaginary component decreases as the curves broaden.

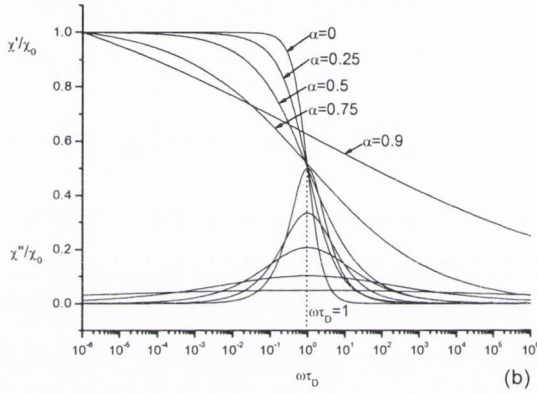


Figure 2.7 (b): The effect of the Cole-Cole parameter α . By increasing α , the curve becomes broader, similar to the case of (a) above, indicating a larger distribution of relaxation times.

Several other empirical expressions have been proposed to describe anomalous relaxation, the best known of which are the Cole-Davidson equation [16-18] where

$$\chi(\omega) = \frac{(\chi_0 - \chi_\infty)}{1 + (i\omega\tau_B)^\beta} + \chi_\infty, \quad 0 < \beta \leq 1 \quad (2.5.13)$$

and the Havriliak-Negami equation, which is a combination of the Cole-Cole and Cole-Davidson equations giving

$$\chi(\omega) = \frac{(\chi_0 - \chi_\infty)}{[1 + (i\omega\tau_B)^\alpha]^\beta} + \chi_\infty. \quad (2.5.14)$$

2.6 Equations of motion of the magnetization vector.

In the previous section the rotational Brownian motion of a spherical particle in the context of the Fokker-Planck and Smoluchowski equations was considered, and its response to an applied force leading to the Debye equation for dielectric relaxation, with the characteristic Debye relaxation time. These equations were then adopted for the case of N magnetic nanoparticles in a ferrofluid. In doing so, it was presumed that the magnetic moment vector was ‘blocked’, and hence the magnetic particle behaved as a rigid body. In the following sections the magnetic moment will be considered to be ‘unblocked’ and free to rotate or deviate independently of the particle itself. The independent internal rotation of the magnetic moment vector, m , gives rise to another relaxation effect, called the Néel relaxation. The Néel relaxation is dependent on the ratio $\sigma = K_V m / k_B T$. It can be considered in the simplest sense as a kind of switching action. When σ is large the probability is that a switch in moment orientation is low, and when σ is small there is a significant or large probability that the moment will switch direction. It will be discussed in detail in section 2.6.1.

It is also possible for the magnetic moment and hence the magnetisation of a ferrofluid to undergo precession about an effective magnetic field (comprising of the internal magnetic field, H_A , and/or a parallel applied static field, H_S). When a small alternating magnetic field is applied perpendicular to the magnetisation, the magnetisation is seen to resonate and absorb energy from the alternating field at a certain frequency. The starting point in the description of the precessional and Néel behaviour of the magnetic moment is the simple gyromagnetic equation of motion for an individual electron (equation 1.15).

Equation 1.15 states that the rate of change of an atomic magnetic moment is equal to a constant times the cross product of the magnetic moment and an applied magnetic field, H , where the constant is, γ , the gyromagnetic ratio i.e.

$$\dot{m} = \gamma(m \times H). \quad (2.6.1)$$

The same equation can be used to describe the precession of a single domain magnetic nanoparticle about an applied field, H . Since the magnetisation vector, M , is in the same direction as the moment, m , we may substitute M for m , to give

$$\dot{M} = \gamma(M \times H). \quad (2.6.2)$$

Equation (2.6.2) describes the motion of the magnetisation vector in the absence of damping. In reality the observable behaviour of the magnetisation vector is of alignment with the field, H . The alignment is due to the collisions between precessing electrons within the particle, which gives rise to a damping effect. To take account of this, Landau and Lifshitz [19] proposed the following equation for the motion of the magnetisation vector in the presence of damping

$$\dot{M} = \gamma(M \times H) + \frac{\alpha\gamma}{M_{sat}}(M \times H) \times M, \quad (2.6.3)$$

where α is a dimensionless damping parameter, which typically has a value of between 0.01 and 0.1 for ferromagnets [20,21-31]. γ and M_{sat} are the gyromagnetic ratio and the saturation magnetisation as before. The second term on the right hand side of equation (2.6.3) predicts the decay of the precessional motion of M about H , until M and H are aligned. The Landau-Lifshitz equation comprises a precessional component plus a decay component.

Another equation which can be used to describe the equation of motion of the magnetisation vector is that proposed by Gilbert [22]. Gilbert proposed an equation describing the dynamic behaviour of M which incorporated the damping of the precessional motion by a term which was proportional to the rate of change of the magnetisation vector. He constructed a gyromagnetic equation which had the form of γ times the cross product of M with an effective field. The effective field consisted of a conservative part, $H_{cons} = -\partial_M U$ and a dissipative part, $-\eta dM/dt$. Gilbert's equation is then given as

$$\frac{dM}{dt} = \gamma M \times \left(-\frac{\partial U}{\partial M} - \eta \frac{dM}{dt} \right), \quad (2.6.4)$$

where

$$\partial_M U = \frac{\partial U}{\partial M} = \frac{\partial}{\partial M_x} i + \frac{\partial}{\partial M_y} j + \frac{\partial}{\partial M_z} k. \quad (2.6.5)$$

is the derivative of the anisotropy magnetic energy density U with respect to the coordinates of M . Brown [23] used equation (2.6.4) as the starting point in his treatment of the dynamic behaviour of M . It is possible to write equation (2.6.4) as an explicit equation for dM/dt [24] so that

$$\dot{M} = g' M_{sat} (M \times H) + h' (M \times H) \times M, \quad (2.6.6)$$

where

$$g' = \frac{\gamma}{(1 + \alpha^2)M_{sat}}, \quad h' = \frac{\alpha\gamma}{(1 + \alpha^2)M_{sat}} = \alpha g', \quad \alpha = \eta\gamma M_{sat}. \quad (2.6.7)$$

The factor h' is also known as the rotary mobility factor and has units of inverse viscosity. By inspection, equation (2.6.7) has the same form as the Landau-Lifshitz equation. It is possible to write the Landau-Lifshitz equation directly from equation (2.6.6) by taking the damping parameter, α , as being very small, so that $\alpha \ll 1$.

By a similar process to that described in section 2.4, Brown was able to derive the Fokker-Planck equation for the density of magnetic moment orientation from equation (2.6.6). The Fokker-Planck equation is then given as [12]

$$\frac{\partial W}{\partial t} = g' \hat{m} (\nabla U \times \nabla W) + h' \nabla \bullet (W \nabla U) + D' \nabla^2 W, \quad (2.6.8)$$

where $\hat{m}$ is a unit vector in the direction of m , and $W(\vartheta, \varphi, t)$ is the density of magnetic moment orientations. D' in (2.6.8) above is the diffusion coefficient. The term multiplied by g' is the precessional term which gives rise to ferromagnetic resonance, whilst the term with h' is the relaxation or alignment term which predicts a decay of the precessional motion of m about the effective field with time constant

$$\tau_0 = \frac{1}{\alpha \omega_{pre}}, \quad (2.6.9)$$

where ω_{pre} is the angular frequency of free precession without damping. If at instant $t = 0$ the vector M deviates from H by an angle θ_0 then the angle between M and H vanishes as

$$\theta(t) = \theta_0 \exp(-t / \tau_0) \quad (2.6.10)$$

For a ferromagnet with low damping, say $\alpha = 0.01$, $\omega_{pre} \tau_0 = 100$ which means that during the relaxation time, τ_0 , the magnetic moment makes one hundred rotations about the effective field.

Following from equation (2.6.8) the diffusion coefficient, D' is given as [12] the mobility factor times the thermal energy per volume, i.e.

$$D' = \frac{\alpha \gamma k_B T}{(1 + \alpha^2) M_{sat} v_m} = \frac{h' k_B T}{v_m}. \quad (2.6.11)$$

For very low potential barriers, i.e. $\sigma \ll 1$, the magnetic moment m will rotate freely with internal diffusion time

$$\tau_d' = \frac{1}{2D'} = \frac{(1 + \alpha^2)M_{sat}v_m}{2\alpha\gamma k_B T} = \frac{v_m}{2h'k_B T}. \quad (2.6.12)$$

In the limits of low ($\alpha \rightarrow 0$) and of high ($\alpha \rightarrow \infty$) damping, the internal diffusion time approaches infinity and alignment of m with the field cannot take place. The reason for this, in the case of low damping, is because of the infinitely persisting undamped precessional motion, and for high damping, because of the absence of all motion, due to the mobility of m being zero. It must be noted that it is important not to confuse τ_d' with the Debye relaxation time. The magnetic viscosity can be defined as

$$\eta_m = \frac{(1 + \alpha^2)M_{sat}}{6\alpha\gamma} = \frac{1}{6h'}. \quad (2.6.13)$$

The magnetic viscosity can be thought of as the impediment to rotation of the magnetic moment within the particle. The magnetic viscosity is inversely proportional to the mobility factor. One would expect that for a high value of η_m the magnetic moment would have difficulty switching direction and hence have a low mobility. In this case the magnetic moment would have to surmount a large barrier height. In the opposite case, where η_m is low, and the mobility high, the magnetic moment will have little difficulty switching directions and surmounting the energy barrier.

2.6.1. Parallel, perpendicular and effective relaxation times

As stated previously, the Néel mechanism of approaching thermal equilibrium (relaxation) is where the magnetic moments within the particles switch direction from one energy minimum over a potential barrier to the other energy minimum. The energy minima arise from the particles anisotropy (discussed in section 2.3) so that in the case of isotropic particles there is no energy barrier to rotation and the moments are free to rotate with internal diffusion time, τ_d' . However for anisotropic particles the moments have to surmount the anisotropy energy barrier which is equal to Kv_m . The potential wells of figure 2.3 are adapted in figure 2.8 to the switching of the magnetic moment. The probability of the magnetic moment reversing is approximately proportional to $\exp(-\sigma)$. The relaxation time proposed by Néel is [3]

$$\tau_N = \tau_0 \exp \sigma, \quad (2.6.1.1)$$

where τ_0 is known as the Néel prefactor, and is equal to τ_d' where τ_d' is as before. Equation (2.6.1.1) can be inverted to give

$$f = f_0 \exp(-\sigma). \quad (2.6.1.2)$$

In this case f is the frequency of the switching or flipping of the magnetic moment. If the anisotropy barrier is large in comparison to the thermal energy, then the frequency of switching will be very small. In this case we can say that the magnetic moment is ‘blocked’. This is shown in figure 2.8 (a). However, if the thermal energy is not too small or comparable to the anisotropy barrier, it is possible for thermal fluctuation to cause the magnetic moment to reverse direction within the particle (figure 2.8 (b)). The potential barrier has very little effect on m and the Néel relaxation time is approximately the same as the internal diffusion time.

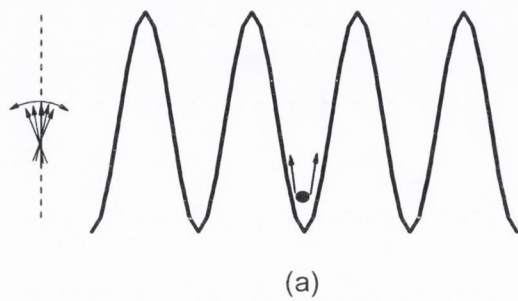


Figure 2.8 (a): Magnetic moment is ‘blocked’, and trapped within the potential well unable to surmount the energy barrier $K_V m$. The left most section of the figure indicates the motion of the magnetic moment. In its blocked state it cannot change direction within the particle and hence can only ‘twitch’ about its axis.

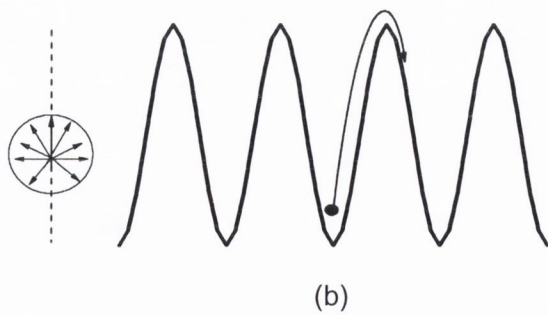


Figure 2.8 (b): Magnetic moment is free to travel between energy minima, and switch direction. In this case the thermal energy is comparable to the energy barrier $K_V m$. The left most section of the figure indicates the motion of the magnetic moment. In its unblocked state, it is free to change direction within the particle at will.

For large particles in which $\sigma \rightarrow \infty$, τ_N also tends to infinity meaning that the probability of a reversal in magnetisation is negligible. This means that there is a well defined particle size where a transition to stable behaviour occurs. This is important for magnetic particles that are used as memory elements.

Equation (2.6.1.1) is only a first approximation to the relaxation time. It deals only with a discrete orientation approximation i.e. Néel's theory considers only a single jump from one energy minimum to the other without allowing the magnetisation vector to spend some time in between these energy minima before jumping. Brown [23] realised that in the limit of $\sigma \rightarrow 0$ the Néel time of precession τ_0 should become equal to τ'_d . He suggested the following expressions for τ_N for low and high anisotropy barriers with

$$\tau_N = \tau'_d (1 + 2\sigma/5) \quad \text{for } \sigma \ll 1 \quad (2.6.1.3)$$

$$\tau_N = \tau'_d \frac{\sqrt{\pi}}{2\sigma^{3/2}} \exp(\sigma) \quad \text{for } \sigma > 2. \quad (2.6.1.4)$$

While Brown's equations provide an improvement on that of Néel, they are still invalid for values of σ between 1 and 2. For $\sigma = 0$ in equation (2.6.1.3) it is clear that τ_N does indeed equal τ'_d .

Based on the effective eigenvalue technique Coffey et al [25] arrived at the following approximate formula valid for all values of σ .

$$\tau_N = \frac{2\tau'_d(\sqrt{\sigma} - D(\sqrt{\sigma}))}{D(\sqrt{\sigma})(1 + 2\sigma) - \sqrt{\sigma}}, \quad \text{for all } \sigma \quad (2.6.1.5)$$

where $D(x)$ represents Dawson's integral which is defined as

$$D(x) = e^{-x^2} \int_0^x e^{t^2} dt. \quad (2.6.1.6)$$

Coffey [26] also derived an exact formula for τ_N for all values of σ , but the calculations for this particular equation are of considerable complexity, and in view of this, equation (2.6.1.5) is considered a satisfactory expression to be used in this work. The best approximate solution to be proposed so far has come from Cregg and Crothers [27] who proposed the following formula for τ_N

$$\tau_N = \frac{\tau'_d(e^\sigma - 1)}{2\sigma} \left(\frac{1}{1 + 1/\sigma} \sqrt{\frac{\sigma}{\pi}} + 2^{-\sigma-1} \right)^{-1}. \quad (2.6.1.7)$$

At this point, having described the Néel relaxation mechanism and the characteristic equations that describe it, it is convenient to consider the effect of an externally applied magnetic field, H_S superimposed on the effective field. The magnitude of H_S is usually comparable to the internal anisotropy or effective field, H_A . To simplify, we neglect the Brownian relaxation mechanism and consider only the Néel mechanism to be operating. Due to anisotropy, the internal relaxation will depend on the direction of the applied field relative to the easy axis. When the field is applied parallel to the easy axis there is a tendency for m to align parallel with the field. Hence the magnetisation in this case is called the parallel magnetisation, $M_{||}$. When the field is removed the magnetic moment attains thermal equilibrium (relaxes) by jumping over the anisotropy barrier, and the parallel magnetisation tends to zero with time constant $\tau_{||}$. The parallel time constant $\tau_{||}$ is equal to the Néel relaxation time, τ_N . The decay of the magnetisation in the parallel case can be written as

$$M_{||}(t) = M_{||}^0 \exp(-t/\tau_{||}) = M_{||}^0 \exp(-t/\tau_N). \quad (2.6.1.8)$$

However if a field H_S is applied perpendicular to the easy axis, the parallel relaxation time cannot be used to describe the decay of the magnetisation. In this case, the magnetic moment, m , deviates in order to respond to the applied field. The magnetisation in this case is denoted as the transverse magnetisation, $M_{\perp}$. The transverse magnetisation decays with the transverse time constant, $\tau_{\perp}$, when the field is suddenly removed. The transverse magnetisation is given by

$$M_{\perp}(t) = M_{\perp}^0 \exp(-t/\tau_{\perp}), \quad (2.6.1.9)$$

where the transverse time constant is given by Coffey et al [25] as

$$\tau_{\perp} = 2\tau_d' \left[\frac{D(\sqrt{\sigma})(2\sigma+1) - \sqrt{\sigma}}{D(\sqrt{\sigma})(2\sigma-1) + \sqrt{\sigma}} \right]. \quad (2.6.1.10)$$

In equation (2.6.1.10), $\tau_{\perp}$ decreases with increasing σ . For $\sigma \rightarrow 0$, $\tau_{\perp} \rightarrow \tau_d'$ and for $\sigma \rightarrow \infty$, $\tau_{\perp} \rightarrow \tau_d' / \sigma$. This behaviour is opposite to that of $\tau_{||}$ or τ_N which increase exponentially with increasing σ .

So far, in the treatment of relaxation times, the effects of the Brownian (Debye) and Néel relaxation mechanisms have been treated independently of each other. When considering the Brownian mechanism, the magnetic moment was treated as 'blocked' so that the magnetic particle behaved as a rigid body. For the treatment of the Néel relaxation the mechanical freedom of the particle to rotate is

considered frozen, so that the magnetic moment can change orientation only by switching direction within the particle from one energy minimum to the other. In the constituent nanoparticles of ferrofluids, both of these effects are observable. It then becomes necessary to combine both relaxation processes into one effective relaxation time. Shliomis [28] proposed that this relaxation time should be described by

$$\tau_{eff} = \frac{\tau_N \tau_B}{\tau_N + \tau_B}. \quad (2.6.1.11)$$

The dominant relaxation time is the smaller one. Small particles tend to relax via the Néel mechanism, whilst the opposite is true for large particles whose dominant relaxation mechanism is by Brownian relaxation. When $\sigma < 1$, $\tau_N \ll \tau_B$ and the Néel relaxation dominates the effective time. When $\sigma > 10$, $\tau_N \gg \tau_B$ so that the Brownian mechanism dominates. The typical value of σ where $\tau_N = \tau_B$ is σ_x where σ_x is in the range $5 < \sigma_x < 7$ [28]. In a ferrofluid, a distribution of particle sizes will exist so that some particles (or aggregates) may relax via the Brownian mechanism and some by the Néel. An observation of the distribution of particle sizes and relaxation times of a typical ferrofluid is given by Fannin [29] showing a critical point at 6nm below which particles relax by Néel relaxation, and above which they approach thermal equilibrium by the Brownian mechanism. This is depicted in figure 2.9 below.

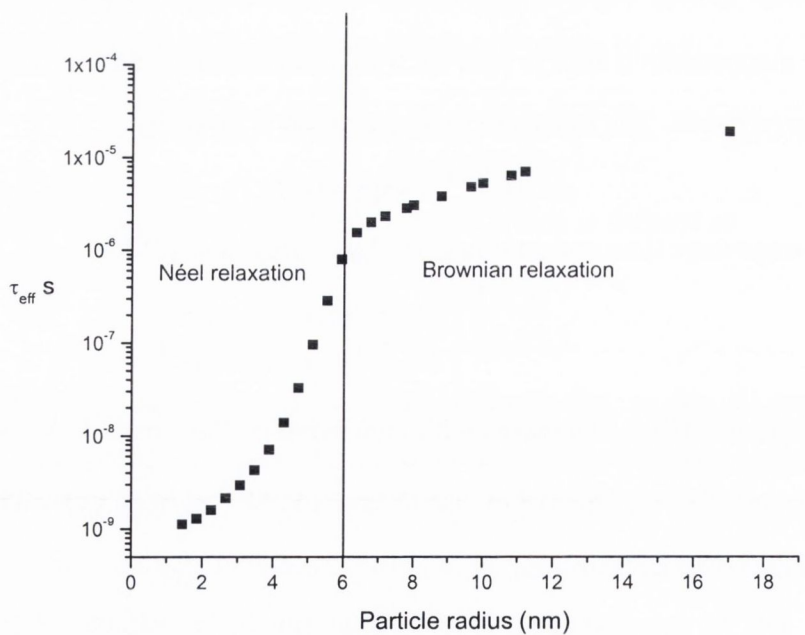


Figure 2.9: Dependence of effective relaxation time on particle radius. The solid line indicates a critical particle radius at $r = 6\text{nm}$, where a transition from Néel to Brownian relaxation takes place.

2.6.2. Review of Superparamagnetism

Whilst it has been alluded to indirectly in the previous sections, the characteristics of superparamagnetism have not yet been discussed. In this section a summary of the primary characteristics of the phenomenon will be given.

Superparamagnetism was first discovered by Elmore [4] in 1937 on a colloidal suspension of Fe_3O_4 particles, and the name describing the phenomenon was coined by Bean [5]. Superparamagnets are unblocked particles that can respond to an applied field. The particles can respond to the applied field by two different mechanisms. Hence they may be considered doubly superparamagnetic. The first mechanism of response is by the spontaneous flipping or switching of the magnetic moment by thermal activation (Néel Mechanism), the second by the external Brownian rotation of the particle in the carrier liquid (for ferrofluids). The decay of the magnetisation in response to an applied field can be characterised by an effective relaxation time which is a combination of both Néel and Brownian relaxation times. Superparamagnetic particles consist of only one magnetic domain and are generally in the size range of 8 – 12 nm in diameter. The magnetisation of an assembly of superparamagnetic particles can be described by the same Langevin function as used in section 1.6.1 for the case of paramagnetism where,

$$M = Nm \left\{ \coth(\xi) - \frac{1}{\xi} \right\}, \quad \text{where } \xi = \frac{mH}{k_B T}. \quad (2.6.2.1)$$

A normalised plot of M versus H is shown in figure 2.10 below.

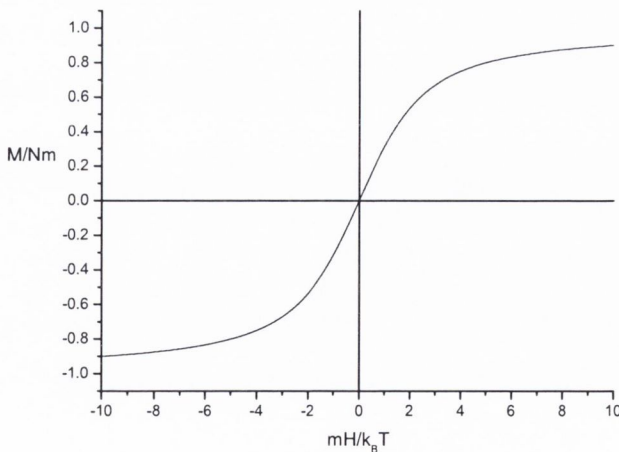


Figure 2.10: Magnetisation curve of a typical ferrofluid exhibiting typical superparamagnetic behaviour.

However, at room temperature, in contrast to paramagnets, superparamagnets have a much greater susceptibility. The M - H curve (figure 2.10) shows that superparamagnetic materials exhibit no hysteresis, have zero remanence, and that the magnetisation process is fully reversible.

2.7. Parallel and perpendicular susceptibilities - modification of susceptibility equations to take account of Anisotropy

In the derivation for the magnetisation of an assembly of paramagnetic atoms equation (1.6.1.7), no consideration was given to the anisotropy of the material. In the following section, equations will be given to describe the magnetisation with the internal equivalent anisotropy field taken into account. Let $\hat{n}$ be a unit vector along the axis of the uniaxial anisotropy. Due to uniaxial anisotropy, the response of the magnetic moment of a magnetic particle is dependant on whether the applied field is directed parallel, or perpendicular, to $\hat{n}$. It is convenient therefore to follow the convention of section 2.6.1, with the parallel and perpendicular magnetisation, to study the susceptibility in terms of parallel and perpendicular components, $\chi_{\parallel}$, $\chi_{\perp}$ respectively. The parallel susceptibility will be given by

$$M_{\parallel}(\xi_m) = M_{sat} \langle \cos \theta \rangle, \quad (2.7.1)$$

where θ is the angle between the field $\hat{h}$ and moment $\hat{m}$ directions (Figure 2.11). Equation (1.6.1.6) gives the average value of $\cos \theta$ by integrating over the angular distribution. However the external field, H , must now be modified in this equation to take account of the anisotropy. This is done by including the internal anisotropy field H_A (equation 2.3.1.6), i.e.

$$H_A = \frac{2K}{M_{sat}} \hat{n} = \frac{2K v_m}{m} \hat{n}. \quad (2.7.2)$$

Thus the ratio of total magnetic energy to thermal energy is

$$\xi_m \cos \theta - \sigma \sin^2 \theta = \frac{mH \cos \theta - K v_m \sin^2 \theta}{k_B T}. \quad (2.7.3)$$

Hence the parallel magnetisation is given by

$$M_{\square}(\xi_m, \sigma) = M_{sat} \langle \cos \theta \rangle = M_{sat} \left\langle \hat{m} \cdot \hat{h} \right\rangle =$$

$$M_{sat} \frac{\int_0^{2\pi} \int_0^{\pi} \cos \theta \exp(\xi_m \cos \theta - \sigma \sin^2 \theta) \sin \theta d\theta}{\int_0^{2\pi} \int_0^{\pi} \exp(\xi_m \cos \theta - \sigma \sin^2 \theta) \sin \theta d\theta} \cong M_{sat} \xi_m \left(1 - \frac{2 \tanh \sigma}{3\sigma} \right). \quad (2.7.4)$$

The above integral is complicated to evaluate and for this reason it is desirable to use the approximate value incorporating the hyperbolic tangent given above.

From equation (2.7.4) the parallel susceptibility is defined as

$$\chi_{\square}(\sigma) = \frac{3\chi_0}{\xi_m} \frac{\int_0^{2\pi} \int_0^{\pi} \cos \theta \exp(\xi_m \cos \theta - \sigma \sin^2 \theta) \sin \theta d\theta}{\int_0^{2\pi} \int_0^{\pi} \exp(\xi_m \cos \theta - \sigma \sin^2 \theta) \sin \theta d\theta} \cong 3\chi_0 \left(1 - \frac{2 \tanh \sigma}{3\sigma} \right), \quad (2.7.5)$$

where χ_0 is the static susceptibility as given by equation (2.5.6).

For small σ parallel susceptibility reduces to χ_0 whilst for large σ it equals $3\chi_0$.

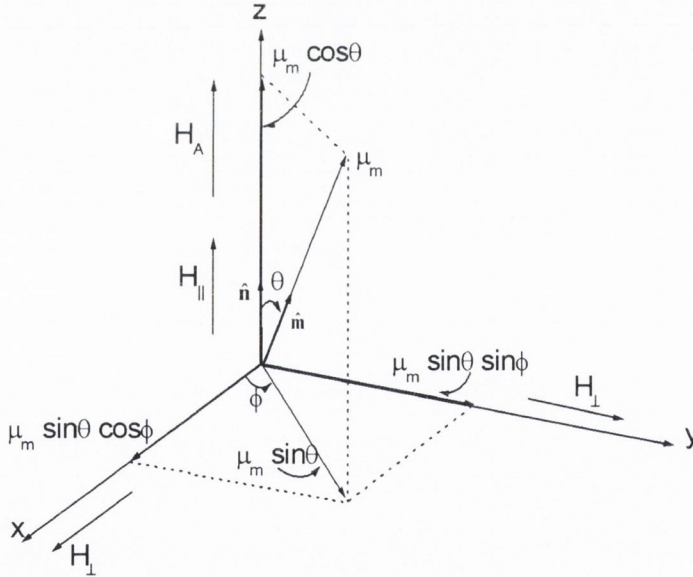


Figure 2.11: Magnetic moment vector shown relative to parallel and perpendicular field directions.

The easy axis lies along the vertical. Note in this graph the magnetic moment is denoted by μ_m .

For the case where the field is perpendicular to the unit vector $\hat{n}$ the following is the expression for the magnetisation;

$$M_{\perp}(\xi_m, \sigma) = M_{sat} \langle \sin \theta \cos \phi \rangle = \frac{M_{sat} \int_0^{2\pi} \int_0^{\pi} \sin \theta \cos \phi \exp(\xi_m \sin \theta \cos \theta - \sigma \sin^2 \theta) \sin \theta d\theta d\phi}{\int_0^{2\pi} \int_0^{\pi} \exp(\xi_m \sin \theta \cos \theta - \sigma \sin^2 \theta) \sin \theta d\theta d\phi}. \quad (2.7.6)$$

This equation is also difficult to evaluate. It may be simplified by making the assumption that the internal energy is small in comparison to the thermal energy so that

$$\xi_m \ll 1, \text{ hence } \exp(\xi_m \sin \theta \cos \phi) \cong 1 + \xi_m \sin \theta \cos \phi. \quad (2.7.7)$$

Equation (2.7.6) can then be written as

$$\begin{aligned} M_{\perp}(\xi_m, \sigma) &= M_{sat} \frac{\int_0^{2\pi} \int_0^{\pi} (\sin^2 \theta \cos \phi + \xi_m \sin^3 \theta \cos^2 \phi) \exp(-\sigma \sin^2 \theta) \sin \theta d\theta d\phi}{\int_0^{2\pi} \int_0^{\pi} \sin \theta \exp(-\sigma \sin^2 \theta) d\theta} \\ &= \frac{M_{sat}}{2} \frac{\int_0^{\pi} \xi_m \sin^3 \theta \exp(-\sigma \sin^2 \theta) d\theta}{\int_0^{\pi} \sin \theta \exp(-\sigma \sin^2 \theta) d\theta} \cong \frac{M_{sat} \xi_m}{3} \frac{\tanh \sigma}{\sigma}. \end{aligned} \quad (2.7.8)$$

The perpendicular susceptibility can then be written as

$$\chi_{\perp}(\sigma) = \frac{3\chi_0}{2\xi_m} \frac{\int_0^{\pi} \xi_m \sin^3 \theta \exp(-\sigma \sin^2 \theta) d\theta}{\int_0^{\pi} \sin \theta \exp(-\sigma \sin^2 \theta) d\theta} \cong \chi_0 \frac{\tanh \sigma}{\sigma}. \quad (2.7.9)$$

For the case of a purely isotropic material, where $\sigma \rightarrow 0$, the perpendicular susceptibility tends to its static value, which is to be expected since for isotropic particles the susceptibility is independent of direction.

The above equations are valid only for the case of a static applied field. Account must be taken for the parallel and perpendicular susceptibility when the applied field is alternating. If the alternating field is applied parallel, the susceptibility can be very well described by the Brownian complex susceptibility, equation (2.5.4). In this case the effective relaxation time, τ_{eff} must be used. If the alternating field is applied perpendicular, the response is one of resonance. Ferromagnetic resonance has been described in detail in section 1.4. It occurs when the frequency of the alternating field matches the frequency of precession of the magnetic moment. If this is not the

case, then the probability that the moment will absorb energy from the applied field is very low and no resonance will occur. If the two frequencies match, then absorption of microwave energy can take place, and ferromagnetic resonance will take place. The resonance is accompanied by a change in sign of the susceptibility. The resonance frequency, ω_{res} is related to the total field $H_S + H_A$ and the gyromagnetic ratio by the equation,

$$\omega_{res} = \frac{d\hat{m}}{dt} = \gamma \hat{m} \times (H_S + H_A), \quad (2.7.10)$$

which is an equation similar to that of the gyromagnetic equation of section 2.6 (equation 2.6.1). H_A is the equivalent internal anisotropy field in the direction of $\hat{m}$. Because the susceptibility is perpendicular, the cross product in equation (2.7.10) reduces to

$$\omega_{res} = \gamma(H_S + H_A). \quad (2.7.11)$$

Raikher and Shliomis [30] derived an equation for the perpendicular susceptibility based on the Landau-Lifshitz equation taking into account the effect of superparamagnetism. However they omitted to cater for the effect of thermal agitation, meaning their equation was valid for high σ only. More recently Coffey and co-workers [25] derived an equation for $\chi_{\perp}(\omega)$ based on the analysis of Gilbert's equation (equation (2.6.4) with

$$\chi_{\perp}(\omega) = \chi_{\perp}(0) \frac{1 + i\omega\tau_2 + \Delta}{(1 + i\omega\tau_2)(1 + i\omega\tau_{\perp}) + \Delta}, \quad (2.7.12)$$

where

$$\Delta = \frac{\sigma\tau_2(\tau_d - \tau_{\perp})}{\sigma^2\tau_d^2}, \quad \text{and} \quad \tau_2 = \tau_d \left(-\sigma - 2 + \frac{4\sigma(\sqrt{\sigma} - D(\sqrt{\sigma}))}{3\sqrt{\sigma} - (3 + 2\sigma)D(\sqrt{\sigma})} \right)^{-1}. \quad (2.7.13)$$

Equation (2.7.12) includes the effect of thermal agitation and hence is exact for all σ . For the case of isotropic particles, with $\sigma \rightarrow 0$, we find that $\Delta \rightarrow 0$ and $\tau_{\perp} \rightarrow \tau_d'$ which means that equation (2.7.12) reduces to a simple Debye-type equation. Also $\chi_{\perp}(0) = \chi_{\parallel}(0) = \chi_0$, this means that for isotropic particles the parallel and perpendicular dynamic susceptibilities are identical. For the opposite case where $\sigma \rightarrow \infty$, then $\tau_{\perp}, \tau_2 \rightarrow \tau_d'/\sigma$ and equation (2.7.12) yields the Landau-Lifshitz equation of ferromagnetic resonance,

$$\chi_{\perp}(\omega) = \chi_0 \frac{\tanh \sigma}{\sigma} \frac{(1 + \alpha^2) \omega_{pre}^2 + i \alpha \omega \omega_{pre}}{(1 + \alpha^2) \omega_{pre}^2 - \omega^2 + i 2 \alpha \omega \omega_{pre}}, \quad (2.7.14)$$

where $\omega_{pre} = 1/\alpha \tau_0$ is the frequency of free precession (equation (2.6.9)). Substituting equation (2.6.9) into equation (2.7.14) gives

$$\chi_{\perp}(\omega) = \chi_0 \frac{\tanh \sigma}{\sigma} \frac{1 + \alpha^2 + i \alpha^2 \omega \tau_0}{1 + \alpha^2 - \alpha^2 \omega^2 \tau_0^2 + i 2 \alpha^2 \omega \tau_0}. \quad (2.7.15)$$

By substituting $\alpha = 1/(\omega_{pre} \tau_0)$ the Landau-Lifshitz equation can be written as

$$\chi_{\perp}(\omega) = \chi_0 \frac{\tanh \sigma}{\sigma} \frac{1 + \omega_{pre}^2 \tau^2 + i \omega \tau_0}{1 + \omega_{pre}^2 \tau_0^2 - \omega^2 \tau_0^2 + i 2 \omega \tau_0}. \quad (2.7.16)$$

The frequency and field dependence of equation (2.7.16) is a function of two parameters. The first, $\omega \tau_0$ is dependent on the frequency, whilst the second $\omega_{pre} \tau_0$ is dependent on the field since $\omega_{pre} \propto \omega_{res} = \gamma(H_A + H_S)$.

Some theoretical plots of the Landau-Lifshitz equation are shown below in figure 2.12. The first shows equation (2.7.15) plotted against frequency, f , and shows a purely resonant profile, whilst the second has been modified to include a Debye-type relaxation term as well as the resonance.

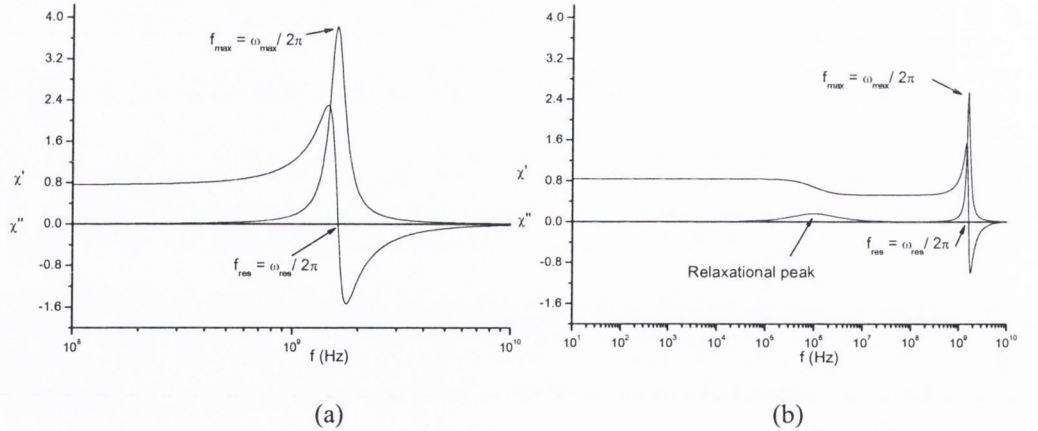


Figure 2.12: Theoretical plot of equation (2.7.15) for case (a): Pure resonance, (b) relaxation and resonance. The values used were $\sigma = 1$, $\alpha = 0.1$, $\tau_0 = 10^{-9}$ s.

The Landau-Lifshitz equation gives the resonance frequency as

$$\omega_{res} = \frac{1 + \alpha^2}{\sqrt{1 - \alpha^2}} \alpha \omega_{pre} = \gamma(H_S + H_A). \quad (2.7.17)$$

α must be less than one for resonance to occur. If α is greater than one the denominator of equation (2.7.17) becomes complex and hence ω_{res} will also be complex. Coffey's equation (2.7.12) can be separated into its real and imaginary parts where

$$\frac{\chi_{\perp}(\omega)}{\chi_0 \frac{\tanh \sigma}{\sigma}} = \frac{(1 + \Delta)^2 + \omega^2 \tau_2^2 - \Delta \omega^2 \tau_2 \tau_{\perp}}{(1 - \omega^2 \tau_2 \tau_{\perp} + \Delta)^2 + \omega^2 (\tau_{\perp} + \tau_2)^2} - i \frac{\omega^3 \tau_2^2 \tau_{\perp} + \omega \tau_{\perp} + \omega \tau_{\perp} \Delta}{(1 - \omega^2 \tau_2 \tau_{\perp} + \Delta)^2 + \omega^2 (\tau_{\perp} + \tau_2)^2}. \quad (2.7.18)$$

$\chi'_{\perp}(\omega)$ goes negative when

$$\omega = \omega_{res} = \frac{1 + \Delta}{\sqrt{\Delta \tau_{\perp} \tau_2 - \tau_2^2}}. \quad (2.7.19)$$

ω_{res} needs to be real for resonance to occur. Substituting for Δ in equation (2.7.19) we arrive at the following condition,

$$\frac{\sigma}{\alpha^2} > \frac{\tau_d'^2}{\tau_{\perp} (\tau_d' - \tau_{\perp})}. \quad (2.7.20)$$

It has been stated previously (section 2.6) that α is typically between 0.01 and 0.1 for ferromagnets. Therefore for $\alpha = 0.1$, the condition for resonance is $\sigma > 5\alpha$, so that σ must be at least 0.5 for resonance to occur. Figures 2.13 (a and b) show the effect of changing the σ , and α parameters on the perpendicular susceptibility, as given by equation (2.7.12).

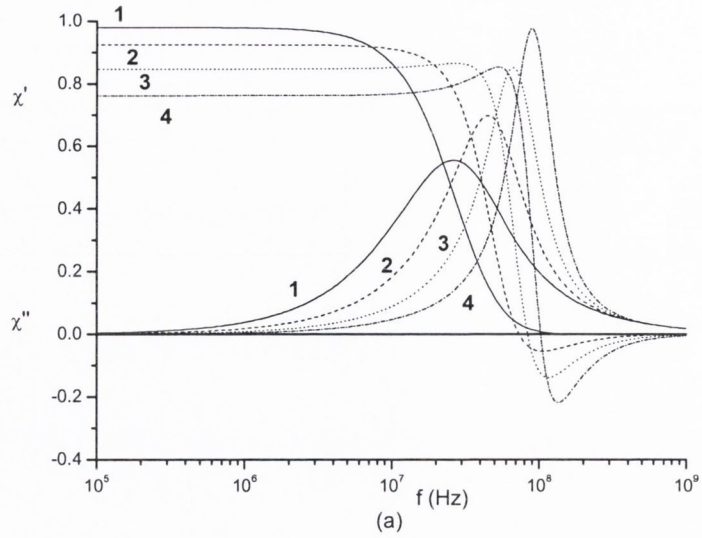


Figure 2.13 (a): Dependence of the perpendicular susceptibility on the parameter σ , calculated from equations (2.7.12, 2.7.13). (1) $\sigma = 0.25$, (2) $\sigma = 0.5$, (3) $\sigma = 0.75$, (4) $\sigma = 1$. Notice for $\sigma = 0.25$, the curve is purely relaxational in character, at $\sigma = 0.5$, resonance is seen to take place where the real component of the susceptibility goes negative.

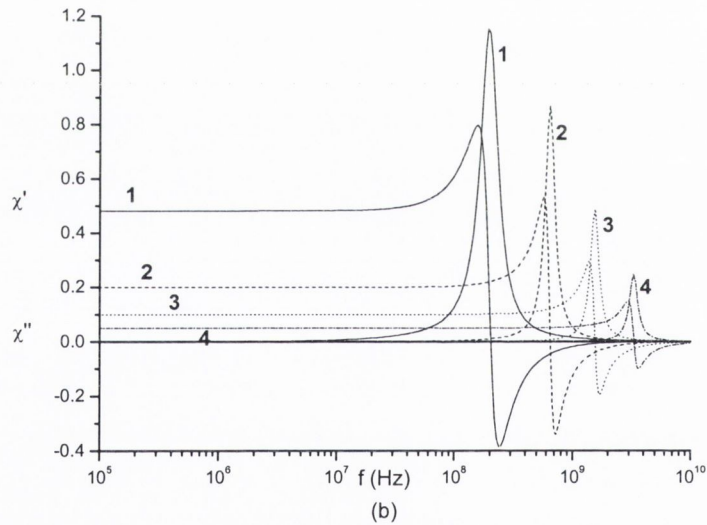


Figure 2.13 (b): Dependence of the perpendicular susceptibility on the parameter σ , calculated from equations (2.7.12, 2.7.13). (1) $\sigma = 2$, (2) $\sigma = 5$, (3) $\sigma = 10$, (4) $\sigma = 20$. Higher values of sigma increase the location of the resonance to higher frequencies.

The dependence of $\chi_{\perp}(\omega)$ on the damping parameter α is shown below. A low value of α , say $\alpha = 0.05$ gives a very sharp profile for $\chi_{\perp}(\omega)$. Increasing α , flattens the susceptibility profile. Using a value of $\alpha = 1$, returns a purely relaxational susceptibility profile.

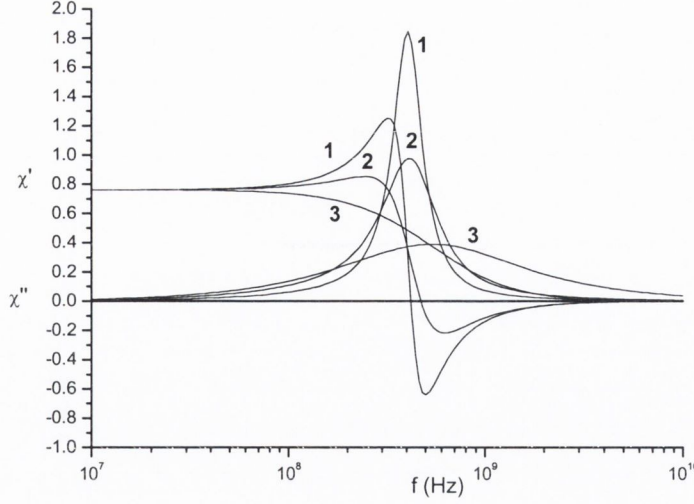


Figure 2.14 : Dependence of the perpendicular susceptibility on the parameter α , calculated from equations (2.7.12, 2.7.13). (1) $\alpha = 0.05$, (2) $\alpha = 0.1$, (3) $\alpha = 1$.

The total susceptibility will be the average susceptibility over the three spatial dimensions shown in figure 2.11. The total susceptibility is given by

$$\chi(\omega) = \frac{1}{3}(\chi_{\square}(\omega) + 2\chi_{\perp}(\omega)), \quad (2.7.21)$$

in which the parallel susceptibility is given by the Debye / Brownian equation and the perpendicular susceptibility by the resonance equation (equation 2.7.12). Equation (2.7.21) becomes

$$\chi(\omega) = \frac{1}{3} \left(\frac{3\chi_0 \left(1 - \frac{2 \tanh \sigma}{3\sigma} \right)}{1 + i\omega\tau_{\square}^{eff}} + 2\chi_0 \frac{\tanh \sigma}{\sigma} \frac{1 + i\omega\tau_2 + \Delta}{(1 + i\omega\tau_2)(1 + i\omega\tau_{\perp}) + \Delta} \right). \quad (2.7.22)$$

The ration of 2:1 in $\chi_{\perp}(\omega)$ to $\chi_{\square}(\omega)$ arises from the fact that there are two axes perpendicular to the applied perpendicular field, whilst there is only one axis parallel to the parallel field.

2.8. Perpendicular Susceptibility of Polydisperse Ferrofluids

The equations presented in section 2.7 account for the case of a monodisperse ferrofluid only. Figures (2.13 a, b) show that the resonant profiles of the susceptibility are quite sharp. These profiles do not correspond to the case of a

realistic system in which the particle radius and anisotropy energy vary from particle to particle. As in section 2.5 probability distribution functions must be used to account for the effect of varying particle size and anisotropy. In a similar fashion to equation (2.5.10) it is possible to write

$$\chi_{\perp}(\omega) = \frac{\int_{r_{\min}}^{r_{\max}} P(r_m) \int_{K_{\min}}^{K_{\max}} \chi_{\perp}(\omega, K, r_m) P(K) dK dr_m}{\int_{r_{\min}}^{r_{\max}} P(r_m) \int_{K_{\min}}^{K_{\max}} P(K) dK dr_m}, \quad (2.8.1)$$

where r_m is the magnetic radius.

The distribution $P(K)$ and $P(r_m)$ result in the elimination of the sharpness of the curves. It is possible to use many different distributions to achieve equation (2.8.1), however a normal or log normal distribution of K , and a log normal or Nakagami distribution of r gives the best results for this work. The log normal distribution is given by

$$P(x) = \frac{1}{x\sigma_{pdf}\sqrt{2\pi}} \exp\left\{-\frac{(\ln x - \mu_{pdf})^2}{2\sigma_{pdf}^2}\right\}, \quad (2.8.2)$$

where σ_{pdf} and μ_{pdf} are the standard deviation and the mean respectively.

In figure 2.15 (a, b), the dependence of the normalised perpendicular susceptibility on the distribution of the anisotropy constant, K , is shown. The first graph shows $\chi_{\perp}(\omega)$ evaluated with the following parameters, $M_{sat} = 0.4$ T, $K = 10^4$ J/m³, $r_m = 4.5$ nm, $\alpha = 0.1$, and starting from the top curve, $\sigma_{pdf} = 0.1, 0.25, 0.5, 0.75, 0.9, 1$. The second graph uses the same values except for the damping parameter α which is now equal to 0.05.

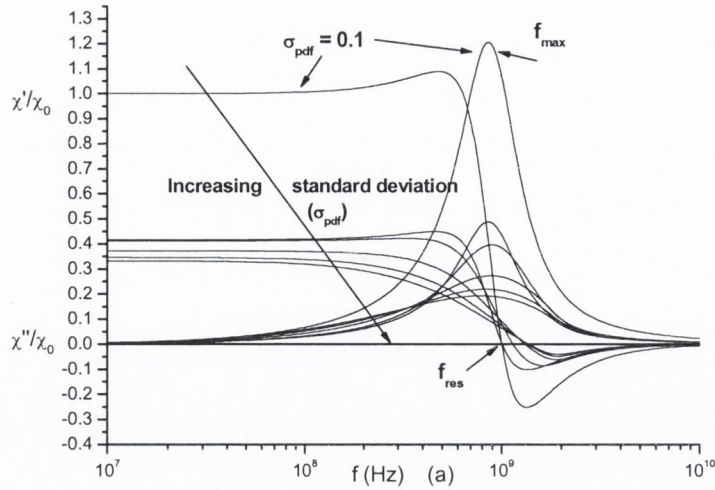


Figure 2.15 (a): Dependence of the normalised $\chi_{\perp}(\omega)$ on the standard deviation of the distribution of anisotropy constant, K . Here $\sigma_{pdf} = 0.1, 0.25, 0.5, 0.75, 0.9, 1$. The top most curve corresponds to $\sigma_{pdf} = 0.1$, and exhibits the sharpest resonant profile.

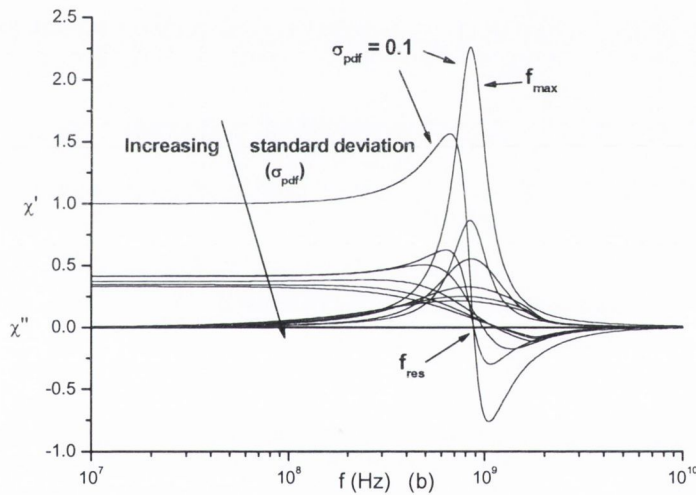


Figure 2.15 (b): As above. The curves in figure 2.15 (b) are sharper than in the corresponding graph above, due to the reduction in damping parameter from $\alpha = 0.1$ to $\alpha = 0.05$.

The effect of increasing the standard deviation is to flatten the susceptibility profile and shift the resonance points to higher frequencies. This flattening effect is to be expected as the broader the distribution is, the greater is the amount of different sizes of particles contributing to resonance. Increasing the standard deviation also leads to a decrease in the initial susceptibility, equation (2.5.6), since the initial susceptibility is dependent on σ and K through the relation $\sigma = K v_m / k_B T$. The effect of changing the damping parameter α is also evident in comparing figures 2.15 (a) and (b). The

value of α is halved from $\alpha = 0.1$, to $\alpha = 0.05$ in graph (b). Reducing α leads to an increase in the sharpness of the susceptibility curve. As damping is reduced, the susceptibility profile tends towards the purely resonant curves of figure 2.13 (b).

The Nakagami probability distribution function (pdf) can be best used to describe the distribution in the radius. The Nakagami pdf is given by

$$P(x) = \frac{2\beta^\beta}{\Gamma(\beta)W^\beta} x^{2\beta-1} \exp\{-\beta x^2/W\}. \quad (2.8.3)$$

β is the width parameter of the distribution, and W is a scale parameter equal to the mean square of x :

$$W = \frac{1}{n} \sum_{i=1}^n x_i^2. \quad (2.8.4)$$

The larger the value of β the narrower is the distribution. Applying the Nakagami distribution to the susceptibility profile of $\chi_\perp(\omega)$ has negligible effect on the width of the resonance peak because only the smallest particles contribute to the magnetic resonance. If the parallel susceptibility was to be included in the calculations the distribution of particle sizes would become important. This is due to the strong dependence of the Néel and Brownian relaxation mechanisms on the particle size.

2.9. Field Dependence of the Parallel Susceptibility

Having considered the frequency dependent susceptibility under the influence of an alternating field in section 2.5, and also under the influence of the combined anisotropy and static field in section 2.7, it is now desirable to consider the effect of a strong d.c field (H_S) superimposed on a comparatively weak alternating field (h_{ac}) on the susceptibility. We presume that $h_{ac} \ll H_S$, so that we operate with such a weak alternating field that only linear behaviour of the magnetisation is considered. The following treatment of the field dependence will be limited to the parallel susceptibility, $\chi_\parallel(\omega)$, so that only relaxation effects are considered. Coffey et al[24] have shown the parallel susceptibility under the influence of H_S and $h_{ac} = H_0 \cos(\omega t)$, to be of the Debye type with a modification to the static susceptibility and the effective relaxation time taking account of the static field dependence. The starting point for their treatment of the problem was Brown's equation (equation (2.6.8)), which they solved by expanding the solution in spherical harmonics. They

considered the rise transient of the magnetisation following the application of a small d.c. field, a large d.c. field having been applied at $t = -\infty$. The response to a weak alternating field superimposed on the bias field (H_S) can be found from the response to the increment in the d.c. field by linear response theory. They arrived at the following expression for the parallel susceptibility with

$$\chi_{\square}(\omega, \xi_m) = \frac{3\chi_0 L'(\xi_m) - \chi_{\infty}}{1 + i\omega\tau_{\square}} + \chi_{\infty} = \frac{3\chi_0(1 - \coth^2(\xi_m) + 1/\xi_m^2) - \chi_{\infty}}{1 + i\omega\tau_{\square}} + \chi_{\infty}, \quad (2.9.1)$$

where

$$\xi_m = \frac{m(H_S + h_{ac})}{k_B T}. \quad (2.9.2 -a)$$

In the above equation L' is the derivative of the Langevin function.

In equation (2.9.1) the static parallel susceptibility can be written in the following manner,

$$\chi_{\square}^S = 3\chi_0 L'(\xi_m) = 3\chi_0(1 - \coth^2(\xi_m) + 1/\xi_m^2). \quad (2.9.2 -b)$$

Equation (2.9.2 -b) is a decreasing function of ξ_m and hence equation (2.9.1) predicts a decrease of the magnitude of the susceptibility with increasing bias field.

The field dependence of the parallel relaxation time, $\tau_{\square}$ is given by

$$\begin{aligned} \tau_{\square}(\xi_m) &= \tau_{eff} \frac{\xi_m L'(\xi_m)}{L(\xi_m)} = \tau_{eff} \frac{\xi_m [1 - 2L(\xi_m)/\xi_m - L^2(\xi_m)]}{L(\xi_m)} \\ &= \tau_{eff} \frac{\xi_m(1 - \coth^2(\xi_m) + 1/\xi_m^2)}{L(\xi_m)}. \end{aligned} \quad (2.9.3)$$

In equation (2.9.3) above, τ_{eff} is the effective relaxation time given by equation (2.6.1.11) where no biasing field is applied. For small values of ξ_m the Langevin function can be approximated by

$$L(\xi_m) = \xi_m / 3, \quad (2.9.4)$$

And so for small ξ_m , substituting equation (2.9.4) into (2.9.3) yields

$$\begin{aligned} \tau_{\square}(\xi_m) &= \tau_{eff} \frac{\xi_m L'(\xi_m)}{L(\xi_m)} = \tau_{eff} \left\{ 1 - \frac{\xi_m^2}{3} \right\}, \text{ so for small } \xi_m \\ &\Rightarrow \tau_{\square}(\xi_m) = \tau_{eff}. \end{aligned} \quad (2.9.5)$$

as expected. If ξ_m is not so small we need to retain higher terms of ξ_m in the Langevin function so that

$$L(\xi_m) = \xi_m / 3 - 2\xi_m^3 / 45, \quad (2.9.6)$$

which results in

$$\tau_{\square}(\xi_m) = \tau_{eff} (1 - 2\xi_m^2 / 15). \quad (2.9.7)$$

In the opposite limit of high ξ_m the predicted relaxation time is virtually instantaneous, the asymptotic behaviour being

$$\tau_{\square}(\xi_m) = \tau_{eff} / \xi_m. \quad (2.9.8)$$

Theoretically, equations (2.9.3) and (2.9.8) predict a decrease in relaxation time with increasing ξ_m . Experimentally this can be interpreted as the blocking of the larger particles with increasing bias field. As H_S increases, a smaller number of the larger particles contribute to the effective relaxation. Hence, smaller particles now contribute to the relaxation, leading to a decrease in the overall relaxation time. This has been verified experimentally, and experimental results for the Bias field dependence of ferrofluids will be given in chapter four. Figure 2.16 (a) contains theoretical plots of equation (2.9.1) evaluated for increasing Bias field from, $H_S = 0$ A/m to $H_S = 50,000$ A/m. The small alternating field is given as 60 A/m for all plots. As predicted by the theory, figure 2.16 (a) shows a decrease in the magnitude of susceptibility and an increase in maximum relaxation frequency, f_{max} (i.e. a decrease in τ_{eff}) with increasing bias.

As in previous sections, the above expressions are only valid for the monodisperse case. Probability functions can be used to achieve a distribution in relaxation times, as before. It is preferable however to modify equation (2.9.1) to take account of the Cole-Cole parameter α . Equation (2.9.1) can be modified so that

$$\chi_{\square}(\omega, \xi_m) = \frac{3\chi_0 L'(\xi_m) - \chi_{\infty}}{1 + (i\omega\tau_{\square})^{1-\alpha}} + \chi_{\infty} = \frac{3\chi_0(1 - \coth^2(\xi_m) + 1/\xi_m^2) - \chi_{\infty}}{1 + (i\omega\tau_{\square})^{1-\alpha}} + \chi_{\infty}, \quad (2.9.9)$$

where ξ_m and $\tau_{\square}$ are as before. Equation (2.9.9) is then the final expression for the modified Debye model of the complex susceptibility taking into account, the dependence of static susceptibility and the parallel relaxation time on the polarising (Bias) field, and the polydispersity of the ferrofluid. Theoretical graphs for equation (2.9.9) are presented in Figure 2.16 (b).

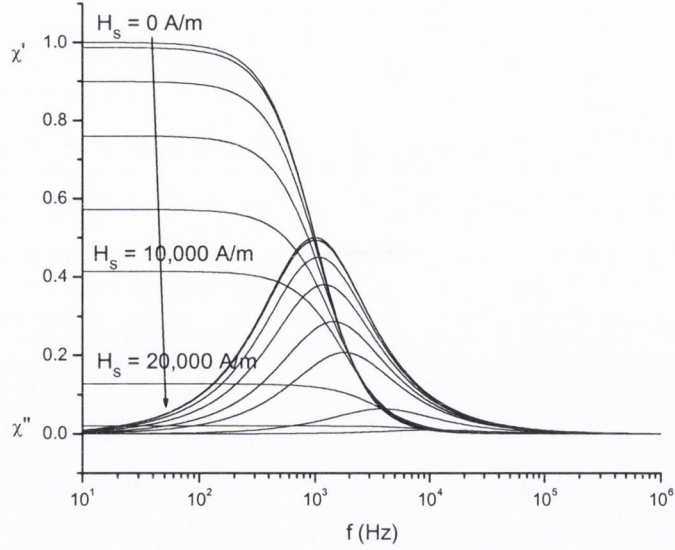


Figure 2.16 (a): Dependence of the complex susceptibility on Bias field, H_s . The values used in the above plots are $\chi_0 = 1, \chi_\infty = 0, m = 1 \times 10^{-24} \text{ Wbm}, h_{ac} = 60 \text{ A/m}, \tau_{eff} = 159.15 \mu\text{s}$. H_s is increased from 0 to 50,000 A/m. A value of 50 kA/m is difficult to realise in the laboratory thus the value of $H_s = 10$ kA/m is nearer the maximum that can be generated with our apparatus. The magnitude of the curve corresponding to $H_s = 50$ KA/m is very small ~ 0.02 .

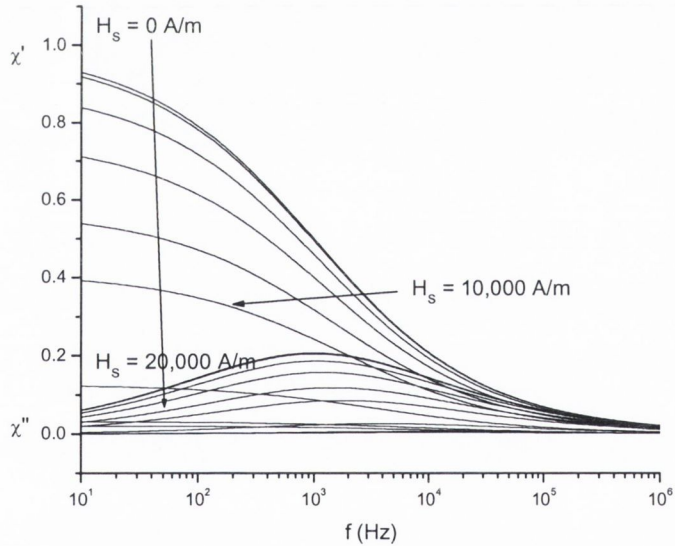


Figure 2.16 (b): Dependence of the complex susceptibility on bias field, H_s . The values used in the above plots are same as in the previous figure. The polydispersity of ferrofluids is taken account of by the Cole-Cole parameter α .

2.10. Relaxational Loss Mechanisms in Ferrofluids

Assuming superparamagnetic behaviour (i.e. no hysteresis) and small particle size so that eddy current heating is negligible, then the only losses that occur in a ferrofluid sample arise from the power dissipation resulting from the orientational relaxation of the magnetic nanoparticles. Following Rosensweig [31] it is possible to derive an equation to describe the volumetric power dissipation in a ferrofluid. From the first law of thermodynamics, for a constant density system of unit volume,

$$dU = \delta Q + \delta W, \quad (2.10.1)$$

where U is the internal energy, and W the magnetic work done on the system. For an adiabatic process, i.e. a process where no heat is lost or gained by the system, $\delta Q = 0$, while the differential magnetic work, δW is given by $\delta W = H \cdot dB$, so that

$$dU = H \cdot dB, \quad (2.10.2)$$

where H is the magnetic field strength (A/m) and B is the induction (T) in the sample. Because the field strength and the induction lie in the same direction, it is possible to rewrite equation (2.10.2) as $dU = H dB$. Knowing that $B = \mu_0 (M + H)$, and substituting into (2.10.2) gives

$$\Delta U = -\mu_0 \oint M dH. \quad (2.10.3)$$

When the magnetisation lags the field the integration in (2.10.3) above yields a positive result so that there will be a conversion of magnetic work to internal energy. Expressing the magnetisation in terms of the complex susceptibility where an alternating magnetic field of the form

$$h_{ac} = H_0 \cos \omega t = \Re \{ H_0 e^{i\omega t} \}, \quad (2.10.4)$$

is applied, gives

$$M(t) = \Re \{ \chi H_0 e^{i\omega t} \} = H_0 (\chi' \cos \omega t + \chi'' \sin \omega t), \quad (2.10.5)$$

where χ' , χ'' are as before, the in-phase and out-of-phase components of the complex magnetic susceptibility respectively. Substituting (2.10.5) for (2.10.3) yields after some manipulation

$$\Delta U = 2\mu_0 H_0^2 \chi'' \int_0^{2\pi/\omega} \sin^2 \omega t dt. \quad (2.10.6)$$

Integrating and multiplying the result by the cyclic frequency $f = \omega / 2\pi$ gives

$$P = f\Delta U = \mu_0 \pi \chi'' f H_0^2. \quad (2.10.7)$$

The dissipated power will be in the form of heat. Clearly P depends strongly on the imaginary susceptibility χ'' , the frequency f , and the magnitude of the alternating field H_0 . For the Debye profile of susceptibility, the maximum value of P will occur when χ'' is at a maximum (at the loss peak). So, depending on the application of the ferrofluid, to maximise or minimise the dissipated power, strong attention must be paid to the value of the loss peak. The effect of particle polydispersity is to flatten the Debye profile of the ferrofluid and hence decrease the maximum of the loss peak. Hence, for applications whereby maximising the losses from the ferrofluid are important, a monodisperse susceptibility profile is highly desirable. The heating effect in ferrofluids will be treated in more detail with experimental examples, in chapter four and five.

2.11. Conclusions

In this chapter the basic theory of ferrofluids and their constituent magnetic nanoparticles have been presented. The properties of single domain particles, and anisotropy were examined. The theory of Debye relaxation as derived from statistical physics, the Fokker-Planck equation and the Langevin equation, has been shown, leading to expressions for the Brownian complex susceptibility and the Cole-Cole equation to describe the frequency response of a ferrofluid system to an external driving magnetic field. Expressions for the relaxation times of the ferrofluid system were given for the cases of the Brownian and Néel relaxation, along with the corresponding perpendicular relaxation times corresponding to ferromagnetic resonance. Equations for the ferromagnetic resonance arising from magnetic moments precessing, are given, as derived by Coffey and Landau and Lifshitz.

In the presence of an external alternating field, the particles rotational movement have been shown to be purely relaxational in a direction parallel to an applied field, and purely precessional in a direction perpendicular to the applied field.

The dependence of the parallel susceptibility on a strong polarising field, H_S is described, along with the dependence of the parallel relaxation on the same field, showing a decrease in the magnitude of susceptibility along with a decrease of

parallel relaxation time, as the field increases. Finally an expression is given for the volumetric power dissipation of a ferrofluid under the effect of an alternating field.

References:

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Chapter Three: Measurement Techniques.

3.1. Introduction

In the following chapter, the relevant techniques for the measurement of $\chi(\omega)$ for a ferrofluid at both low (< 10 MHz), and high (>10 MHz) frequencies will be presented. In both cases, the measurements performed are based on the changes of impedance with frequency of an inductor containing a ferrofluid, as measured by a suitable instrument. At low frequencies, in the range $10 \text{ Hz} < f < 10 \text{ MHz}$, $\chi(\omega)$ can be determined using the slit toroid technique [1], in conjunction with a Hewlett Packard 4192A auto balanced bridge. The frequency resolution of the bridge is high, at 1 mHz, and the range of signal level available is 5mV to 1.1 V, with a 5 mV resolution. The simplest method of measuring $\chi(\omega)$ is by observing the change in impedance of an inductive coil placed in an alternating magnetic field, (i) when the coil is full of ferrofluid, and (ii) when it is empty. The ratio $\frac{\Delta L(\omega)}{L(\omega)}$ is proportional to

$\chi'(\omega)$ where $\Delta L = L_{\text{full}} - L_{\text{empty}}$ whilst $\frac{\Delta R(\omega)}{\omega L(\omega)}$ is proportional to $\chi''(\omega)$ where

where $\Delta R = R_{\text{full}} - R_{\text{empty}}$. Maoirov [2] performed measurements on $\chi(\omega)$ using a cylindrical inductor filled with magnetic fluid. However the use of a cylindrical inductor limits the frequency range in which impedance measurements can be performed. This limit arises, because at frequencies below some kHz, the inductance of an empty cylindrical inductor is miniscule in comparison to the minimum inductance measurement the instrument is capable of. The inductance of an empty cylindrical inductor with outer and inner radii, r_2 and r_1 is given by

$$L = \frac{\Phi_B(t)}{I(t)} = \frac{\mu_0 l}{2\pi} \ln \frac{r_2}{r_1}. \quad (3.1.1)$$

In equation (3.1.1), $\Phi_B(t)$ is the magnetic flux and $I(t)$ is the current. For a cylindrical inductor of dimensions $r_1 = 1.5 \text{ mm}$, $r_2 = 3.5 \text{ mm}$, length $l = 10 \text{ mm}$, L is calculated as $L = 1.7 \times 10^{-8} \text{ H}$. This is well below the minimum value measurable by the bridge which is of the order of mH. To counteract these inadequacies, the slit toroid technique is used, which has been shown to be accurate over a broad range of frequencies [3]. This will be covered in further detail in section 3.2.

At high frequencies between 10 MHz and 16 GHz, measurements are performed using a Transmission Line, incorporating a test cell, and a suitable network analyser. Two different network analysers are used, one a Hewlett Packard (HP) 8753C is used to perform measurements between 10 MHz and 6 GHz, and the second, a HP 8722 D is used in the 100 MHz to 16 GHz frequency range. In both cases a coaxial transmission line is connected to a single port of the analyser. The technique used here is based on the original works of Roberts and von Hippel [4]. Microwaves are transmitted from the analyser (source) along the transmission line, into the test cell, from which they are reflected back to the source. The ratio of the reflected to incident voltage, is the reflection coefficient, S_{11} . S_{11} can take values between -1 and 1. It is related to the characteristic impedance (Z_0) of the transmission line and the impedance of the unknown load (Z_x) by the equation

$$S_{11} = \frac{Z_x - Z_0}{Z_x + Z_0}, \quad (3.1.2)$$

which can be rearranged to read

$$Z_x = Z_0 \frac{1 + S_{11}}{1 - S_{11}}. \quad (3.1.3)$$

The analyser automatically calculates the value of Z_x in its real (R_x) and imaginary (X_x) components. These can then be converted via a complex set of equations to expressions for $\mu(\omega)$, $\varepsilon(\omega)$, and $\chi(\omega)$. When the transmission line is short circuited, it behaves as an inductor, enabling magnetic measurements ($\mu(\omega)$) to be performed. When it is terminated in an open circuit, the transmission line behaves as a capacitor enabling electric measurements ($\varepsilon(\omega)$) to be made. The combined results from both open and short measurements can be used to form a set of simultaneous equations to give more accurate equations to describe $\mu(\omega)$ and $\varepsilon(\omega)$, than are possible by measuring $\mu(\omega)$ and $\varepsilon(\omega)$ separately. The test cell, in which the ferrofluid is placed, is located in the end section of the transmission line. The diameter of the inner conductor of the coaxial line is 3mm, whilst the outer conductor has diameter of 7mm. The depth of the measurement cell ranges from $d = 9.5\text{mm}$ to $d = 1.04\text{mm}$. For good measurement accuracy, the sample depth must be large enough to ensure sufficient interaction of the sample with the incident radiation, whilst also being small enough to ensure the absence of dimensional resonance [4]. Generally speaking, the lower the measurement frequency the deeper the test cell. For example, the test cell with depth, $d = 9.5\text{mm}$ has been found to be accurate in the frequency

range of $10\text{ MHz} < f < 3\text{ GHz}$, whilst a depth of 1.04 mm is used in the very high frequency region where $f > 6\text{ GHz}$. Equations for $\mu(\omega)$, $\varepsilon(\omega)$, and $\chi(\omega)$ are derived in sections 3.4, 3.5 and 3.6 respectively.

3.2. Slit toroid technique

The slit toroid technique of Fannin et al. [1] involves the placing of the ferrofluid in an alternating magnetic field which is generated within a high permeability toroidal inductor. Generally the toroid would be made from a mu-metal or similar magnetic alloy, or ferrite. A narrow slit of length L_1 is cut in the toroid, such that the length of the slit is far less than the remaining length, L_2 , of the overall circumference, (L_1+L_2) of the toroid. The ratio of L_1 to L_2 can be written as $\gamma_g = L_1 / L_2, \ll 1$. Figure 3.1 shows a typical toroid used in the course of the measurements. This toroid has been found to be suitable for measurements in the range $10\text{ Hz} < f < 1\text{ MHz}$.

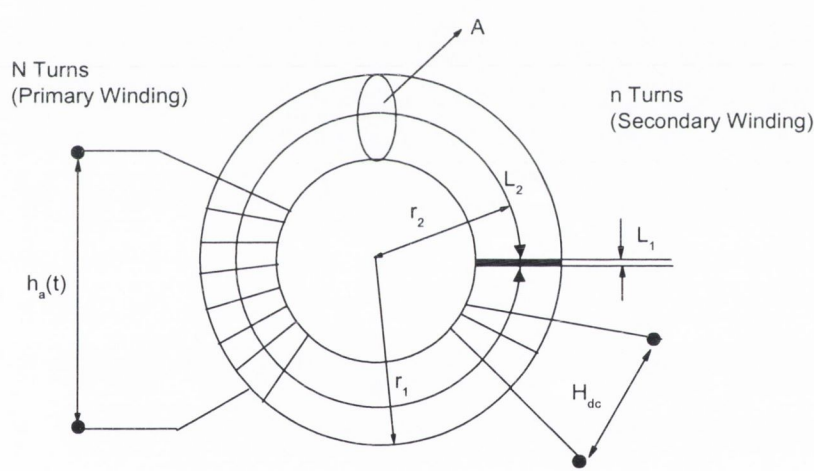


Figure 3.1: Experimental Toroid.

The dimensions of the Toroid shown in figure 1 are given in Table 1 below.

Table 1: Details of Toroid 1.

Outside Radius (r_1)	28.6 mm
Inside Radius (r_2)	19.05 mm
Mean Circumference	150 mm
Cross Sectional Area (A)	90.70 mm^2
Slit length (L_1)	0.3 mm

The primary winding is connected to the terminals of the impedance analyser where it is fed with an alternating current. For $N = 20$, an alternating magnetic field $h_a = H_0 \cos \omega t$ is generated, with magnitude $H_0 = 60$ A/m.

A full derivation of the equations for $\mu(\omega)$ for the toroidal technique, will be given in appendix A. Here only the final result will be considered. Consider a toroid of rectangular cross section A , relative permeability μ_r with a slit length L_l and mean length L_2 . μ_{eff} is the effective permeability of the cut toroid. The impedance measured across N primary turns on the toroid is given by

$$Z(\omega) = R_w + i\omega\mu_{eff}L_0 \quad (3.2.1)$$

where R_w is the d.c. resistance of the primary winding and

$$L_0 = \frac{\mu_{eff}N^2 A}{L_2(1 + \gamma_g)}. \quad (3.2.2)$$

With the slit empty, the impedance is denoted by

$$Z_e = R_w + \frac{i\omega\mu_r L_0}{1 + \mu_r \gamma_g} \quad (3.2.3)$$

and when the slit is full of ferrofluid

$$Z_f = R_w + \frac{i\omega\mu_r L_0}{1 + \gamma_g \mu_r / \mu_1} \quad (3.2.4)$$

where μ_1 is the permeability of the ferrofluid. After much algebraic manipulation, an expression for the complex permeability, μ_1 , of the ferrofluid is reached, with

$$\mu'_1 - i\mu''_1 = \frac{-\gamma_g(Z_f - R_w)(Z_e - R_w)}{(Z_f - R_w)(i\omega L_0 + \gamma_g R_w - \gamma_g Z_e) - (Z_e - R_w)i\omega L_0}. \quad (3.2.5)$$

Thus, by making the empty and full measurements Z_e and Z_f , one can determine μ'_1 and μ''_1 for the fluid in the slit, and using the relations $\mu'_1 = \chi' + 1$ and $\mu''_1 = \chi''$, one can easily determine the complex susceptibility of the ferrofluid.

It is possible to further extend the slit toroid technique, so that polarised measurements may be performed. This is easily accomplished by adding a secondary winding fed by a stabilised direct current power supply. It is possible to generate a polarising field, H_S , of value up to 15 kA/m.

Large alternating magnetic fields may also be generated using the slit toroid technique. To do this, it is necessary to wind approximately 100 primary windings onto the toroid, in such a way that the spacing between each winding is equal, so that

the magnetic flux density is assumed to be uniform over the cross section of the toroid. External software such as Labview [6] or Matlab [7] must be used with the analyser to perform the constant current measurements necessary to generate large alternating fields. Table 2 shows the dimensions for a toroid used to generate the large alternating magnetic fields required for the work presented in chapter 5.

Table 2: Details of Toroid 2

Outside Radius (r_1)	37.5 mm
Inside Radius (r_2)	21 mm
Mean Circumference	218 mm
Cross Sectional Area (A)	236.3 mm ²
Slit length (L_1)	0.3058 mm

At high enough frequencies, an inductor such as the toroid will resonate, due to its fringe capacitance. This reduces the effective frequency range of the toroid. For the toroid in Table 1, resonance occurs at approximately 10 MHz. The frequency of resonance is given by $\omega_{res} = 1/\sqrt{LC}$, and will occur at lower frequencies for toroids with higher amounts of turns. Hence, the large number of turns required to generate a large alternating field will reduce the measurement range of the toroid. The toroid in Table 2 is limited to an upper frequency of 10 kHz.

3.3. Basic Transmission Line Theory

A lossless transmission line can be modelled as an equivalent circuit consisting of inductors, L , in series, and capacitors, C , in parallel. For our case, the distance from the port of the analyser to the cell containing the ferrofluid, is denoted by the length x . The cell has length d . Depending on the termination applied to the cell, it can behave as either a pure inductor, or as a pure capacitor. The rest of the line will remain both inductive and capacitive. The line has a characteristic impedance denoted Z_0 , where $Z_0 = \sqrt{L/C} = 50\Omega$. An equivalent circuit for a transmission line terminated in a load impedance Z_x is shown in figure 3.2. The line has a propagation constant γ_0 where

$$\gamma_0 = \alpha_0 + i\beta_0 \tag{3.3.1}$$

where α_0 is the attenuation factor, $\beta_0 = 2\pi/\lambda$ is the phase coefficient, and λ is the operating wavelength in the line.

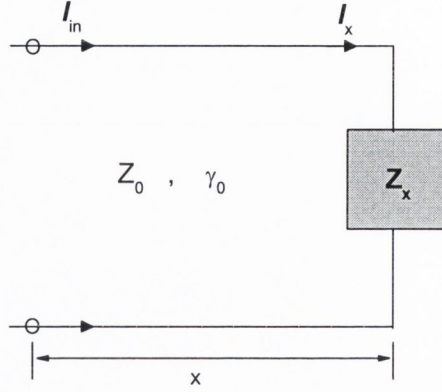


Figure 3.2: Equivalent circuit of a transmission line terminated in a load impedance Z_x .

The input impedance at a distance x from the load is given by the following equation [8]:

$$Z_{in} = \frac{V_{in}}{I_{in}} = \frac{V_x \cosh(\gamma_0 x) + Z_0 I_x \sinh(\gamma_0 x)}{I_x \cosh(\gamma_0 x) + (V_x / Z_0) \sinh(\gamma_0 x)}. \quad (3.3.2)$$

Assuming a very low loss in the line, $\alpha_0 \approx 0$, so that equation (3.3.1) becomes

$\gamma_0 = i\beta_0$. Using the identities $\cosh(ix) = \cos(x)$, and $\sinh(ix) = i\sin(x)$

the input impedance given by equation (3.3.2) becomes

$$Z_{in} = Z_0 \left\{ \frac{Z_x \cos(\beta_0 x) + iZ_0 \sin(\beta_0 x)}{Z_0 \cos(\beta_0 x) + iZ_x \sin(\beta_0 x)} \right\}. \quad (3.3.3)$$

Dividing (3.3.3) above and below by $\cos \beta_0 x$ we obtain,

$$Z_{in} = Z_0 \left\{ \frac{Z_x + iZ_0 \tan(\beta_0 x)}{Z_0 + iZ_x \tan(\beta_0 x)} \right\}. \quad (3.3.4)$$

Equation (3.3.4) is the input impedance of a lossless line terminated by a load impedance of Z_x where x is the distance from the load to the measurement plane. In the special case where the load is a short circuit, the input impedance is given by

$$Z_{in} = iZ_0 \tan(\beta_0 x). \quad (3.3.5)$$

3.4. Measurement of the complex relative permeability

Consider the model and equivalent circuit consisting of an air-filled coaxial transmission line terminated with a toroidal sample of material and a short circuit as depicted in figure 3.3. The sample has a thickness or depth d . The air filled section of the line is characterised by the characteristic impedance Z_0 and the propagation constant γ_0 . Both are known quantities. The unknown quantity of interested is the impedance of the load, or of the section of the line filled with sample, given by Z_1 , and the corresponding propagation constant, γ_1 .

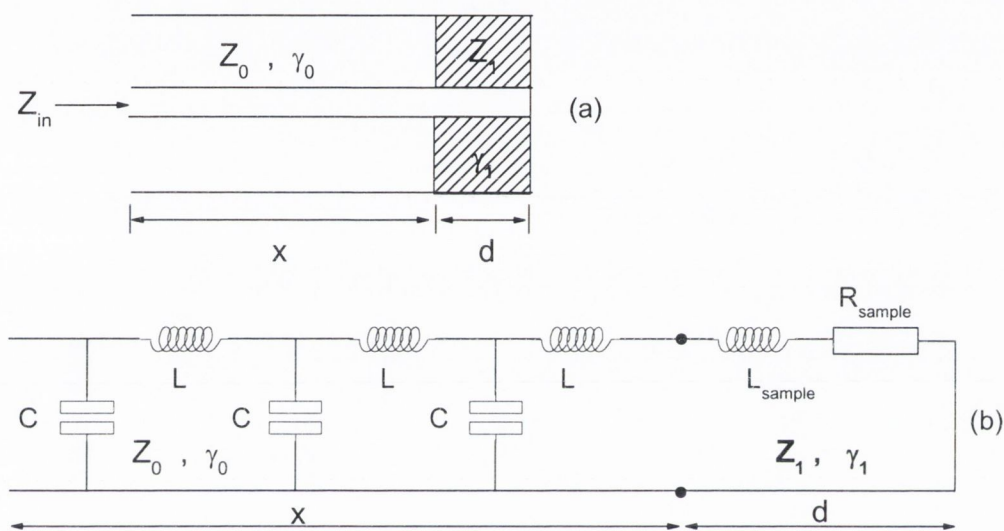


Figure 3.3 (a): Model of coaxial transmission line terminated in toroidal sample terminated in short circuit. **Figure 3.3 (b):** Equivalent circuit of short terminated transmission line with Inductive Impedance of sample denoted by R_{sample} and L_{sample} .

The arrangement in figures 3.3 (a) and (b) can be modelled in the same way as that of figure 3.2, by letting the load impedance Z_x include the section of line marked ' d ', so that the length d , with characteristic impedance Z_1 , and propagation constant γ_1 sees an input impedance of Z_x .

Considering the section of the line containing the load only, the input impedance Z_x can be written in the same form as equation (3.3.5) so that

$$Z_x = Z_1 \tanh(\gamma_1 d). \quad (3.4.1)$$

The intrinsic impedance of a medium is given by [8]

$$Z = \sqrt{\frac{\mu_1}{\varepsilon_1}} \quad (3.4.2)$$

where μ_1 and ε_1 are the absolute values of complex permeability and complex permittivity of the medium. The propagation factor of the medium is

$$\gamma_1 = i\omega\sqrt{\varepsilon_1\mu_1} \quad (3.4.3)$$

where ω is the angular frequency. From equations (3.4.2) and (3.4.3) it is possible to write a relationship between the intrinsic impedance and propagation factor where

$$Z = \frac{i\omega\mu_1}{\gamma_1}. \quad (3.4.4)$$

The characteristic impedance of a coaxial line containing a medium such as a dielectric can be written as [8]

$$Z_1 = \frac{1}{2\pi} Z \ln\left(\frac{r_o}{r_i}\right) \quad (3.4.5)$$

where r_o is the radius of the outer conductor, and r_i is the radius of the inner conductor. Using equations (3.4.4) and (3.4.5) equation (3.4.1) can now be written as

$$Z_x = A_c \frac{i\omega\mu_1}{\gamma_1} \tanh(\gamma_1 d) \quad (3.4.6)$$

where $A_c = \frac{1}{2\pi} \ln\left(\frac{r_o}{r_i}\right)$. Assuming that the sample depth is far less than the

wavelength of electromagnetic radiation in the sample, it is possible to simplify equation (3.4.6). With $\gamma_1 d \ll 1$, $\tanh(\gamma_1 d) \approx \gamma_1 d$ so that

$$Z_x = iA_c \omega \mu_1 d. \quad (3.4.7)$$

Equation (3.4.7) gives an equation for the load impedance in terms of the permeability of the medium. It is now possible to solve equation (3.3.4) using equation (3.4.7) giving an expression for the input impedance at a distance x from the face of the load as

$$Z_{in} = Z_0 \left\{ \frac{i\omega A_c \mu_1 d + iZ_0 \tan(\beta_0 x)}{Z_0 - \omega A_c \mu_1 d \tan(\beta_0 x)} \right\}. \quad (3.4.8)$$

Solving (3.4.8) for μ_1 gives

$$\mu_1 = Z_0 \left\{ \frac{Z_{in} - iZ_0 \tan(\beta_0 x)}{i\omega A_c d Z_0 + Z_{in} \omega A_c d \tan(\beta_0 x)} \right\}. \quad (3.4.9)$$

Equation (3.4.9) gives an expression for the permeability in terms of the input impedance, which is what is desired. However, it is inconvenient to deal with the dimensions of the transmission line, so it is desirable to eliminate the constant factor A_c . This can be done in the following manner. The velocity of propagation of EM waves in the line is given by

$$v = \frac{1}{\sqrt{LC}} \quad (3.4.10)$$

where L and C are the inductance and capacitance per unit length of the line respectively. The characteristic impedance of the lossless part of the line is given by

$$Z_0 = \sqrt{\frac{L}{C}} = 50\Omega \quad (3.4.11)$$

and is purely resistive. The angular frequency can be expressed as

$$\omega = 2\pi f = \frac{2\pi v}{\lambda} = \frac{2\pi}{\lambda\sqrt{LC}}. \quad (3.4.12)$$

Equation (3.4.9) can be rewritten as

$$\mu_1 = \frac{Z_0}{\omega A_c d} \left\{ \frac{Z_{in} - iZ_0 \tan(\beta_0 x)}{iZ_0 + Z_{in} \tan(\beta_0 x)} \right\} = \frac{Z_0}{\omega A_c d} \left\{ \frac{(Z_{in}/Z_0) - i \tan(\beta_0 x)}{i + (Z_{in}/Z_0) \tan(\beta_0 x)} \right\}. \quad (3.4.13)$$

Substituting (3.4.11) and (3.4.12) into (3.4.13) gives

$$\mu_1 = \frac{\lambda}{2\pi A_c d} L \left\{ \frac{(Z_{in}/Z_0) - i \tan(\beta_0 x)}{(Z_{in}/Z_0) \tan(\beta_0 x) + i} \right\}. \quad (3.4.14)$$

Assuming that the lossless section of the line is filled with air, the inductance per unit length can be written as $L = A_c \mu_0$ (3.4.15)

Substituting (3.4.15) into equation (3.4.14) gives

$$\frac{\mu_1}{\mu_0} = \frac{\lambda}{2\pi d} \left\{ \frac{(Z_{in}/Z_0) - i \tan(\beta_0 x)}{(Z_{in}/Z_0) \tan(\beta_0 x) + i} \right\}. \quad (3.4.16)$$

We now have an equation for the permeability of a sample material in terms of the known characteristics of the transmission line, and the input impedance as seen by the sample material.

Noting that $Z_{in} = R_{in} + iX_{in}$, $\mu_r = \mu_1/\mu_0$ and that $Z_0 = R_0 = 50 \Omega$, one can write equation (3.4.16) in terms of the real and imaginary components of the relative complex permeability with

$$\mu_r' = \frac{\lambda}{2\pi d} \left\{ \frac{R_{in}^2 \tan(\beta_0 x) + (X_{in} - R_0 \tan(\beta_0 x))(X_{in} \tan(\beta_0 x) + R_0)}{(R_{in} \tan(\beta_0 x))^2 + (X_{in} \tan(\beta_0 x) + R_0)^2} \right\} \quad (3.4.17)$$

and

$$\mu_r'' = \frac{\lambda}{2\pi d} \left\{ \frac{R_{in}(X_{in} \tan(\beta_0 x) + R_0) - (X_{in} - R_0 \tan(\beta_0 x))(R_{in} \tan(\beta_0 x))}{(R_{in} \tan(\beta_0 x))^2 + (X_{in} \tan(\beta_0 x) + R_0)^2} \right\}. \quad (3.4.18)$$

Since $\mu'(\omega) = 1 + \chi'(\omega)$ and $\mu''(\omega) = \chi''(\omega)$, it is possible to determine the complex susceptibility of a ferrofluid sample from the impedance measurements of the short circuited transmission line.

3.5. Measurement of the complex relative permittivity

The measurement of the complex permittivity, $\epsilon(\omega)$, follows a very similar procedure to that of $\mu(\omega)$. The only difference is that the transmission line is terminated in an open circuit. The equivalent circuit for the open circuited transmission line is shown in figure 3.4. The open circuit ensures that the line behaves as a pure capacitor.

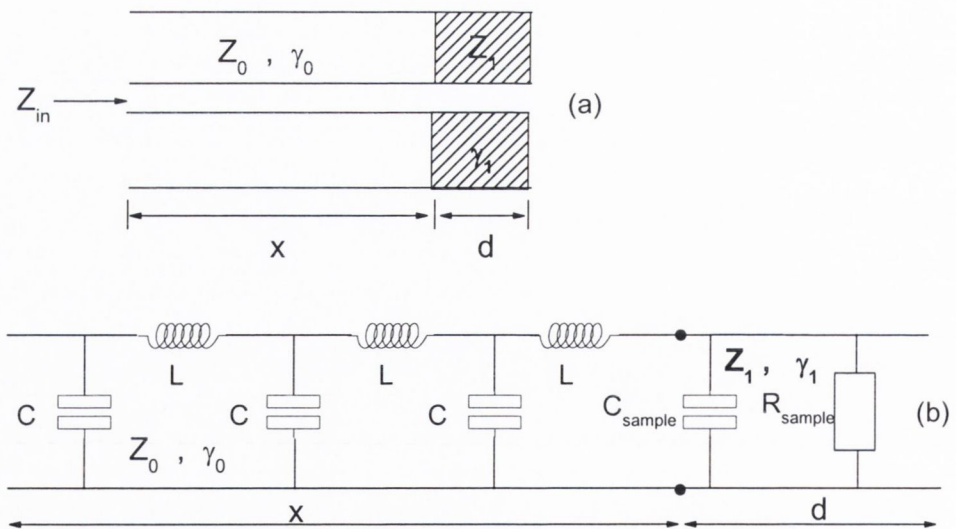


Figure 3.4 (a): Model of coaxial transmission line terminated in toroidal sample terminated in open circuit. **Figure 3.4 (b):** Equivalent circuit of open terminated transmission line with capacitive impedance of sample denoted by R_{sample} and C_{sample} .

The open circuit ensures that within the sample, the electric field is large, and the magnetic field small, provided that the wavelength of EM radiation within the sample is much less than the sample thickness.

Proceeding as before, the load impedance is given as

$$Z_x = Z_l \coth(\gamma_l d). \quad (3.5.1)$$

The intrinsic impedance of the sample medium can be written as

$$Z = \frac{\gamma_l}{i\omega\epsilon_l} \quad (3.5.2)$$

where ϵ_l is the complex absolute permittivity of the medium. Using equation (3.4.5) the equation for the load impedance can be written as

$$Z_x = A_c \frac{\gamma_l}{i\omega\epsilon_l} \coth(\gamma_l d) \quad (3.5.3)$$

Again assuming that the sample depth is far less than the wavelength of electromagnetic radiation in the sample, it is possible to simplify equation (3.5.3).

With $\gamma_l d \ll 1$, $\coth(\gamma_l d) \approx \frac{1}{\gamma_l d}$ so that

$$Z_x = \frac{A_c}{i\omega\epsilon_l d}. \quad (3.5.4)$$

Substituting equation (3.5.4) into equation (3.3.4) gives

$$Z_{in} = Z_0 \left\{ \frac{(A_c / i\omega\epsilon_l d) + iZ_0 \tan(\beta_0 x)}{Z_0 + (A_c / \omega\epsilon_l d) \tan(\beta_0 x)} \right\}. \quad (3.5.5)$$

Solving (3.5.5) for ϵ_l gives

$$\epsilon_l = \frac{A_c}{\omega Z_0 d} \left\{ \frac{(Z_0 / Z_{in}) - i \tan(\beta_0 x)}{(Z_0 / Z_{in}) \tan(\beta_0 x) + i} \right\}. \quad (3.5.6)$$

The capacitance per unit length for an air filled length of line is given as

$$C = \epsilon_0 / A_c \quad (3.5.7)$$

using this, and recalling equations (3.4.11) and (3.4.12), equation (3.5.6) can be rewritten as

$$\frac{\epsilon_l}{\epsilon_0} = \epsilon_r = \frac{\lambda}{2\pi d} \left\{ \frac{(Z_0 / Z_{in}) - i \tan(\beta_0 x)}{(Z_0 / Z_{in}) \tan(\beta_0 x) + i} \right\}. \quad (3.5.8)$$

Once more, equation (3.5.8) can be broken up into its real and imaginary components giving

$$\varepsilon_r' = \frac{\lambda}{2\pi d} \left\{ \frac{(R_0 + X_{in} \tan(\beta_0 x))(R_0 \tan(\beta_0 x) - X_{in}) - R_{in}^2 \tan(\beta_0 x)}{(R_0 \tan(\beta_0 x) - X_{in})^2 + R_{in}^2} \right\} \quad (3.5.9)$$

and

$$\varepsilon_r'' = \frac{\lambda}{2\pi d} \left\{ \frac{(R_0 + X_{in} \tan(\beta_0 x))R_{in} + (R_{in} \tan(\beta_0 x))(R_0 \tan(\beta_0 x) - X_{in})}{(R_0 \tan(\beta_0 x) - X_{in})^2 + R_{in}^2} \right\}. \quad (3.5.10)$$

3.6. Combined method for measuring complex permeability and permittivity

Section 3.1 discussed the relationship between sample depth and measureable frequency range. The general conclusion was that the lower the frequency of measurement the deeper the test cell. At frequencies of 10 MHz to approximately 3 GHz a test cell of depth 9.5 mm is used, whilst at higher frequencies test cells of depth 1.94 mm and 1.04 mm are used to measure up to 6 GHz and 16 GHz respectively. Magnetic measurements require the application of a short circuit to the transmission line, so that the electric field within the material being measured is eliminated. However as the sample depth decreases in line with increasing frequency, the sample depth becomes an appreciable fraction of the wavelength of the radiation in the line. Under these conditions, the electric field in a short circuited line is not eliminated. Thus it is no longer possible to measure μ independent of ε . This can lead to measurement errors. To improve the model, two sets of measurements are taken, one for short circuit, the other with an open circuit. Both sets of measurements are placed into simultaneous equations where μ and ε can be determined in software.

Equations (3.4.1) and (3.5.1) can be relabelled to give

$$Z_{xsc} = Z_1 \tanh(\gamma_1 d) \quad (3.6.1)$$

and

$$Z_{xoc} = Z_1 \coth(\gamma_1 d). \quad (3.6.2)$$

Writing the characteristic impedance for the length of the line containing the sample as

$$Z_1 = \sqrt{\frac{L_1}{C_1}} = \sqrt{\frac{A_c \mu_1}{(\varepsilon_1 / A_c)}} = \sqrt{\frac{A_c^2 \mu_1}{\varepsilon_1}} = A_c \sqrt{\frac{\mu_1}{\varepsilon_1}}, \quad (3.6.3)$$

and using equation (3.3.2) it is possible to write the input impedances for short and open circuits as

$$Z_{insc} = Z_0 \left\{ \frac{A_c \sqrt{\mu_1/\varepsilon_1} \tanh(\gamma_1 d) + Z_0 \tanh(\gamma_0 x)}{Z_0 + A_c \sqrt{\mu_1/\varepsilon_1} \tanh(\gamma_1 d) \tanh(\gamma_0 x)} \right\} \quad (3.6.4)$$

and

$$Z_{inoc} = Z_0 \left\{ \frac{A_c \sqrt{\mu_1/\varepsilon_1} \coth(\gamma_1 d) + Z_0 \tanh(\gamma_0 x)}{Z_0 + A_c \sqrt{\mu_1/\varepsilon_1} \coth(\gamma_1 d) \tanh(\gamma_0 x)} \right\}. \quad (3.6.5)$$

Solving (3.6.4) and (3.6.5) for $\sqrt{\mu_1/\varepsilon_1}$ gives two expressions namely:

$$\sqrt{\frac{\mu_1}{\varepsilon_1}} \tanh(\gamma_1 d) = \frac{Z_0}{A_c} \left\{ \frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \right\}, \quad (3.6.6)$$

and

$$\sqrt{\frac{\mu_1}{\varepsilon_1}} \coth(\gamma_1 d) = \frac{Z_0}{A_c} \left\{ \frac{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}{Z_{inoc} \tanh(\gamma_0 x) - Z_0} \right\}. \quad (3.6.7)$$

In a similar way to equation (3.6.3) Z_0 can be written as

$$Z_0 = A_c \sqrt{\frac{\mu_0}{\varepsilon_0}}. \quad (3.6.8)$$

Substituting (3.6.8) into equations (3.6.6) and (3.6.7) and dividing across by $\sqrt{\mu_0/\varepsilon_0}$ gives

$$\sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh(\gamma_1 d) = \frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0}, \quad (3.6.9)$$

and

$$\sqrt{\frac{\mu_r}{\varepsilon_r}} \coth(\gamma_1 d) = \frac{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}{Z_{inoc} \tanh(\gamma_0 x) - Z_0}. \quad (3.6.10)$$

We now have two equations in two unknowns, μ_r , ε_r . Taking the product of equations (3.6.9) and (3.6.10) produces an expression for μ_r/ε_r where

$$\mu_r/\varepsilon_r = P + iQ = \frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \times \frac{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}{Z_{inoc} \tanh(\gamma_0 x) - Z_0}. \quad (3.6.11)$$

P and Q denote the real and imaginary parts of the right hand side of equation (3.6.11).

Dividing equation (3.6.9) by equation (3.6.10) yields

$$\tanh^2(\gamma_1 d) = R + iS = \frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \times \frac{Z_{inoc} \tanh(\gamma_0 x) - Z_0}{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}, \quad (3.6.12)$$

with R and S denoting the real and imaginary parts of the right hand side of equation (3.6.12).

Equation (3.4.3) tells us that $\gamma_1 = i\omega\sqrt{\varepsilon_1\mu_1}$ so that equation (3.6.12) becomes

$$\tanh^2(i\omega d\sqrt{\varepsilon_1\mu_1}) = R + iS \Rightarrow \tanh(i\omega d\sqrt{\varepsilon_1\mu_1}) = \sqrt{R + iS}. \quad (3.6.13)$$

Knowing $\tanh(i\mathcal{G}) = i\tan(\mathcal{G})$, equation (3.6.13) can be written as

$$i \tan(\omega d\sqrt{\varepsilon_1\mu_1}) = \sqrt{R + iS}. \quad (3.6.14)$$

Now, dividing across by i and solving for $\varepsilon_1\mu_1$ gives

$$\varepsilon_1\mu_1 = \frac{1}{\omega^2 d^2} \left[\tan^{-1}(-i\sqrt{R + iS}) \right]^2. \quad (3.6.15)$$

To convert to relative values, it is necessary to divide both sides by $\varepsilon_0\mu_0$ so that

$$\varepsilon_r\mu_r = \frac{1}{\varepsilon_0\mu_0\omega^2 d^2} \left[\tan^{-1}(-i\sqrt{R + iS}) \right]^2 = X + iY. \quad (3.6.16)$$

$X + iY$ can be written as

$$X + iY = \frac{1}{\varepsilon_0\mu_0\omega^2 d^2} \left\{ \tan^{-1} \left(-i \sqrt{\frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \times \frac{Z_{inoc} \tanh(\gamma_0 x) - Z_0}{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}} \right) \right\}^2. \quad (3.6.17)$$

Once more, X and Y represent the real and imaginary components of equation (3.6.17). By combining equations (3.6.11) and (3.6.16) it is possible to arrive at expressions for μ_r and ε_r where

$$\mu_r = \sqrt{(P + iQ)(X + iY)}, \quad (3.6.17)$$

giving

$$\mu_r = \left\{ \left(\frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \times \frac{Z_{inoc} \tanh(\gamma_0 x) - Z_0}{Z_0 \tanh(\gamma_0 x) - Z_{inoc}} \right) \times \left[\frac{1}{\varepsilon_0\mu_0\omega^2 d^2} \left\{ \tan^{-1} \left(-i \sqrt{\frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \times \frac{Z_{inoc} \tanh(\gamma_0 x) - Z_0}{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}} \right) \right\}^2 \right] \right\}^{\frac{1}{2}}. \quad (3.6.18)$$

and

$$\varepsilon_r = \sqrt{(X + iY)/(P + iQ)}, \quad (3.6.19)$$

giving

$$\varepsilon_r = \left\{ \left(\frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \times \frac{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}{Z_{inoc} \tanh(\gamma_0 x) - Z_0} \right) \div \left[\frac{1}{\varepsilon_0 \mu_0 \omega^2 d^2} \left\{ \tan^{-1} \left(-i \sqrt{\frac{Z_0 \tanh(\gamma_0 x) - Z_{insc}}{Z_{insc} \tanh(\gamma_0 x) - Z_0} \times \frac{Z_{inoc} \tanh(\gamma_0 x) - Z_0}{Z_0 \tanh(\gamma_0 x) - Z_{inoc}}} \right) \right\}^2 \right] \right\}^{\frac{1}{2}}. \quad (3.6.20)$$

The above are equations for the complex permeability and permittivity in terms of the parameters P , Q , X , and Y which can be determined from impedance measurements.

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Chapter 4: Experimental Results

4.1. Introduction

Chapter 3 presented equations for calculating $\chi(\omega)$ from impedance measurements in the low (< 10 MHz), and high (> 10 MHz) frequency regions. In the following chapter, the experimental results from these measurements will be presented, and analysed in terms of the theory presented in chapters 1 and 2. Section 4.2 will examine the use of dielectric formalism to analyse $\chi(\omega)$ and the Debye and Cole-Cole equations for the Brownian susceptibility will be extended to describe the susceptibility of a ferrofluid which exhibits a bimodal distribution of particles sizes.

The cyclical application of a biasing field to a ferrofluid will be examined in detail in section 4.3. The theoretical effects of the application of a biasing or polarising field are documented in section 2.9. However, previous to this work, to my knowledge there has been no investigation as to whether the application of a cyclic polarising field has any lasting effects on the ferrofluid. Analysis is given, in an attempt to address this important question, by cycling the biasing field forward and reverse, and comparing the $\chi(\omega)$ data obtained in each direction. The analysis was extended further, by reversing the polarity of the biasing field, and comparing the measured susceptibilities at individual values of frequency and applied field. The results are interpreted in terms of the Weierstrass Theorem [1], and conditions are given to determine whether the fluid exhibits Isotropic behaviour, i.e. whether the susceptibility is independent of the polarity (or direction) of the biasing field.

Section 4.4 investigates $\chi(\omega)$ of a magnetic microsphere-based colloidal system. The results obtained defy the conventional Langevin theory for the field dependence of a ferrofluid. In this section an attempt is made to quantify this unusual behaviour.

Equations were derived in chapter three to calculate the complex permeability and permittivity of a ferrofluid, measured at radio frequencies, using the transmission line measurement technique. It was shown how it is possible to calculate $\mu(\omega)$, and hence $\chi(\omega)$, in a simple way using a short circuit termination, and in a more complex way, by combining short and open circuit measurements into a set of

simultaneous equations. Section 4.5 investigates the difference between computing $\chi(\omega)$ using the simple short circuited method of section 3.4, and the more complex combined, open-and short-circuited method of section 3.5. Susceptibility measurements plotted against biasing field will be presented, demonstrating the ferromagnetic resonance of the magnetic moments in the ferrofluid, indicated by the change in sign of the real component of $\chi(\omega)$. These measurements will be used to show how important material parameters, such as the anisotropy constant, K , the precessional decay time, τ_0 , and the gyromagnetic constant, γ , can be determined. Verification of the field dependence of $\chi(\omega)$, according to the equation of Landau and Lifshitz, will be demonstrated through the use of Cole Cole plots of $\chi(\omega)$ at a constant frequency against variable field.

4.2. The use of dielectric formulism to analyse $\chi(\omega)$

For a dielectric material, the relationship between $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ and their dependence on frequency can be modelled by a method first proposed by Cole and Cole [2]. Their method involves plotting $\varepsilon''(\omega)$ as a function of $\varepsilon'(\omega)$. This method has been successfully adopted for the analysis of ferrofluid data where $\chi''(\omega)$ is plotted as a function of $\chi'(\omega)$. The simplest Cole-Cole plot is for the Debye equation (equation 2.5.4), which describes a semicircle of radius $\frac{\chi_0 - \chi_\infty}{2}$, with centre on the $\chi'(\omega)$ axis at $\chi' = \frac{\chi_0 + \chi_\infty}{2}$. The maximum value $\chi''(\omega)$ occurs when $\chi' = \frac{\chi_0}{2}$, i.e. when $\omega\tau_B = 1$ and $\chi_\infty = 0$. The Cole-Cole plot for the Debye equation is shown in figure 4.1 (a), along with the corresponding plot of $\chi(\omega)$ against frequency. Plotting the Cole-Cole equation used to describe the Brownian susceptibility (equation 2.5.12), also yields a circular arc, but in this case, the centre of the circle lies below the horizontal axis. The circular arc cuts the $\chi'(\omega)$ axis at an angle of $\Omega = \alpha\pi/2$. Figure 4.2 shows the susceptibility data against frequency plotted for equation (2.5.12). The parameter α is the same as that used to model the distribution of relaxation times in equation (2.5.12). By fitting a semi circle to the experimental data expressed in the Cole-Cole format, it is possible to evaluate the value of α . The value

obtained from the Cole-Cole plot should be comparable to that used in the fitting of equation (2.5.12) to the $\chi(\omega)$ data.

Figure 4.3 (a) shows the Cole-Cole plot for an isoparaffin based cobalt ferrite ferrofluid (fluid 1), of saturation magnetisation, $M_{sat} = 363$ G. Fitting to a semicircle yields an angle of $\Omega = 38.9^\circ$, which corresponds to a value of $\alpha = 0.432$ Figure 4.3 (b) shows the same data graphed in the frequency domain and fitted to equation (2.5.12). The value of α obtained from the fit was $\alpha = 0.43$ which is in close agreement to that obtained from the Cole-Cole diagram. It should be noted that the loss peak in figure 4.3 (b) occurs at 550 Hz, which is quite a low value indicating a large particle or aggregate size.

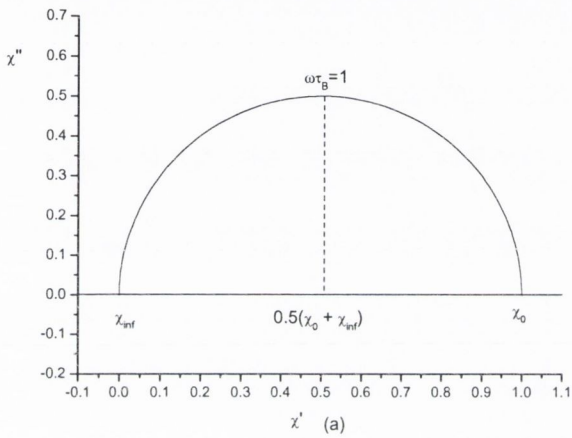


Figure 4.1 (a): Cole-Cole plot of the theoretical Debye equation (equation 2.5.4).

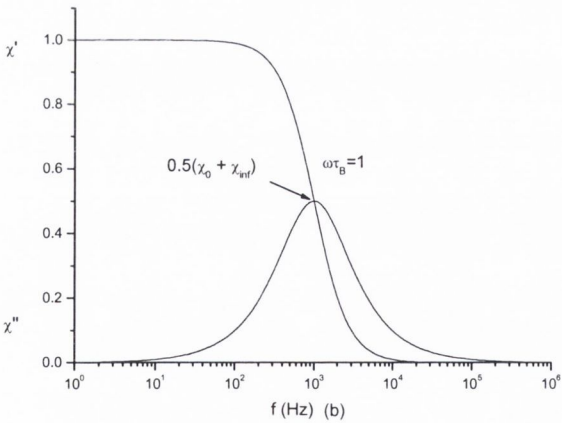


Figure 4.1 (b): Plot of the theoretical Debye equation (equation 2.5.4) against frequency.

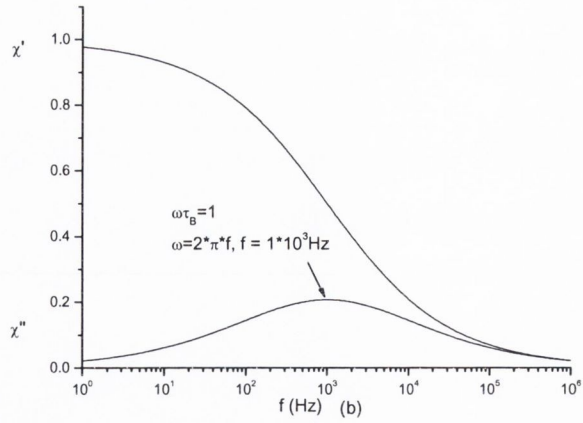


Figure 4.2 : Plot of the equation for the Brownian susceptibility (equation 2.5.12) against frequency. The value of α used is 0.5.

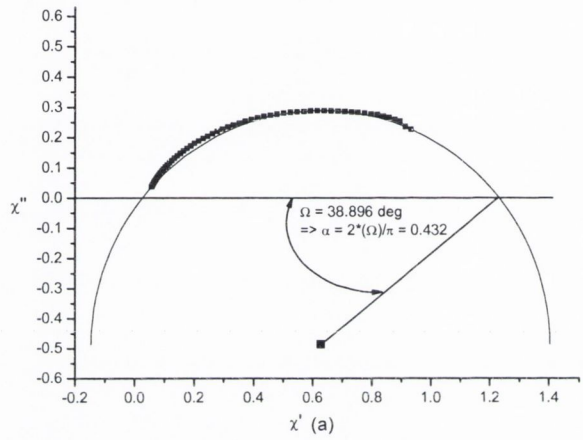


Figure 4.3 (a): Cole-Cole plot and fit of the susceptibility data for a cobalt ferrite in isoparaffin ferrofluid (fluid 1). Fitting a semicircle to the data yields a value of $\alpha = 0.432$ for the Cole-Cole distribution parameter.

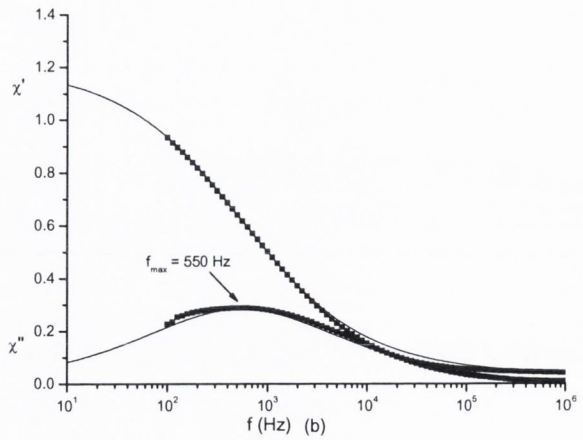


Figure 4.3 (b): Susceptibility data for the ferrofluid of fig 4.3 (a). The data is fitted to equation (2.5.12). The fit yields a value of $\alpha = 0.43$ for the Cole-Cole distribution parameter.

Under certain conditions, it is possible for a ferrofluid to contain a double or bimodal distribution of particle sizes. The bimodal distribution manifests itself as a double loss peak in the susceptibility spectrum. An analysis of such a ferrofluid is given in [3] where the application of a biasing field is found to induce a double loss peak over the frequency range measured. It is possible to modify the standard Debye and Cole-Cole equations to take account of a bimodal distribution. Equation (2.5.4) can be rewritten as [4]

$$\chi(\omega) = (\chi_0 - \chi_\infty) \left\{ \frac{A}{1 + i\omega\tau_1} + \frac{B}{1 + i\omega\tau_2} \right\} + \chi_\infty \quad (4.2.1)$$

where A and B represent a two particle fraction such that, $A + B \leq 1$ and $A, B \leq 1$. τ_1 , τ_2 represent the average relaxation times of the individual sections of the overall susceptibility. For A or $B = 0$, equation (4.2.1) reverts to the original Debye equation (equation 2.5.4). Figure 4.4 (a) shows a theoretical plot of a susceptibility spectrum displaying two loss peaks, in accordance with equation (4.2.1), whilst figure 4.4 (b) shows the corresponding bimodal Cole-Cole plot.

Due to the presence of a distribution of particle sizes and relaxation times, equation (4.2.1) is not sufficient to describe $\chi(\omega)$. The Cole-Cole equation must be modified in the same way to include a two particle fraction, giving

$$\chi(\omega) = (\chi_0 - \chi_\infty) \left\{ \frac{A}{1 + (i\omega\tau_1)^{(1-\alpha_1)}} + \frac{B}{1 + (i\omega\tau_2)^{(1-\alpha_2)}} \right\} + \chi_\infty \quad (4.2.2)$$

where α_1 and α_2 are the Cole-Cole distribution parameters describing τ_1 and τ_2 respectively.

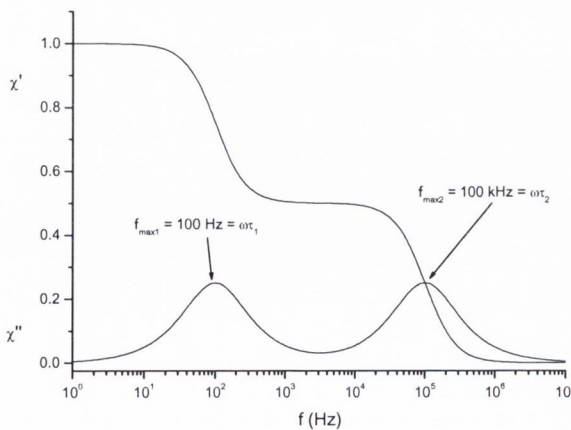


Fig 4.4 (a): Theoretical plot of susceptibility spectra displaying two loss peaks.

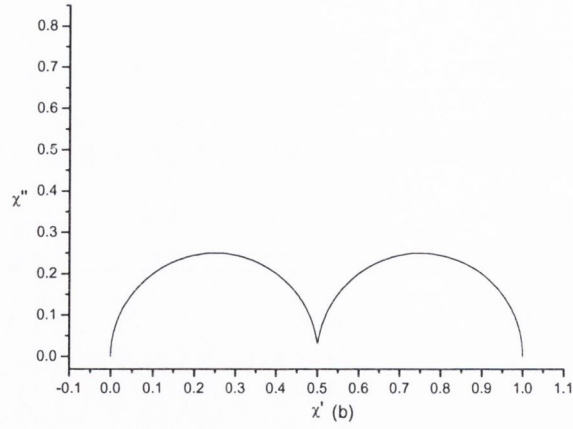


Fig 4.4 (b): Cole-Cole plot of susceptibility data of figure 4.4 (a).

The fluid investigated in [3] is a colloidal suspension of magnetite particles of mean radius 5 nm, in water, with oleic acid as surfactant (fluid 2). M_{sat} is 363 Gauss. Measurements of $\chi(\omega)$ were performed over the range of 200 Hz to 1 MHz, and the polarising field was applied in 15 increments from 0 – 13.6 kA/m. Figures 4.5 and 4.6 show the susceptibility plotted against frequency. Figure 4.5 shows the effect of the polarising field on the evolution of $\chi'(\omega)$, with $\chi'(\omega)$ decreasing as the polarising field, H , is increased. This is as predicted by theory as shown in section 2.9. The dashed lines in figure 4.5 correspond to the unpolarised susceptibility measurement. There is no loss peak in the frequency range measured, indicating a well dispersed ferrofluid, with an absence of aggregates. For clarity, the remaining $\chi''(\omega)$ plots are shown in figure 4.6. As predicted, the susceptibility decreased with increasing H . However as H is increased from zero, a loss peak begins to appear, first at $H = 4.5$ kA/m, with a peak frequency of $f_{max} = 39$ kHz. As H is increased further, two separate loss peaks begin to appear, until at the maximum value of applied field at $H = 13.6$ kA/m, two distinct peaks occur at $f_{max} = 1.7$ kHz, and 35 kHz.

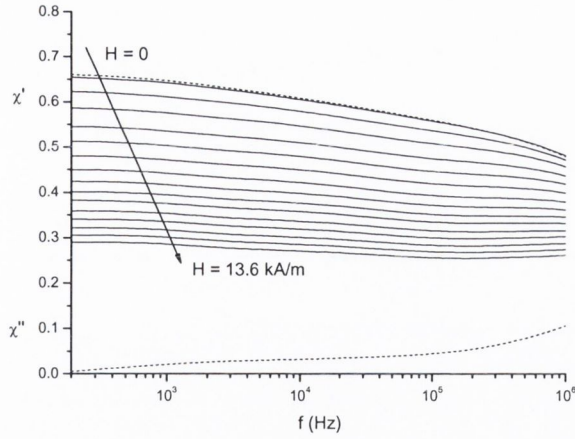


Figure 4.5: Plots of the unpolarised susceptibility spectra (dashed line) and the remaining $\chi'(\omega)$ spectra against f , for increasing H .

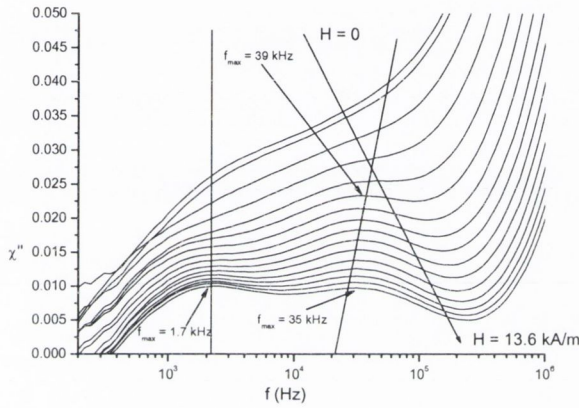


Figure 4.6: Variation of $\chi''(\omega, H)$ against f (Hz) plotted against increasing H , exhibiting bimodal loss peaks at $f_{max}=1.7$ kHz, and 35kHz at $H = 13.6$ kA/m.

The data presented in figures 4.5 and 4.6 has been fitted to equation (4.2.2) for selected values of applied field, at $H = 5.54, 8.18$, and 13.6 kA/m. These are plotted in figures 4.7 (a) – 4.9 (a). An enlarged view of the fit to $\chi''(\omega)$, which is the area of interest, is shown in figures 4.7 (b) – 4.9 (b), along with the values of f_{max} and α for each section of the bimodal distribution. The susceptibility spectra are then plotted in Cole-Cole format (figures 4.7 (c) – 4.9 (c)), with each section of the bimodal distribution fitted individually to a depressed circular arc. This yields values of α_1 , and α_2 corresponding to each loss peak of the $\chi(\omega)$ spectrum. The values of $\alpha_{1,2}$ yielded from the Cole-Cole plots, compare favourably with those obtained from the fit of equation (4.2.2), verifying the values obtained. A comparison between the values of α yielded from the two different methods is shown in table 4.1.

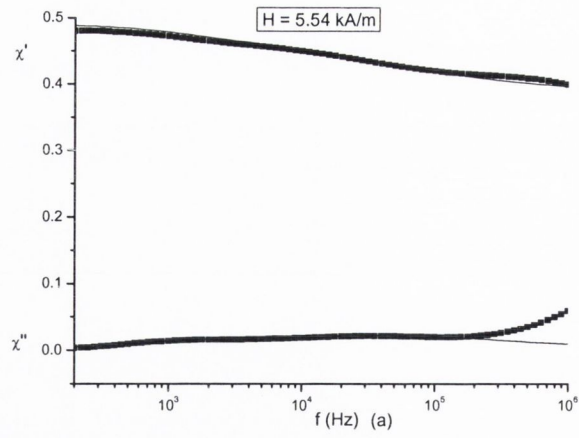


Figure 4.7 (a): Fit of $\chi(\omega)$ to equation (4.2.2) at $H = 5.54$ kA/m.

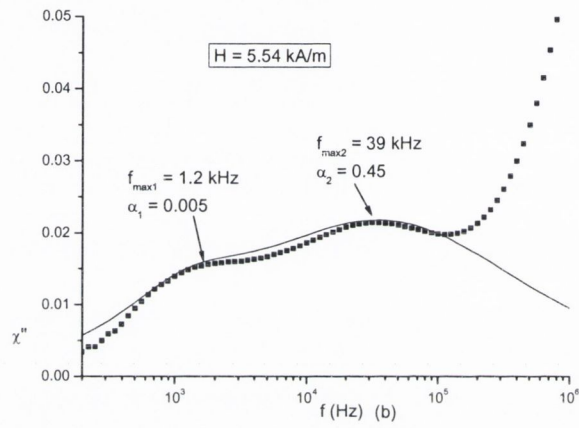


Figure 4.7 (b): Fit of $\chi''(\omega)$ to equation (4.2.2) at $H = 5.54$ kA/m.

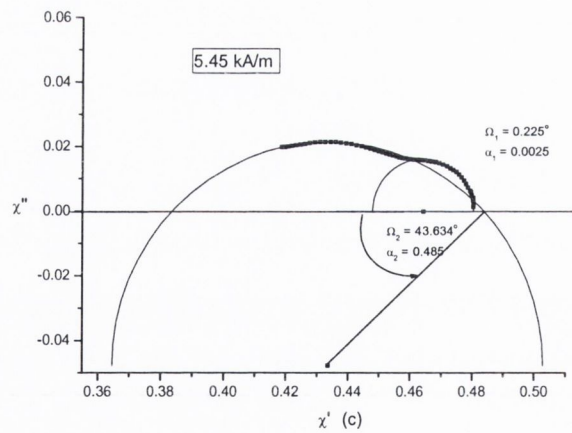


Figure 4.7 (c): Cole-Cole plot of $\chi(\omega)$ fitted to circular arcs at $H = 5.54$ kA/m.

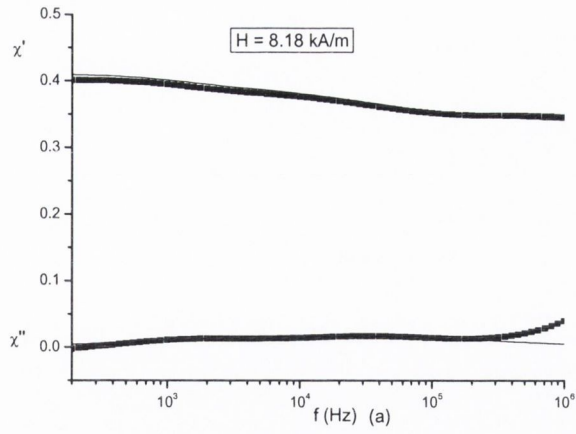


Figure 4.8 (a): Fit of $\chi(\omega)$ to equation (4.2.2) at $H = 8.18$ kA/m.

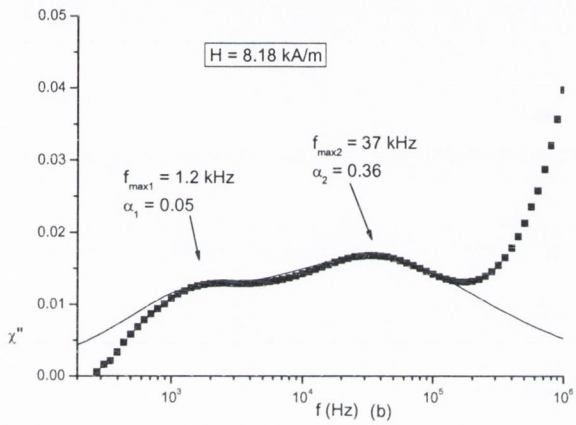


Figure 4.8 (b): Fit of $\chi''(\omega)$ to equation (4.2.2) at $H = 8.18$ kA/m.

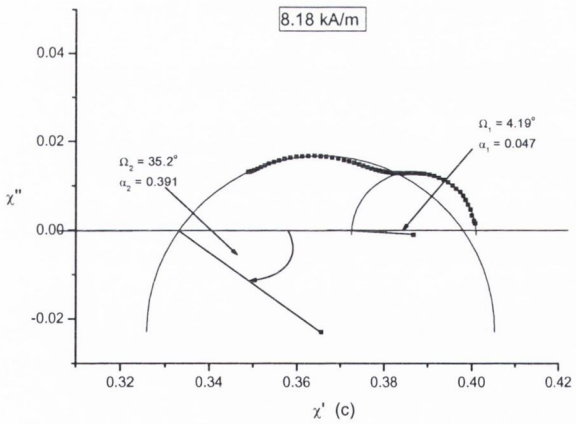


Figure 4.8 (c): Cole-Cole plot of $\chi(\omega)$ fitted to circular arcs at $H = 8.18$ kA/m.

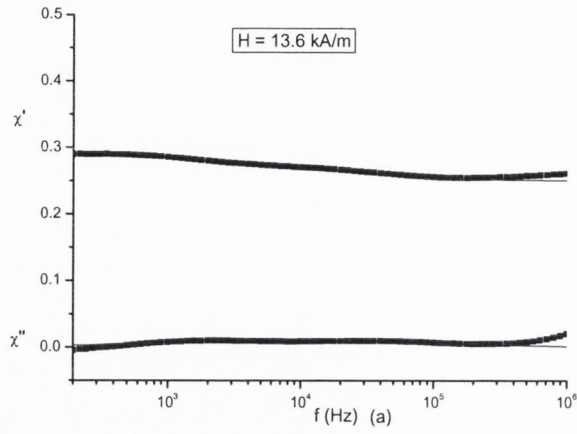


Figure 4.9 (a): Fit of $\chi(\omega)$ to equation (4.2.2) at $H = 13.6$ kA/m.

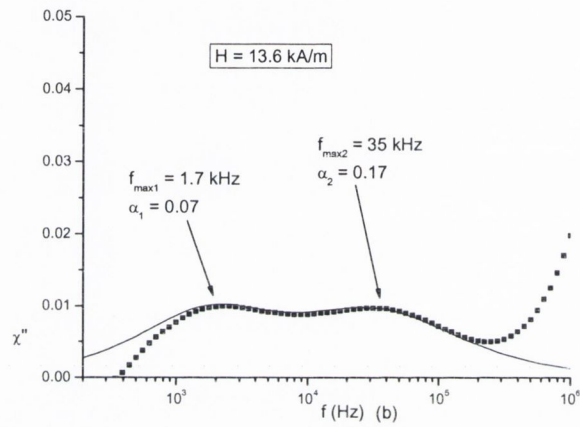


Figure 4.9 (b): Fit of $\chi''(\omega)$ to equation (4.2.2) at $H = 13.6$ kA/m.

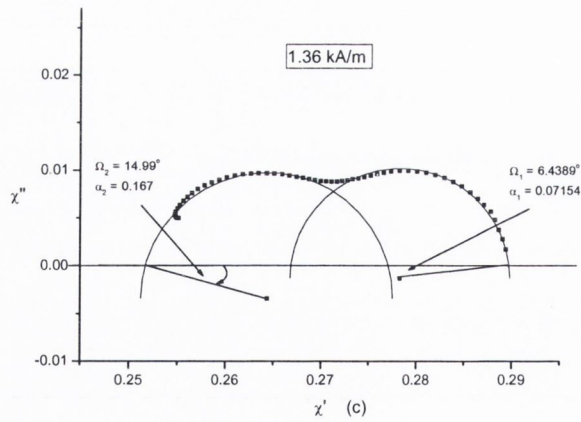


Figure 4.9 (c): Cole-Cole plot of $\chi(\omega)$ fitted to circular arcs at $H = 13.6$ kA/m.

Table 4.1

Comparison of α from fit to equation (4.2.2) and Cole-Cole plots.

H (kA/m)	f_{max1} kHz	f_{max2} kHz	α_1 fit	α_2 fit	α_1 Cole- Cole	α_2 Cole- Cole
5.45	1.2	39	.003	.45	.0025	.485
8.18	1.2	37	.05	.36	.047	.391
13.6	1.7	35	.07	.17	.072	.167

Table 4.1 shows an increase of α_1 with increasing applied field, H . On the other hand, α_2 decreased from a value of approximately 0.45, to 0.17. These values are to be expected from examination of figure 4.5. As H increases, the prominence of the loss peak located in the lower end of the susceptibility spectrum centred on f_{max1} increases, and this would imply an increase in the distribution of relaxation times at f_{max1} as evidenced by the increase in α_1 . Conversely, the width of the loss peak centred on f_{max2} is decreasing with increasing H , which corresponds to the observed decrease in α_2 . The values of α obtained from two separate fitting exercises are a close match, confirming the validity of the use of equation (4.2.2) to describe the susceptibility spectrum of a ferrofluid displaying a bimodal distribution of relaxation times.

4.3. Investigation of the effects of biasing field on the properties of a ferrofluid

The application of a biasing field to a ferrofluid has been well documented in [5] where the dependence of the susceptibility and the relaxation time have been proven to follow equations (2.9.1 and 2.9.3), resulting in a reduction in the magnitude of both $\chi'(\omega)$ and $\chi''(\omega)$, and a decrease in the effective relaxation time. The analysis presented in this section addresses the question as to whether the application of a strong polarising field causes any irreversible effects in the ferrofluid. The starting point of the analysis is to investigate whether the bias field has introduced any hysteresis into the sample. This can be done by measuring $\chi(\omega)$ as the bias field is decreased from its maximum value to zero (reverse measurement), as well as when it is increased from zero to its maximum (forward measurement). The two measurements are then compared. The absence of

hysteresis should be evident, if both forward and reverse measurements are of equal magnitude over the measured frequencies. In [6], measurements are presented of the frequency and field dependence of forward and reverse measurements of a 100 Gauss magnetite in water sample (fluid 3) of mean radius 5.5nm, and of the isoparaffin based cobalt ferrite fluid (fluid 1) used in section 4.2. The polarising field applied was increased in 15 steps of 910 A/m, from 0-13.6 kA/m, and then decreased in the same number of steps from 13.6kA/m to 0A/m. The results for fluid 1 are shown in figures 4.10 and 4.11. Apart from the profiles corresponding to the unpolarised plots, there is little difference between the profiles, indicating an absence of hysteresis. From figure 4.11, it is obvious that the variation in f_{max} for increasing values of H is almost identical to that for decreasing values of H , indicating that the effective relaxation time, and hence the aggregate size corresponding to each value of H , has not changed due to application of forward and reverse values of the applied field.

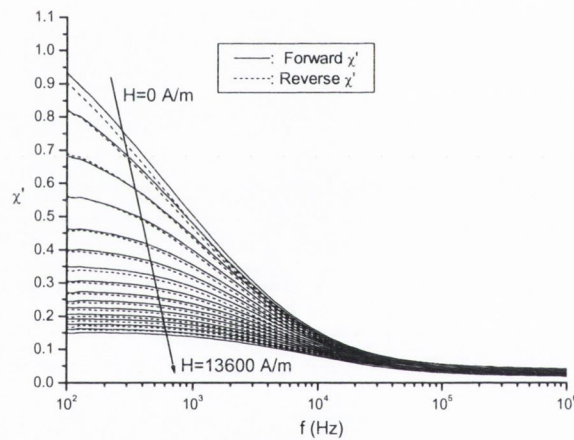


Figure 4.10: Plot of $\chi'(\omega, H)$ (forward and reverse) against f (Hz) for fluid 1.

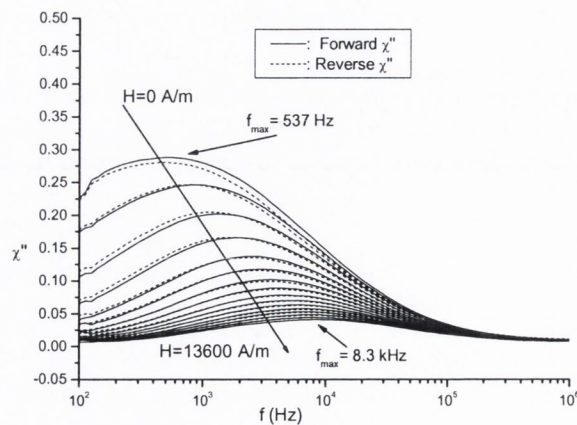


Figure 4.11: Plot of $\chi''(\omega, H)$ (forward and reverse) against f (Hz) for fluid 1.

Figure 4.11 shows an increase in f_{max} from 537 Hz to 8.3 kHz. This is indicative of a decrease in effective relaxation time with a corresponding apparent decrease in average hydrodynamic aggregate size. By means of equation (2.5.3) the corresponding effective aggregate radius is found to vary from 33 to 13nm. The aggregate radii for the reverse measurement are found to be equal to those above, confirming the absence of any hysteresis, as the particles have reverted to their original state.

Figures 4.12 (a-c) show plots of $\chi'(\omega, H)$ and $\chi''(\omega, H)$ obtained for the water based magnetite sample (fluid 3). For clarity, not all of the polarised profiles are shown.

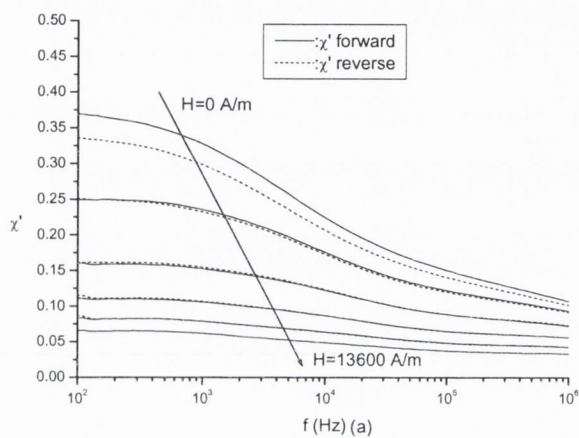


Figure 4.12 (a): Plot of $\chi'(\omega, H)$ (forward and reverse) against f (Hz) for fluid 3.

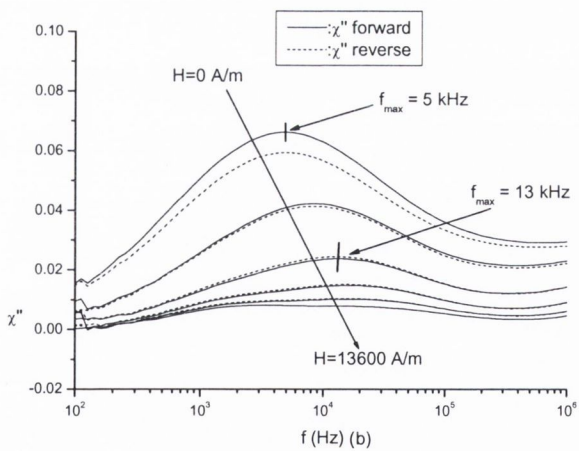


Figure 4.12 (b): Plot of $\chi''(\omega, H)$ (forward and reverse) against f (Hz) for fluid 3.

The unpolarised loss peak occurs at $f_{max} = 5$ kHz which corresponds to an average radius of 22nm, indicating the aggregation of the particles. With increasing H , f_{max} increases, as was the case with the previous sample. At $H = 5.5$ kA/m, f_{max} has

reached a value of 13 kHz. With further increase of H , the loss peak begins to separate out until at $H = 13.6$ kA/m, a bimodal loss peak is apparent, with loss peaks of frequency, $f_{\max A} = 3.3$ kHz, and $f_{\max B} = 20.6$ kHz.

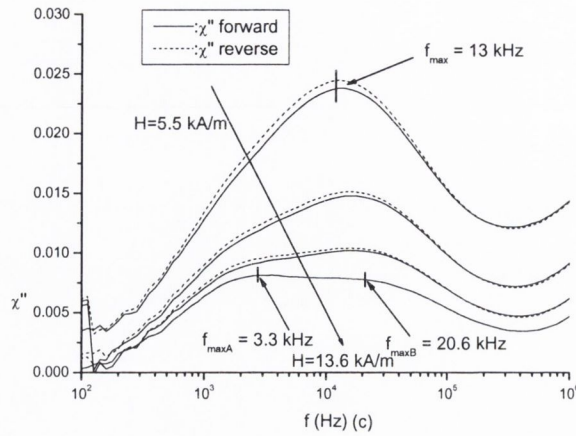


Figure 4.12 (c): Plot of $\chi''(\omega, H)$ (forward and reverse) against f (Hz) over polarising field range, $H = 5.5$ -13.6 kA/m.

This indicates the presence of two different aggregate sizes in the sample, the corresponding average radii being 25 nm, and 13.6 nm. With decreasing H , the dispersion peaks revert to their original profile at $H = 5.5$ kA/m, thereby confirming that no permanent aggregate size species have been induced by the polarising process.

4.3.1. Cyclical variation of the polarising field

Measurements investigating the isotropic properties of the field dependence of ferrofluids have been presented in [7, 8, 9]. By cycling the polarising field over the range ± 13.6 kA/m, it is possible to determine whether the direction of the polarising field has any permanent effects on the properties of the ferrofluid. In [8] measurements were performed on fluid 3 from 200 Hz to 1MHz, cycling the polarising field from 0-13.6kA/m (Forward Positive Measurement), 13.6 – 0 kA/m (Reverse Positive Measurement), 0- -13.6 kA/m (Negative Forward) and -13.6 – 0 kA/m (Negative Reverse). Figure 4.13 (a-b) shows the normalised cycled measurement of $\chi(\omega)$ over the field and frequency range specified, the magnitudes of H used were: 0, 2.73, 5.45, 8.18, 10.9, and 13.6 kA/m.

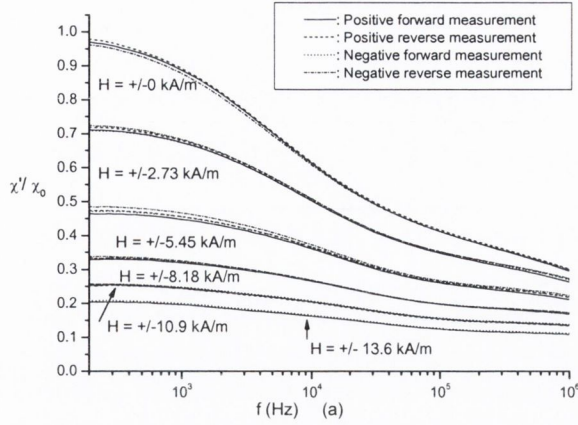


Figure 4.13 (a): Plots of $\chi'(\omega, H)$ against $f(\text{Hz})$ over polarising field range $0 \rightarrow \pm 13.6 \text{ kA/m}$.

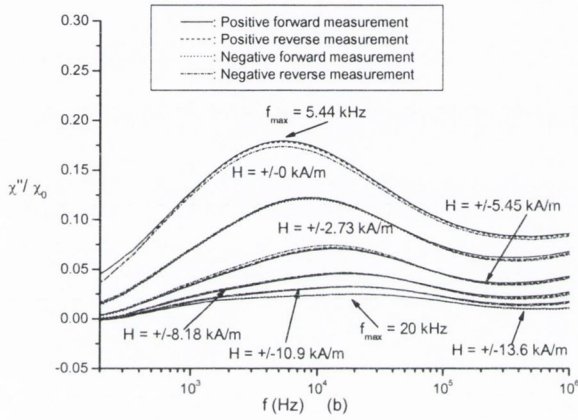


Figure 4.13 (b): Plots of $\chi''(\omega, H)$ against $f(\text{Hz})$ over polarising field range $0 \rightarrow \pm 13.6 \text{ kA/m}$.

It is apparent from figures 4.13 (a) and (b) that there is very little difference between the profiles of $\chi'(\omega, H)$ and $\chi''(\omega, H)$ at each value of H , indicating that the cyclical variation of the polarising field has not introduced any hysteresis into the sample.

A magnetic fluid can be deemed isotropic in relation to the direction of H , if a plot of the graph of $\chi(\omega, H)$ vs. H is symmetrical about the vertical axis. This is demonstrated with the aid of the Weierstrass hypothesis [1] in [7, 8, 9], which states that ‘any continuous function, i.e. $\chi(\omega, H)$, on a closed and bounded interval, can be uniformly approximated on that interval by polynomials, to any degree of accuracy’. We may write,

$$\chi(\omega, H) = a_0(\omega) + a_1(\omega)H + a_2(\omega)H^2 + a_3(\omega)H^3 + a_4(\omega)H^4 + \dots \quad (4.3.1.1)$$

For $\omega = 0$,

$$\chi(0, H) = a_0(0) + a_1(0)H + a_2(0)H^2 + a_3(0)H^3 + a_4(0)H^4 + \dots \quad (4.3.1.2)$$

If the fluid is Isotropic, then $\chi(\omega, H) = \chi(\omega, -H)$.

Consequently, under such conditions,

$$\begin{aligned} a_0(\omega) + a_1(\omega)H + a_2(\omega)H^2 + a_3(\omega)H^3 + a_4(\omega)H^4 + \dots = \\ a_0(\omega) - a_1(\omega)H + a_2(\omega)H^2 - a_3(\omega)H^3 + a_4(\omega)H^4 - \dots, \end{aligned} \quad (4.3.1.3)$$

$$\text{which is only possible if } a_1(\omega) = a_3(\omega) = a_5(\omega) = 0. \quad (4.3.1.4)$$

Hence we would expect to be able to approximate $\chi(\omega, H)$ by a polynomial whose odd coefficients are zero or close to zero. Hence we expect to be able to expand $\chi(\omega, H)$ in a series of even powers of H , i.e.

$$\chi(\omega, H) = a_0(\omega) + a_2(\omega)H^2 + a_4(\omega)H^4 + \dots + a_{2n}(\omega)H^{2n}, \quad (4.3.1.5)$$

which means that a graph of $\chi(\omega, H)$ vs. H is symmetrical about the vertical axis.

Furthermore, if χ is complex, then $\chi(\omega, H) = \chi'(\omega, H) - i\chi''(\omega, H)$. Then the polynomial coefficients a_n can be written as follows

$$a_0(\omega) = a_0'(\omega) - ia_0''(\omega), a_2(\omega) = a_2'(\omega) - ia_2''(\omega), \dots, a_n(\omega) = a_n'(\omega) - ia_n''(\omega).$$

Hence,

$$\begin{aligned} \chi(\omega, H) = a_0'(\omega) + a_2'(\omega)H^2 + a_4'(\omega)H^4 + \dots + a_{2n}'(\omega)H^{2n} \\ - i(a_0''(\omega) + a_2''(\omega)H^2 + a_4''(\omega)H^4 + \dots + a_{2n}''(\omega)H^{2n}). \end{aligned} \quad (4.3.1.6)$$

Comparing real and imaginary components gives

$$\chi'(\omega, H) = a_0'(\omega) + a_2'(\omega)H^2 + a_4'(\omega)H^4 + \dots + a_{2n}'(\omega)H^{2n} \quad (4.3.1.7)$$

and

$$\chi''(\omega, H) = a_0''(\omega) + a_2''(\omega)H^2 + a_4''(\omega)H^4 + \dots + a_{2n}''(\omega)H^{2n}. \quad (4.3.1.8)$$

Thus, as with equation (4.3.1.3), this means that, in the case of a ferrofluid being isotropic, a plot of the individual complex components vs. H is also symmetrical about the vertical axis.

The isotropic properties of fluid 4, which is a 600 G suspension of cobalt particles in L9 oil, of mean radius 5nm and viscosity 65cP, are shown below. As with the results of the cyclical variation of H for fluid 3, the plots of $\chi'(\omega, H)$ and $\chi''(\omega, H)$ against f (figures 4.14 (a), (b)), over the polarising range, show very little difference between the profiles at each value of H , indicating that over the complete cycle of polarisation, the fluid remains unaltered.

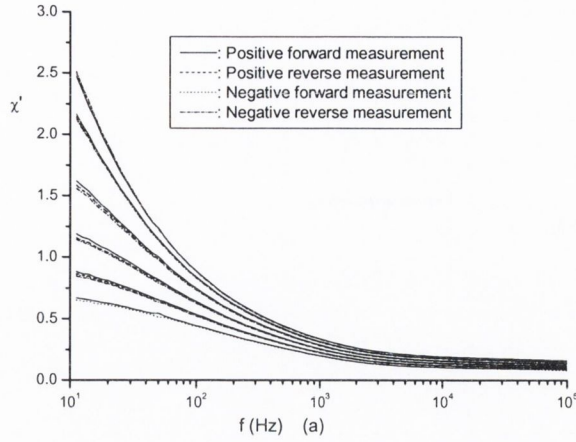


Fig 4.14 (a): Plots of $\chi'(\omega, H)$ against f (Hz) over polarising field range $0 \rightarrow \pm 13.6$ kA/m .

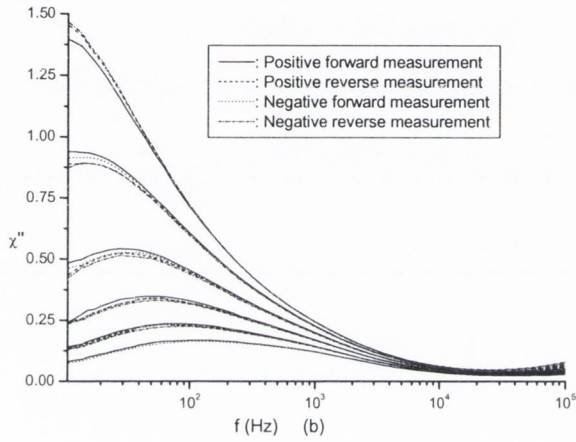


Figure 4.14 (b): Plots of $\chi''(\omega, H)$ against f (Hz) over polarising field range $0 \rightarrow \pm 13.6$ kA/m .

In terms of the model, for the fluid to be isotropic, we have stated that the graph of $\chi(\omega, H)$ vs. H must be symmetrical about the vertical axis. This property is demonstrated by the following examples.

(i): Figures 4.15 (a) and 4.15 (b) show the χ' and χ'' data as a function of H at a frequency of 20 Hz.

(ii): Figures 4.16 (a) and 4.16 (b) show the χ' and χ'' data as a function of H at a frequency of 100 Hz.

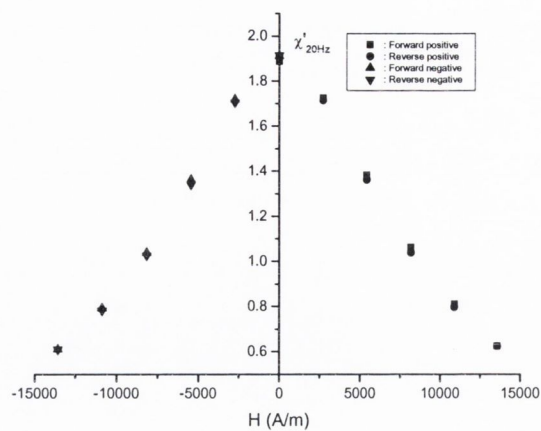


Fig 4.15 (a): Plot of χ' against H at 20 Hz.

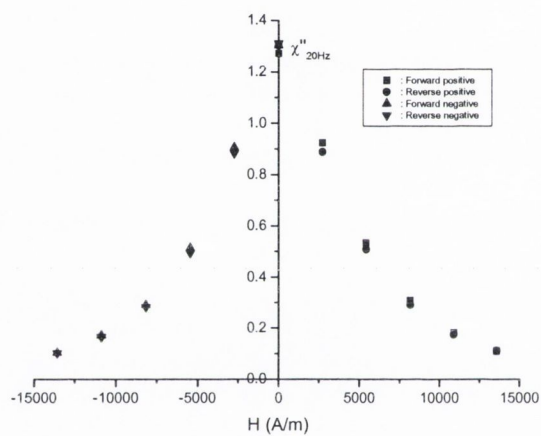


Fig 4.15 (b): Plot of χ'' against H at 20 Hz.

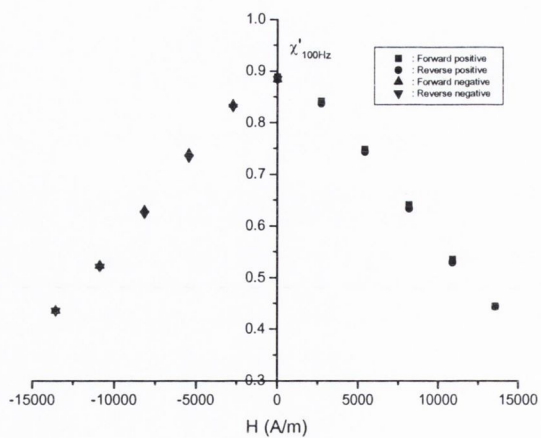


Fig 4.16 (a): Plot of χ' against H at 100 Hz.

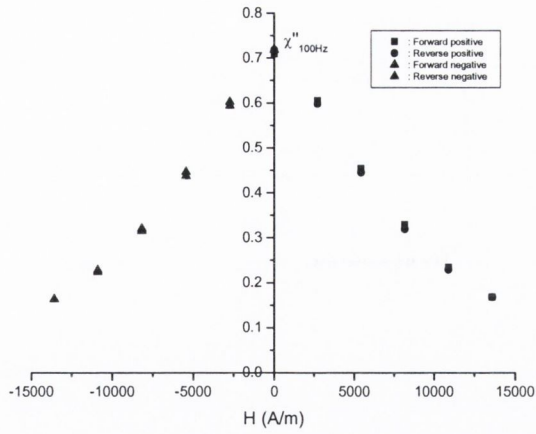


Fig 4.16 (b): Plot of χ'' against H at 100 Hz.

To further emphasise the symmetry of the data, the plots may be fitted to a polynomial or to Gaussian curves, which are naturally symmetric. Figure 4.17 (a) and (b) show the data at 100 Hz fitted to a 9th order polynomial. When evaluated at $H = 10 \text{ kA/m}$, the odd numbered products of $a_n(\omega)H^n$ are negligible in comparison to the even numbered $a_{2n}(\omega)H^{2n}$, thus confirming the condition given in equation (4.3.14).

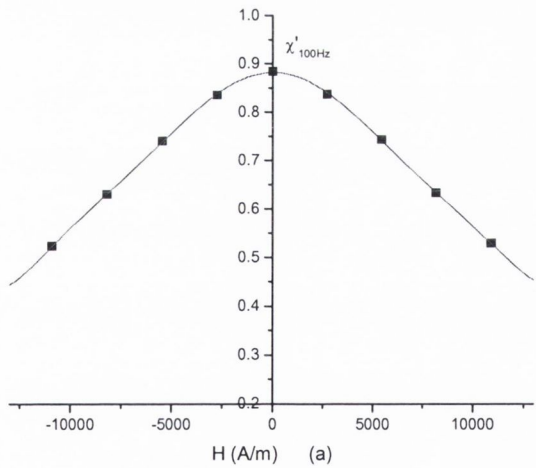


Fig 4.17 (a): 9th order polynomial fit to χ' against H data at 100 Hz.

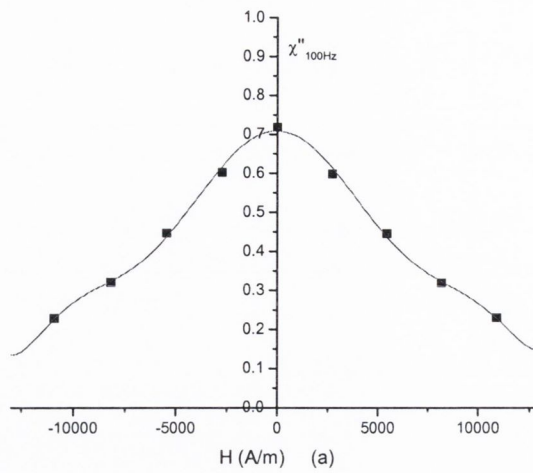


Fig 4.17 (b): 9th order polynomial fit to χ'' against H data at 100 Hz.

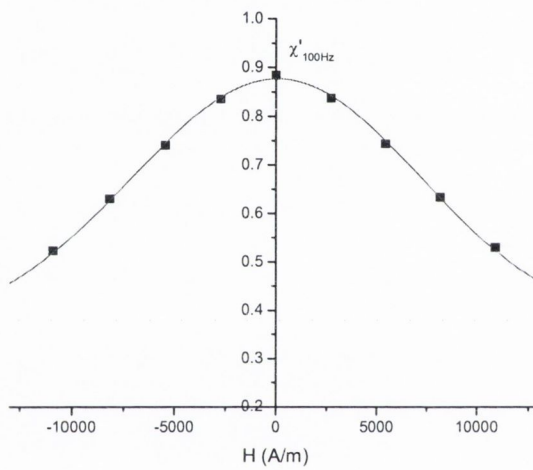


Fig 4.18 (a): Gaussian fit to χ' against H data at 100 Hz.

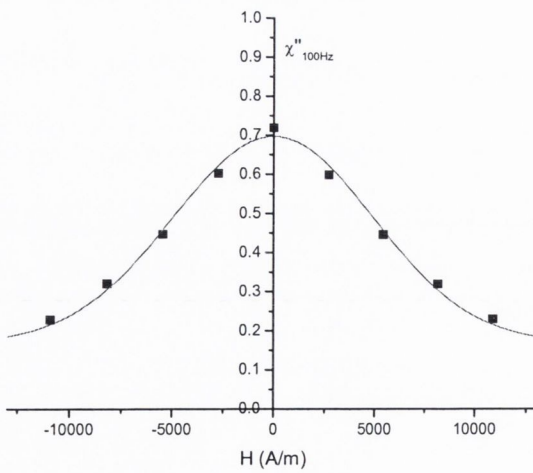


Fig 4.18 (b): Gaussian fit to χ'' against H data at 100 Hz.

Figures 4.18 (a) and (b) show a Gaussian curve fitted to the data at 100 Hz. Gaussian curves possess a natural symmetry, which further still, emphasises the symmetry of the plot of χ' and χ'' against H , with the peak of the Gaussian centred exactly on the vertical axis close to the maximum value of χ in both cases.

Thus, through the use of cyclical measurements of $\chi(\omega, H)$, the Weierstrass hypothesis, and the symmetry of plots of χ', χ'' vs. H , the isotropic nature of two different ferrofluids, has been demonstrated. Both of these fluids have vastly different composition, one oil based containing cobalt particles, the other water-based containing magnetite particles, yet the results are the same, confirming their isotropic properties.

4.4. Investigation of the complex susceptibility of magnetic microspheres

Magnetic beads, or magnetic microspheres as they are more commonly known, are an interesting class of material, which are of great current interest, particularly in the area of biomedical diagnosis [10]. The microspheres investigated in this section have a diameter of 200nm and were supplied by Ademtech [11]. They are made by evaporating an octane solvent in emulsions of an organic ferrofluid. Emulsions are colloidal systems consisting of droplets of a liquid dispersed in another immiscible one, the droplets being stabilised by a surfactant. Once the solvent is evaporated, the solid-like spheres contain 50 % volume fraction of maghemite particles of approximately 10 nm mean radius. The mean radius size was obtained from Dynamic Light Scattering measurements. The surfactant in the case of these microspheres is oleic acid. The microspheres are surrounded in a polymer shell, to ensure isolation of the magnetic core from its surroundings, which is an important consideration in the use of the microspheres for biological applications. Figure 4.19 below shows a TEM micrograph [11] of the polymer-coated beads as supplied by Ademtech. The 200 nm bead is of similar appearance to the beads used in our study.

Measurements were made for the first time, of $\chi(\omega, H)$ for two samples of magnetic microspheres, and of their constituent maghemite nanoparticles in the frequency range 200 Hz to 1 MHz. The results have been published in [12, 13] and will be examined in further detail in this section.

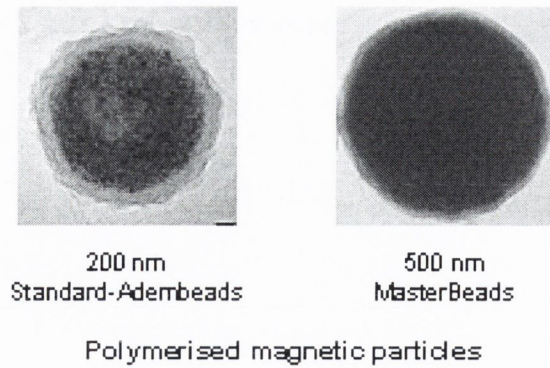


Figure 4.19: TEM micrograph of polymer coated magnetic microspheres / beads [11].

Fluid 5 is the original colloidal microsphere suspension described above, whilst fluid 6 is a more dilute version of the same suspension and does not possess a polymer shell. Fluid 7 is a colloidal suspension of the maghemite nanoparticles used in both fluids 5 and 6.

The first question in the analysis of $\chi(\omega)$ is which relaxation mechanism is dominant? There are four possible methods by which the magnetisation of a suspension of magnetic microspheres can relax. These are, (i): by Brownian or Néel relaxation of the microspheres themselves, (ii): by Brownian relaxation of the inner maghemite nanoparticles, and (iii): by the Néel relaxation of the inner nanoparticles. The microspheres have been demonstrated to form chains, and self organise [10, 11]. The chaining of 500 nm microspheres is shown in figure 4.20.

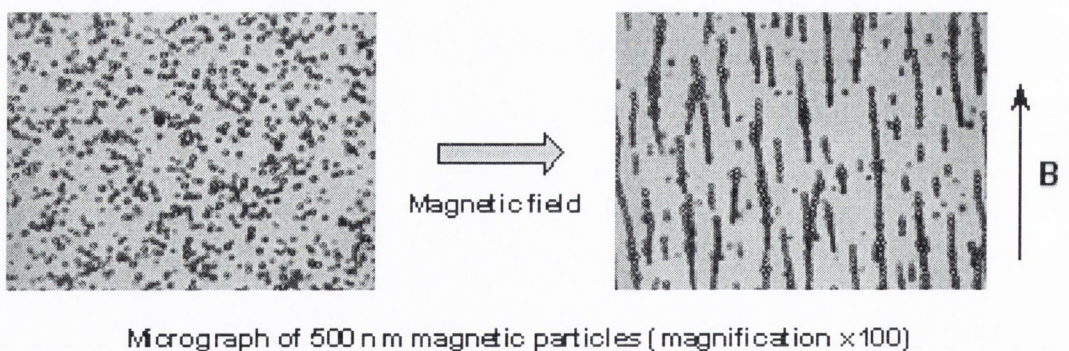


Figure 4.20: TEM micrograph of magnetic microspheres forming chains [11].

This chaining effect must be kept in mind when considering the complex susceptibility. Regarding (ii) above, the maghemite particles are extremely confined (closely packed) inside the microspheres, and therefore due to the elimination of their mechanical degree of freedom, they cannot experience Brownian relaxation. This is

verified by figure 4.21, where the unpolarised $\chi(\omega)$ spectra for fluid 7 are plotted against frequency. The profile of the plots is flat, showing the absence of an absorption peak and of Debye-type behaviour, which would otherwise indicate the presence of aggregates, and thus this fluid may be regarded as a well dispersed colloid.

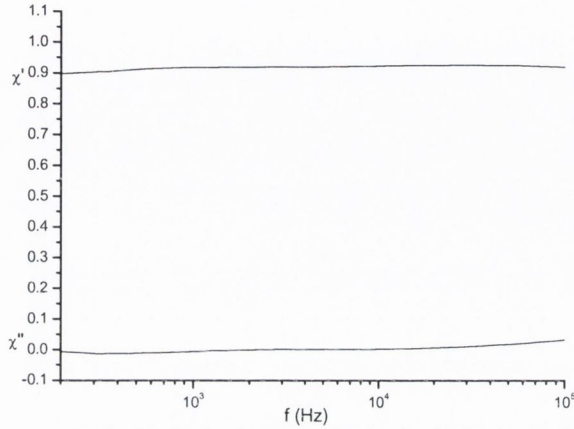


Figure 4.21: Plots of $\chi'(\omega)$ and $\chi''(\omega)$ against f (Hz) over the range 200-10⁵ Hz for fluid 7.

Higher frequency measurements were also made for fluid 7, in the range 100 MHz to 6 GHz. These results will be presented in greater details in the next section of this chapter. The high frequency measurement indicated the presence of ferromagnetic resonance, and yielded a value of effective anisotropy field, $H_A = 47.8$ kA/m. Knowing the value of H_A it is possible to arrive at a value for the anisotropy constant, $K = M_{sat} H_A / 2 \approx 10^4$ J/m³. Figure 4.22 shows the susceptibility spectrum of both complex components for fluid 5. Comparatively speaking, the measured susceptibility is quite weak, which meant that below 200 Hz no useful signal was obtained. The static susceptibility, χ_0 , given by equation (2.5.6) was taken to be equivalent to the value of $\chi'(\omega)$ at 400 Hz. Figure 4.23 shows a plot of χ_0 against H . Interestingly, both figures 4.22 and 4.23 show a general trend of increasing χ_0 , $\chi'(\omega)$, and $\chi''(\omega)$ with increase in polarising field. This is in contrast to what normally happens for ferrofluid, where the equivalent components decrease with increasing field. Furthermore no loss peak is evident for the unpolarised measurement and for the first polarised measurement. At a value of $H = 1.8$ kA/m, an absorption peak emerges at a frequency of $f_{max} = 1.06$ kHz, and increases to $f_{max} = 2.5$ kHz for $H = 13.6$ kA/m.

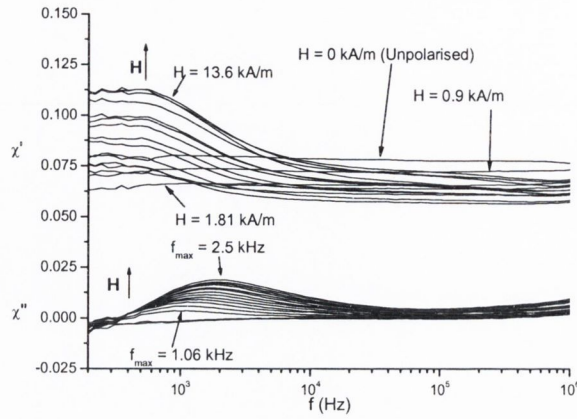


Figure 4.22: Plot of $\chi'(\omega)$ and $\chi''(\omega)$ against f (Hz) for fluid 5, for $H = 0$ - 13.6 kA/m.

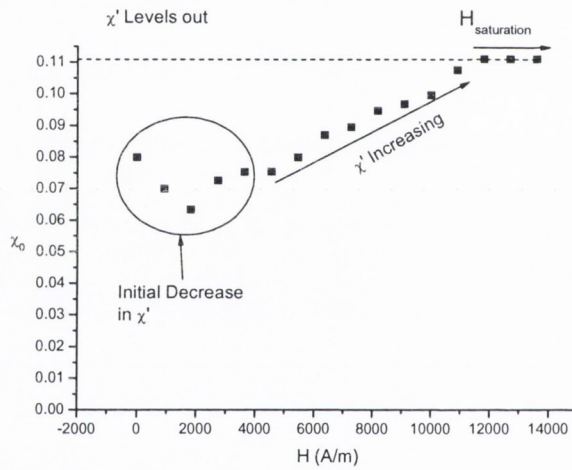


Figure 4.23: Plot of χ_0 against H for $H = 0$ - 13.6 kA/m.

An attempt must now be made to attribute the observed absorption peak to the relevant relaxation mechanism. Considering (i) the Brownian relaxation of the microspheres, it is convenient to express equation (2.5.3) in terms of the frequency of the maximum absorption, f_{max} . This gives

$$\tau_B = \frac{1}{2\pi f_{max}} = \frac{4\pi\eta r^3}{k_B T}, \text{ giving } f_{max} = \frac{k_B T}{8\pi^2 r^3 \eta_h} \quad (4.4.1)$$

Assuming that the viscosity of the carrier does not change, the increase in f_{max} over the polarising field range corresponds to a decrease in the effective hydrodynamic radius, r , of the spheres, something which is only possibly if the structure of the

spheres breaks down. The manufacturer has indicated that the polymer shell prevents the microspheres from changing shape, meaning that the increase in f_{max} cannot be attributed to a change in the radius of the microspheres. The viscosity of water is 1 cP, and with microspheres of radius 100nm measured at room temperature, the Brownian relaxation time is $\tau_B = 3 \times 10^{-3}$ s.

This corresponds to a value of f_{max} as given by equation (4.4.1) of 50 Hz, which is well outside the frequency range where the loss-peaks were detected.

Having eliminated the possibility of the Brownian relaxation of the microspheres being responsible for the observed absorption, it is now time to consider whether the Néel relaxation of the microspheres is the cause of the absorption. The simplest approximation of the Néel relaxation time given by equation (2.6.1.1) is $\tau_N = \tau_0 \exp(\sigma)$, $\sigma = K v_m / k_B T$. (4.4.2)

Thus for spheres of radius 100 nm, with $K \approx 10^4 J / m^3$ (as determined by the high frequency measurements), and $\tau_0 = 10^{-9}$ s we get a value of $\sigma = 1 \times 10^4$ which gives an exponentially large relaxation time, corresponding to an undetectable (almost zero) frequency.

However, if the Néel time is evaluated for a smaller particle of radius 10nm, the value of σ is equal to 10.5 and $\tau_N = 3.6 \times 10^{-5}$ s. This corresponds to an f_{max} of approximately 4 kHz which is comparable to the frequency of the observed loss peaks. Thus from the above calculation of the Brownian and Néel relaxations times, it appears that the loss peaks detected are due to the Néel relaxation of the constituent maghemite nanoparticles.

The next question that arises is why do the complex components of $\chi(\omega)$ increase with increase in H ? Recalling equation (2.5.12) $\chi(\omega)$ can be written in the following way

$$\chi(\omega) = \chi_0 \left(\frac{1}{1 + \omega^2 \tau_{eff}^2} - i \frac{\omega \tau_{eff}}{1 + \omega^2 \tau_{eff}^2} \right) \quad (4.4.3)$$

where χ_∞ is neglected. Clearly from equation (4.4.3), both complex components of $\chi(\omega)$ are directly proportional to χ_0 . Recalling equation (2.5.6)

$$\chi_0 = \frac{N m_{sp}^2}{3 \mu_0 k_B T} \quad (4.4.4)$$

all parameters are fixed, except for the magnetic moment of the spheres, m_{sp} . Thus an increase in m_{sp} could be due to the fact that the individual spheres, and magnetic

moments in the spheres become more aligned with increasing H . This would lead to an increase in $\chi'(\omega)$ and $\chi''(\omega)$, which is what has been observed. Indeed, if a chain of microspheres were to form at a certain value of H , which the manufacturer has indicated as happening (figure 4.20), then the effective magnetic moment of the chain could be regarded as the summation of the individual magnetic moments of the spheres, so that $m_{chain} = \Sigma m_{sp}$. Indeed, if the theory of the chaining of the microspheres holds, an estimate can be made of the critical H value where the individual microspheres begin to assemble. A ‘timeline’ can be established describing the change in behaviour of the microspheres with increasing H . Figures 4.24 (a) and (b) below show an enlargement of the susceptibility spectra of figure 4.22.

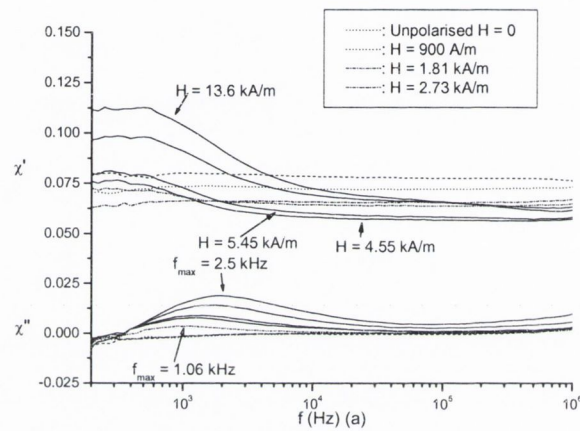


Figure 4.24 (a): Spectra of selected $\chi'(\omega)$ and $\chi''(\omega)$ for fluid 5.

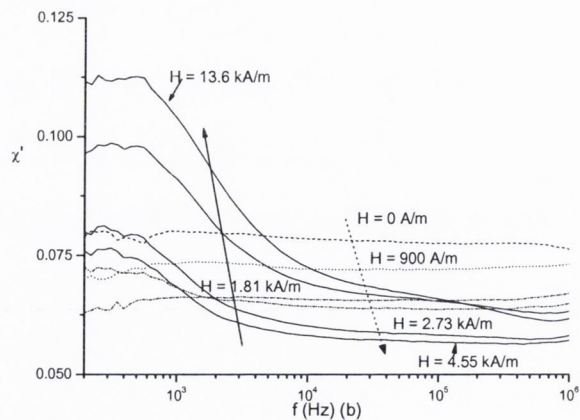


Figure 4.24 (b): Spectra of selected $\chi'(\omega)$ for fluid 5. The broken lines show the $H = 0, 0.9, 1.81, 2.73$ kA/m measurements.

For the values of $H = 0 \rightarrow 2.7 \text{ kA/m}$, $\chi'(\omega)$ decreases as predicted by theory, and $\chi''(\omega)$ is flat with an absence of an absorption peak. At $H = 2.7, 3.6 \text{ kA/m}$ an absorption peak appears in the $\chi''(\omega)$ profile, and $\chi'(\omega)$ continues to decrease. At this point ($H = 3.6 \text{ kA/m}$), H is now strong enough to turn some of the magnetic moments of the maghemite nanoparticles into its direction. However, on the colloidal scale, the microspheres are still well dispersed. $\chi'(\omega)$ continues to decrease until $H = 4.55 \text{ kA/m}$. After this value of H , $\chi'(\omega)$ begins to increase. At this point, the microspheres have begun to form chains. The effective moment of the chain causes the increase in $\chi'(\omega)$. $\chi'(\omega)$ continues to increase with H , until at approximately 12 kA/m , the field begins to saturate the maghemite particles, and the rate of increase in $\chi'(\omega)$ slows down (figure 4.23). The ‘timeline’ for the above described process is shown in figures 4.25 (a) and (b).

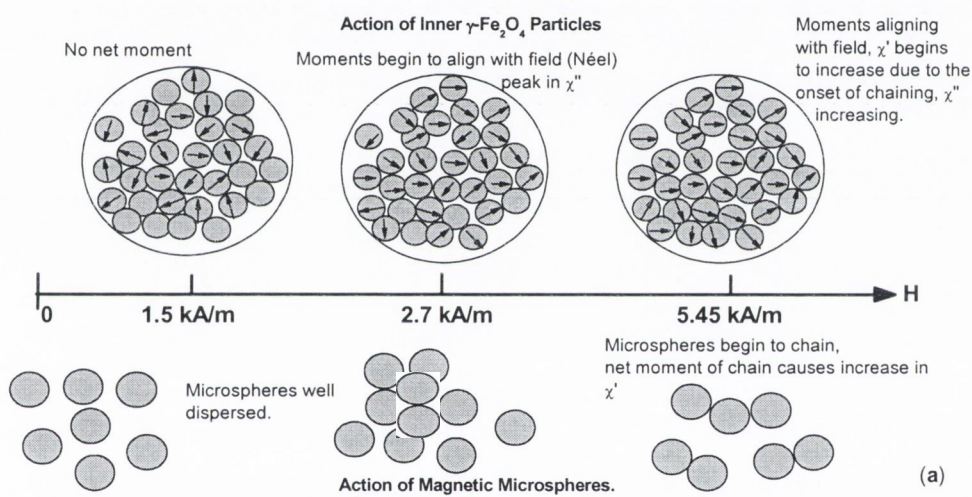


Figure 4.25 (a): Evolution of microsphere magnetisation process with increasing H .
 $H = 0\text{-} 5.45 \text{ kA/m}$.

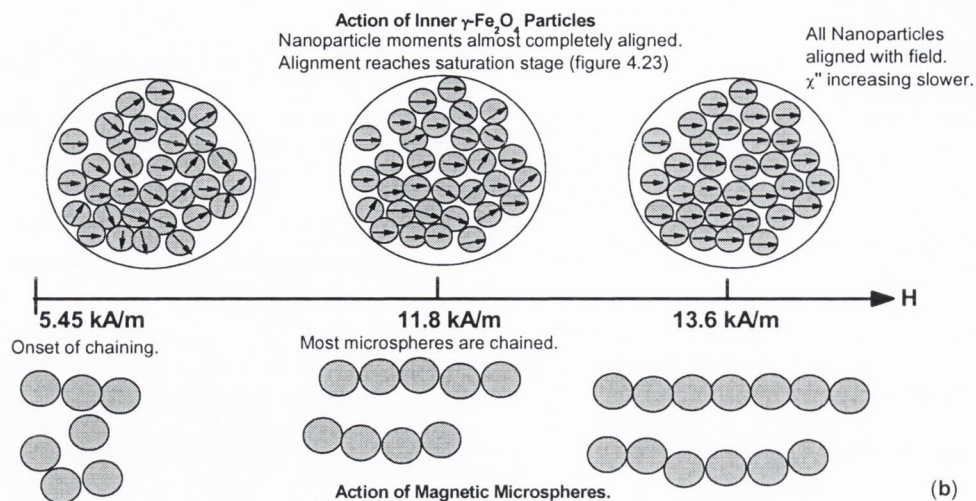


Figure 4.25 (b): Evolution of microsphere magnetisation process with increasing H .
 $H = 5.45 - 13.6$ kA/m.

As more and more maghemite particles become more aligned with increasing H , one would expect to see a change in the distribution of relaxation times of the inner particles. To analyse this, the data was plotted in Cole-Cole format and fitted to a semi circle. Selected results are shown below in figure 4.26 (a) and (b) and in table 4.2.

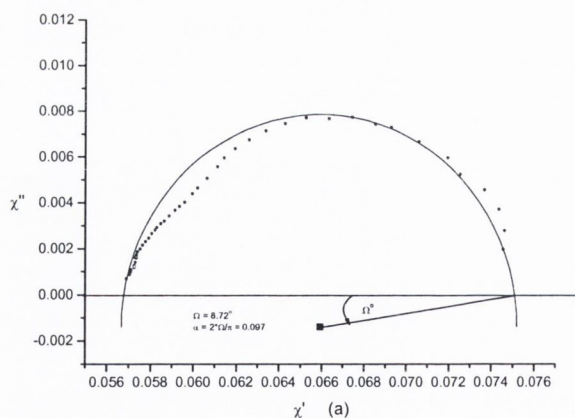


Figure 4.26 (a): Cole-Cole plot for fluid 5. $H = 5.45$ kA/m.

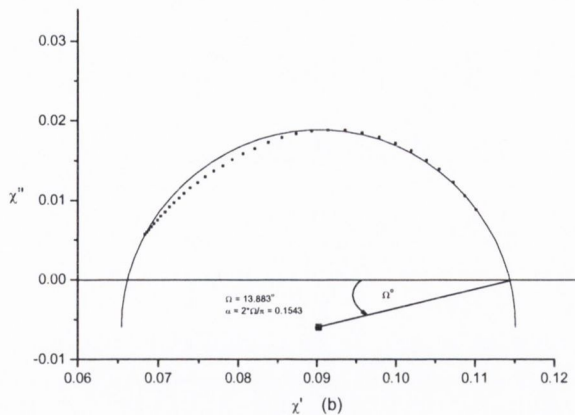


Figure 4.26 (a): Cole-Cole plot for fluid 5. $H = 13.6$ kA/m.

Table 4.2. Results of Cole-Cole fitting for fluid 5.

$H(\text{kA/m})$	2.73	4.55	6.36	8.18	10	12.7	13.6
α	0.1	0.1	0.112	0.132	0.101	0.14	0.154

Overall, as table 4.2 shows, there is a general increase in α , from $\alpha = 0.1$ at $H = 2.73$ kA/m, to $\alpha = 0.154$ at $H = 13.6$ kA/m, indicating a change in the distribution of relaxation times inside the microspheres, possibly indicating that more particles are contributing to relaxation as H increases.

Similar measurements were carried out for fluid 6, which is a more dilute version of fluid 5, and does not have a polymer shell. However, the measurement included a reverse polarisation, where the field was decreased in 16 steps from 13.6 – 0 kA/m, as in section 4.3. The reverse polarisation revealed a hysteresis effect in the fluid. Figures 4.27 and 4.28 show the forward and reverse polarisations for fluid 6.

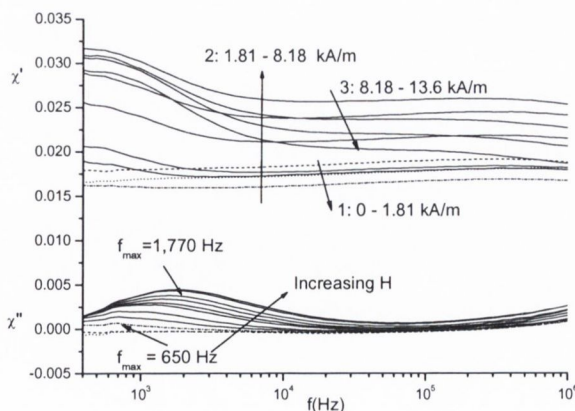


Figure 4.27: Plot of $\chi'(\omega)$ and $\chi''(\omega)$ forward against f (Hz) for fluid 6, for $H = 0$ - 13.6 kA/m.

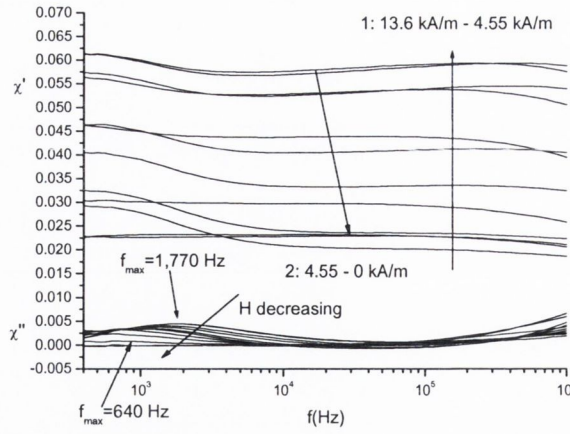


Figure 4.28: Plot of $\chi'(\omega)$ and $\chi''(\omega)$ reverse against f (Hz) for fluid 6, for $H = 0$ - 13.6 kA/m.

The broken lines in figure 4.27 represent the unpolarised and $H = 0.9, 1.81$ kA/m measurements. As with fluid 5, initially $\chi'(\omega)$ decreases and the profile of $\chi''(\omega)$ is flat. After 1.81 kA/m a loss peak appears and $\chi'(\omega)$ begins to increase. At a value of 8.18 kA/m, $\chi'(\omega)$ begins to decrease again, however $\chi''(\omega)$ continues to increase. The decrease in $\chi'(\omega)$ after 8.18 kA/m could possibly be explained by the absence of the polymer shell surrounding the microspheres. If a strong enough field were to cause the deformation of each individual microsphere, due to the absence of the structure of the shell, the chains between individual microspheres could be broken, resulting in the effective moment of the chain decreasing, and hence the decrease in $\chi'(\omega)$.

With decreasing H , the reverse polarisation shows a further increase in $\chi'(\omega)$ until a value of $H = 4.55$ kA/m, when it decreases again. Decreasing H causes $\chi''(\omega)$ to reverse itself fully back to its original state with an absence of a peak in its profile. The strange hysteretic behaviour of $\chi'(\omega)$ can be best observed in figure 4.29, where the zero susceptibility for forward and reverse polarisation is plotted against H .

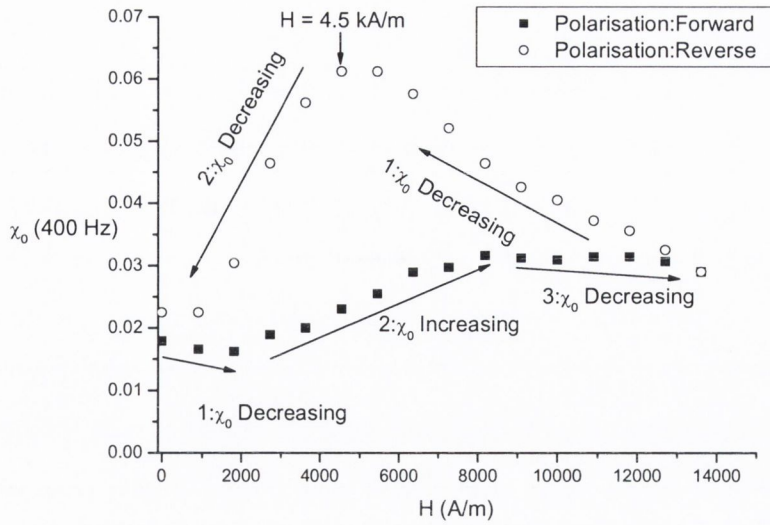


Figure 4.29: Plot of χ_0 against H for $H = 0 - 13.6 - 0$ kA/m.

The interesting point to note in figure 4.29 is that after $H = 4.5$ kA/m in the reverse polarisation, χ_0 falls quickly back to almost its initial value in the forward polarisation. This would seem to indicate that $H = 4.5$ kA/m is a critical point at which the structure of the fluid changes. Despite the upward and downward swings in χ_0 over the course of the polarisation cycle, once H is switched off, the fluid seems to return to its original state, meaning that no permanent hysteresis is induced in the fluid.

In summary, a series of measurements of $\chi(\omega, H)$ for two colloidal suspensions of magnetic microspheres, filled with maghemite nanoparticles, have been presented, showing unusual behaviour in defiance of the accepted theory. Both components of susceptibility showed a general rise in magnitude with increasing polarising field. The increase in $\chi''(\omega)$ was shown to be due to the Néel relaxation of the inner maghemite nanoparticles, whilst the increase in $\chi'(\omega)$ was attributed to the chaining of the individual microspheres, causing an increase in effective magnetic moment. Measurements were taken for forward and reverse polarisation, cycling over the field range. Hysteresis behaviour was observed over the course of the cycle, but after the removal of the applied field, no appreciable permanent effect was evident. The approximate value of $H = 4.5$ kA/m, appears to be a critical value for the formation or degradation of chains of microspheres in the measured fluids.

4.5. High Frequency Susceptibility Measurements ($f > 10$ MHz)

Equations have been presented in chapter 3 for the calculation of the complex permeability and permittivity by means of the open and short circuited transmission line technique, and by means of combining the equations for μ and ϵ to obtain a more accurate expression over the frequency range. This section will initially perform a comparison between the separate short circuited method, and the combined open and short-circuited method, for measuring the complex susceptibility of a ferrofluid at frequencies greater than 20 MHz. The need for the combined method arises because of the inaccuracies inherent in performing measurements at frequencies and sample depths where the wavelength of radiation in the transmission line is comparable to the sample depth. Under such conditions, the electric field in a short circuited transmission line is not eliminated, and it becomes impossible to measure μ independently of ϵ . Results will be presented for measurements taken over three overlapping frequency ranges, 20 MHz – 3GHz, 100 MHz – 6GHz, and 1 GHz to 16 GHz. One would expect both methods to provide the same results at the lower frequencies of each range, and the difference between the methods to become significant at the higher ends of each range. Figures 4.30 (a) and (b) show unpolarised measurements performed on a suspension of 400 Gauss magnetite particles of mean radius 5 nm, dispersed in an isoparaffin carrier (fluid 8). Figure 4.30 (a) is in the frequency range 20 MHz to 3 GHz, whilst figure 4.30 (b) is in the range 100 MHz to 6 GHz.

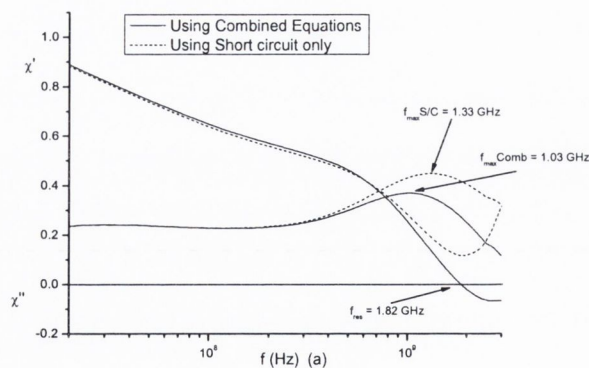


Figure 4.30 (a): Plots of $\chi(\omega)$ for fluid 8 in the frequency range 20 MHz to 3 GHz.

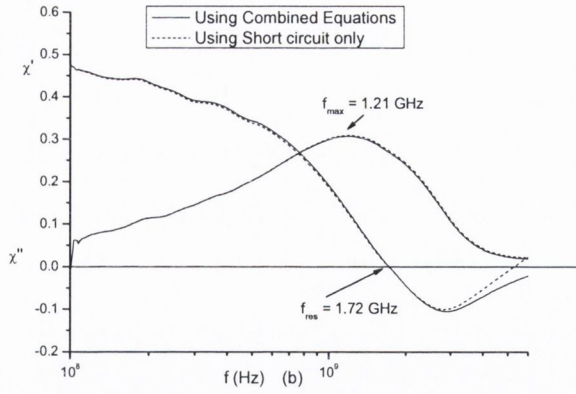


Figure 4.30 (b): Plots of $\chi(\omega)$ for fluid 8 in the frequency range 100 MHz to 6 GHz.

Figure 4.30 (c) shows $\chi(\omega)$ in the frequency range of 1 GHz to 16 GHz. The fluid used in this case is fluid 4 used in section 4.3. A different fluid to that of the previous plots is used, because it resonates at a higher frequency well inside the range measured.

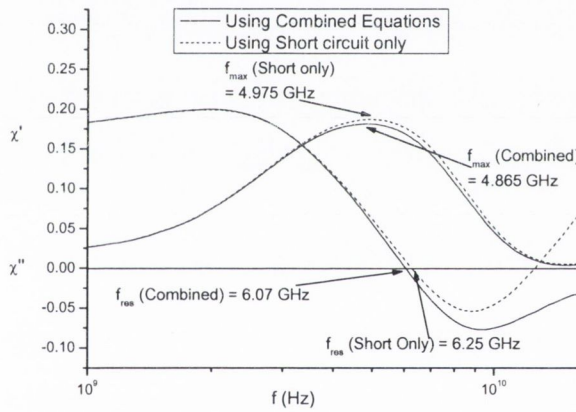


Figure 4.30 (c): Plots of $\chi(\omega)$ for fluid 4 in the frequency range 1 GHz to 16 GHz.

It is very clear from the above figures that the accuracy of the short circuited measurement technique breaks down at higher frequencies. As expected, the plots of $\chi(\omega)$ are very similar in the lower frequency sections of the measured range. This is because the wavelength of the incident radiation in the sample is very much greater than the sample depth at these particular frequencies. It must be noted that the results shown in figure 4.30 (a) show a large difference at $f > 800$ MHz between $\chi(\omega)$ calculated by the short circuited method and that of the combined method. This difference is due to the unsuitability of the 9.5 mm cell for measurements in excess

of 800 MHz. For electro-magnetic radiation oscillating at 800 MHz, the corresponding wavelength is 0.375 m which is 40 times greater than the cell depth. The next frequency range covered, is from 100 MHz to 6 GHz. This measurement is performed with a cell of depth 1.94mm. At 800 MHz, the wavelength is as before, but is now 193 times greater than the cell depth, which leads to increased accuracy. Figure 4.30 (b) shows $\chi'(\omega)$ resonating at $f_{res} = 1.72$ GHz, with an associated absorption peak at $f_{max} = 1.21$ GHz. Both f_{res} and f_{max} are the same for the combined and short circuit (s/c) measurement. However, $\chi'(\omega)$ calculated from the s/c crosses back over the $y = 0$ axis after the resonance point. This should not happen, and is not predicted by any of the relevant theory given in section 2.7. This is not the case for $\chi'(\omega)$ calculated using the combined method. Moving on to the highest frequency region in figure 4.30 (c), the inaccuracies in the s/c method really become obvious. The susceptibility differs substantially from the combined measurement at frequencies greater than 10 GHz. At this value of frequency, the wavelength of radiation is 0.03 m which is only 30 times greater than the cell depth.

The application of a biasing field parallel to the fluid in conjunction with the probing perpendicular field causes the resonance point to shift to higher frequencies. The relationship between resonance frequency and applied field is given by equation (2.7.17) which states that

$$\omega_{res} = 2\pi f_{res} = \gamma(H_S + H_A). \quad (4.5.1)$$

Applying a polarising field allows us to see what happens to $\chi(\omega)$ at frequencies higher than its unpolarised value. The following values of H_S have been applied to fluids 4 and 8: $H_S = 0, 15.2, 35.7, 69.2, 102.4, 135.5$, and 168.4 kA/m. The polarised results are plotted below for the ranges 100 MHz to 6 GHz, and 1GHz to 16 GHz, in figures 4.31 (a-c) and 4.32 (a-c).

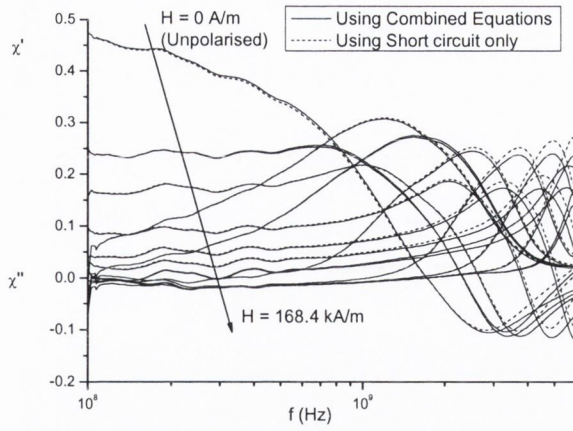


Figure 4.31 (a): Polarised plots of $\chi(\omega)$ for fluid 8 in the frequency range 100 MHz to 6 GHz.

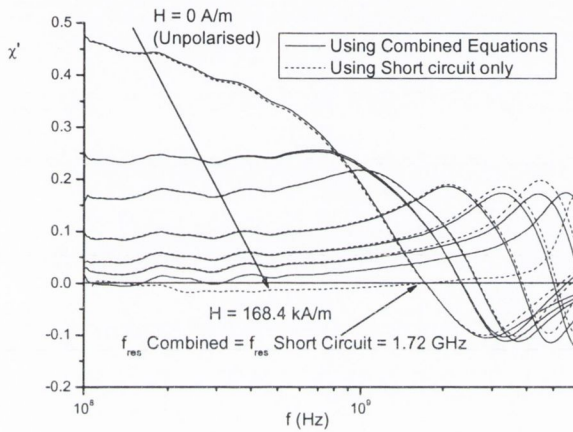


Figure 4.31 (b): Polarised plots of $\chi'(\omega)$ for fluid 8 in the frequency range 100 MHz to 6 GHz.

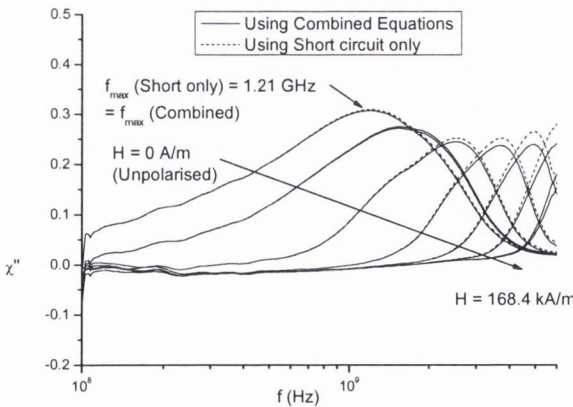


Figure 4.31 (c): Polarised plots of $\chi''(\omega)$ for fluid 8 in the frequency range 100 MHz to 6 GHz.

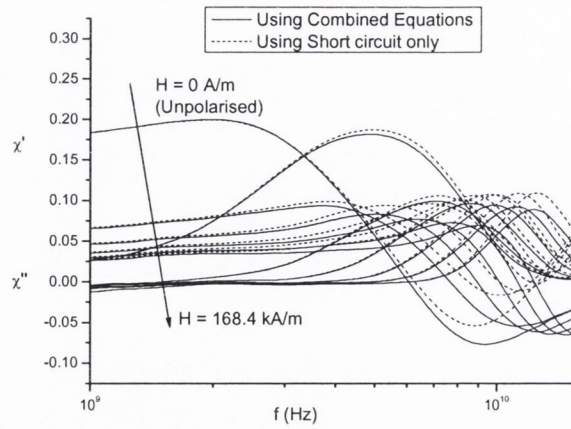


Figure 4.32 (a): Polarised plots of $\chi(\omega)$ for fluid 4 in the frequency range 1 GHz to 16 GHz.

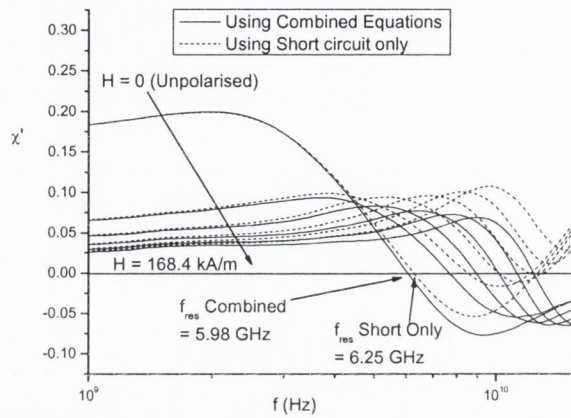


Figure 4.32 (b): Polarised plots of $\chi'(\omega)$ for fluid 4 in the frequency range 1 GHz to 16 GHz.

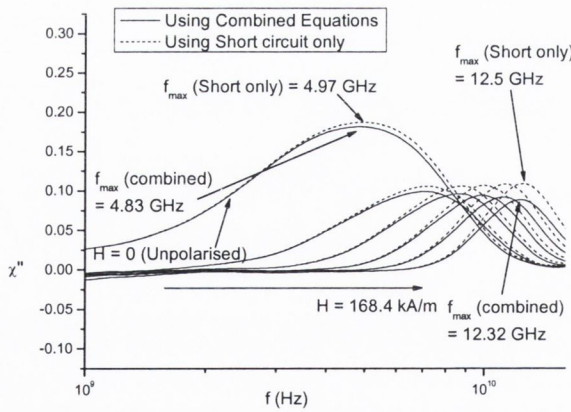


Figure 4.32 (c): Polarised plots of $\chi''(\omega)$ for fluid 4 in the frequency range 1 GHz to 16 GHz.

The diminished accuracy of the s/c technique is obvious in the $\chi'(\omega)$ component for fluid 4. The ‘depth’ of the resonance, i.e. the depth below the $y = 0$ axis to which $\chi'(\omega)$ extends to is diminishing with increase in H_S . Finally at a value of $H_S = 102.4$ kA/m, the resonance disappears. This occurs after 12 GHz at a wavelength of 0.025m, which is almost 25 times the cell depth.

4.5.1. Estimation of material parameters from high frequency measurements of $\chi(\omega)$.

Important material parameters such as the average internal anisotropy field, H_A , the anisotropy constant, K , the gyromagnetic ratio, γ , the damping parameter, α , and the precessional decay time τ_0 can be estimated by measuring the complex susceptibility. Equation (4.5.1) can be rewritten in the following way.

$$\omega_{res} = 2\pi f_{res} = \gamma(H_S + H_A) \Rightarrow f_{res} = \frac{\gamma}{2\pi}(H_{eff}). \quad (4.5.1.1)$$

The equation for a straight line is $y = mx + c$.

Clearly if $c = 0$ then $y = mx$ (4.5.1.2)

Comparing equations (4.5.1.2) and (4.5.1.1), it is clear that the former describes a straight line with slope $\gamma/2\pi$. Hence plotting f_{res} against H will yield a straight line, the value of which at the intercept with the x axis will equal the value of H_A . Figure 4.33 (a-c) below, shows the susceptibility spectra for fluid 7, for which low frequency plots of $\chi(\omega)$ were given in section 4.4. The susceptibility was calculated using the combined method.

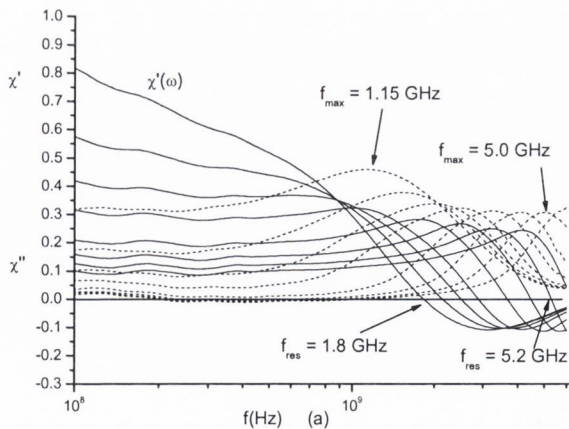


Figure 4.33 (a): Plot of $\chi'(\omega)$ (solid line) and $\chi''(\omega)$ (dashed line) against f (Hz) for fluid 7.

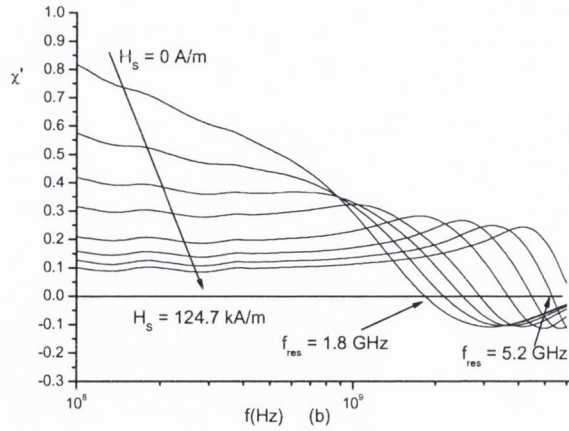


Figure 4.33 (b): Plot of $\chi''(\omega)$ against f (Hz) for fluid 7.

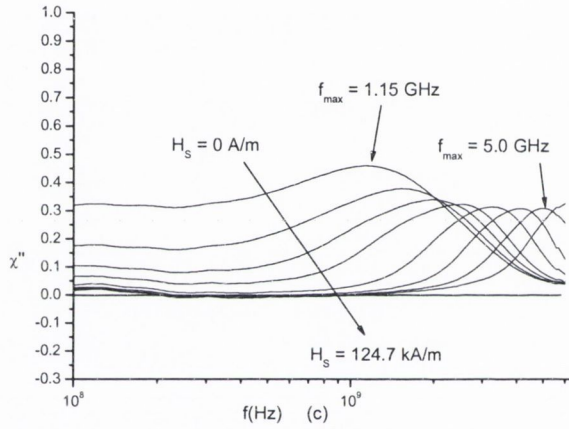


Figure 4.33 (a): Plot of $\chi'(\omega)$ against f (Hz) for fluid 7.

Figure 4.34 below shows the plot of f_{res} against H_s . As expected there is a linear relationship between f_{res} and H_s . The equivalent anisotropy field was determined as being 47.8 kA/m. Using a value of $M_{sat} = 0.4$ T the anisotropy constant, K , is determined as $K = 0.956 \times 10^4 \approx 10^4 \text{ J/m}^3$. The gyromagnetic ratio was determined to be $\gamma = 2.1875 \times 10^5 \text{ m/As} \approx 2.2 \times 10^5 \text{ m/As}$, which is as expected for maghemite.

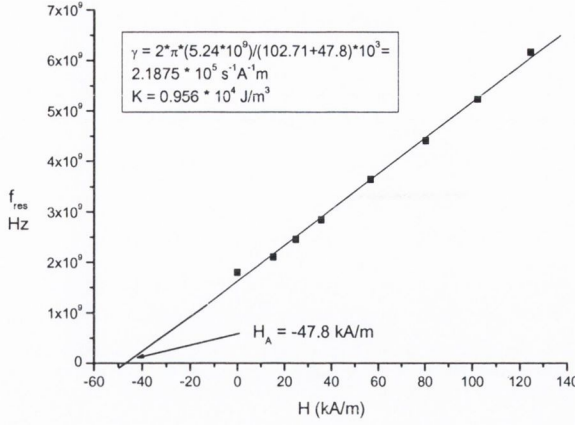


Figure 4.34: Plot of f_{res} vs. H for fluid 7.

The values for the material parameters can also be found by fitting the equations of resonance derived by Coffey [14] and Landau and Lifshitz as proposed by Raikher and Shliomis [15]. This has been shown for constant field and variable frequency in [16] where values for K , the particle radius r , and the damping parameter α were obtained, all of which compared well with known values. It is also possible to fit the equation of Landau and Lifshitz to the $\chi(\omega)$ data for the case of constant frequency and variable field. The Landau and Lifshitz equation, (2.7.16) is given by

$$\chi_{\perp}(\omega) = \chi_{\perp}(0) \frac{1 + \omega_{\text{pre}}^2 \tau_0^2 + i\omega\tau_0}{1 + \omega_{\text{pre}}^2 \tau_0^2 - \omega^2 \tau_0^2 + i2\omega\tau_0}, \quad (4.5.1.3)$$

which may be written in the equivalent form [17],

$$\chi_{\perp}(\omega) = \chi_{\perp}(0) \frac{1 + a^2 + ix}{1 + a^2 - x^2 + 2ix}, \quad (4.5.1.4)$$

where $x = \omega\tau_0$ and $a = \omega_{\text{pre}}\tau_0$, where ω_{pre} is the angular precession frequency and τ_0 is the time constant for the decay of precessional motion. If the parameter x is kept constant and the parameter a varies, the resultant Cole-Cole plot of $\chi(\omega)$ is a circle. Results for such a fitting procedure have been presented in [18], where a colloidal suspension of magnetite of $M_{\text{sat}} = 900$ G dispersed in isopar M, was fitted to equation (4.5.1.4) above for the case of constant frequency. Results will be given here for fluid 7, which will serve to confirm the values of K and γ obtained from figure 4.34.

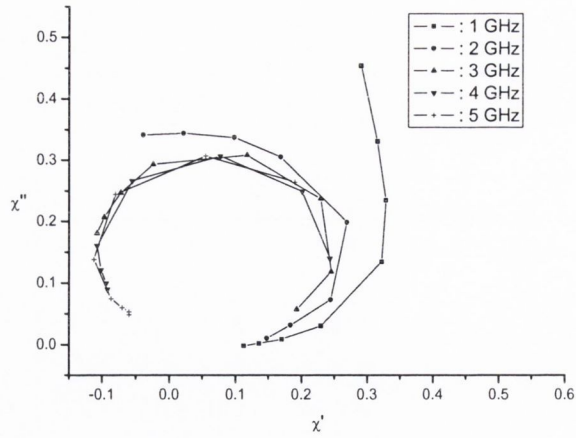


Figure 4.35: Cole-Cole plot of $\chi''(\omega)$ against $\chi'(\omega)$ for fluid 7 at constant frequencies of 2.7, 3, 4, 5 GHz.

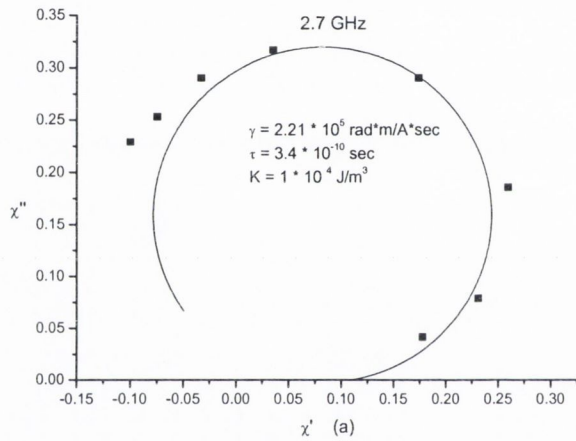


Figure 4.36 (a): Cole-Cole plot of $\chi''(\omega)$ against $\chi'(\omega)$ for fluid 7 at a constant frequency of 2.7 GHz.

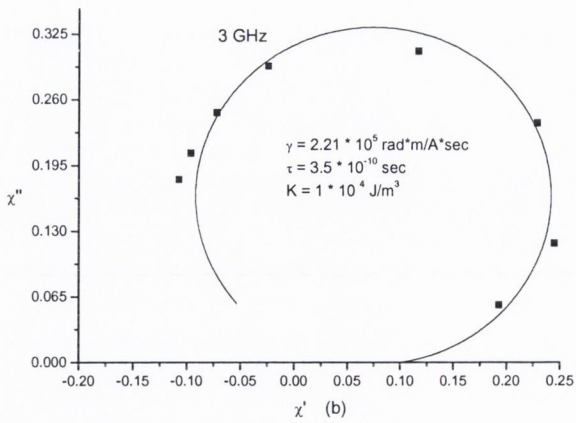


Figure 4.36 (b): Cole-Cole plot of $\chi''(\omega)$ against $\chi'(\omega)$ for fluid 7 at a constant frequency of 3 GHz.

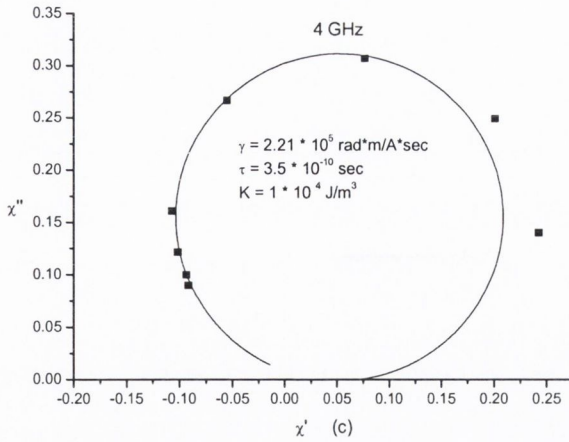


Figure 4.36 (c): Cole-Cole plot of $\chi''(\omega)$ against $\chi'(\omega)$ for fluid 7 at a constant frequency of 4 GHz.

Figure 4.35 shows the Cole-Cole plots of equation (4.5.1.4) over the polarising field range at frequencies of 2.7, 3, 4, 5 GHz. It clearly shows the variation in the Cole-Cole plots, as they gradually approach a circular shape, as indicated in figures 4.36 (a), (b) and (c). The fitting parameters used were $\gamma = 2.21 \times 10^5$ m/As, $K = 10^4$ J/m³, $M_{sat} = 0.4$ T, and $\tau_0 = 3.5 \times 10^{-10}$ s. These values are almost equal to those obtained from the plot of f_{res} vs. H_S , thus confirming the accuracy of the fit.

4.6. Conclusion

Measurements of $\chi(\omega)$ have been presented ranging from near d.c. to 16 GHz. These measurements are obtained by performing impedance measurements on the ferrofluid over the frequency ranges of interest, by using a suitable sample holder and impedance / network analyser. The results obtained from the impedance measurements, have been analysed in terms of the expressions given by Debye [19, 20] and Cole and Cole [2] for the low frequency region, and in terms of the equations of Landau and Lifshitz [14] for the high frequency region.

The Cole-Cole equation was modified to describe the susceptibility of a ferrofluid exhibiting a bimodal distribution of relaxation times, and fits were performed on the experimental data. The values of Cole-Cole distribution parameter yielded from the fit, compared favourably to those obtained from the Cole-Cole plots of the susceptibility data.

The effect of biasing field on the hysteresis and isotropic properties of the ferrofluid was examined in section 4.3. Measurements were performed for two different ferrofluids. Fluid 3 comprised of magnetite particles dispersed in water whilst fluid 1 was a suspension of cobalt nanoparticles in paraffin. The results obtained showed the absence of any hysteresis over the frequency and field range measured. The cycling of the biasing field over positive and negative values of H showed that the susceptibility was independent of the direction of applied H . Symmetry of the graph of $\chi(\omega, H)$ about the vertical axis was the condition given for a fluid to be isotropic. This was demonstrated with the aid of the Weierstrass hypothesis which stated that $\chi(\omega, H)$ could be approximated by a polynomial. Upon expansion of the Weierstrass hypothesis, it was found that the odd coefficients of a polynomial used to fit $\chi(\omega, H)$ should be zero or close to zero, for the condition of isotropy to be met. This was demonstrated by fitting a ninth order polynomial to the susceptibility data of fluid 1, thus proving the isotropic nature of that fluid. To further emphasise the symmetry of $\chi(\omega, H)$, the data was fitted to a Gaussian curve. The Gaussian curve was centred directly on the vertical axis at almost exactly the central value of $\chi(\omega, H)$.

The $\chi(\omega)$ for a suspension of magnetic microspheres was presented in section 4.4. To our knowledge, this is the first such measurement undertaken. In contrast to the accepted theory of the field dependence of $\chi(\omega)$, a general trend of increasing $\chi'(\omega)$ and $\chi''(\omega)$ was observed. The increase in $\chi''(\omega)$ was attributed to the gradual alignment of the inner maghemite particles contained in the microspheres, causing an increase in the magnetic moment of the spheres, and hence an increase in χ_0 . The maghemite particles were shown to undergo Néel relaxation. $\chi'(\omega)$ was shown to decrease with increasing H at first, and then increase after a critical value of H had been reached. This was attributed to the individual microspheres forming chains. The effective magnetic moment of the chain is the sum of the individual moments. As H increases, more microspheres chain up, thus increasing the effective moment of the chains, which leads to the observed increase in $\chi'(\omega)$. Measurements were also performed over forward and reverse polarisations on a weaker sample of microspheres. These measurements revealed a large hysteresis effect in the fluid. However, it was determined that once the field was removed, the microspheres

reverted to their original non-chained equilibrium state, and no permanent hysteresis was introduced in the fluid.

Finally, section 4.5 gives a comparison between the two techniques used to measure $\chi(\omega)$ at high frequencies. The first technique uses an equation for μ based on the short circuited transmission line technique, the second uses simultaneous equations based on the measurement of susceptibility when the line is terminated in both an open and a short circuit. The analysis shows inaccuracies in the short circuit method at high measurement frequencies when the wavelength of radiation in the line has become comparable to the sample depth. It is shown how the equation of Landau and Lifshitz as modified by Raikher and Shliomis can be fitted in Cole-Cole format to the susceptibility data yielding important information about the material parameters of the fluid. The results obtained were compared to those obtained from a different method where the resonance frequency is plotted against the applied field. The results were a good match, thus confirming the validity of the fits.

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Chapter 5: Non Linear Susceptibility of a Ferrofluid system.

5.1. Introduction

When a strong alternating field, h_a , is applied to a dielectric system it may be possible to observe nonlinear dielectric effects in that system.

In the case of a magnetic system, the magnetisation of the system, M , can be shown to be a function dependant on the square of h_a .

M is proportional to h_a in the linear region of magnetisation, corresponding to the region C to C' in figure 5.1 (c). In this region, the susceptibility of the material is independent of h_a and can be described by the simple Debye equation given by (2.5.4). In the higher field region corresponding to the points between B and B' in figure 5.1 (b), the Magnetisation/(Polarisation) becomes nonlinear and is no longer proportional to h_a . In this region it can shown that the susceptibility can be represented by the Debye equation minus a term dependent on the square of the probing alternating field. Thus the susceptibility may be written as $\chi(\omega) = \chi_{lin}(\omega) - \Delta\chi(\omega)$, where $\chi_{lin}(\omega)$ is the susceptibility as described by the Debye equation and $\Delta\chi(\omega)$ is the nonlinear increment which is dependant on h_a^2 .

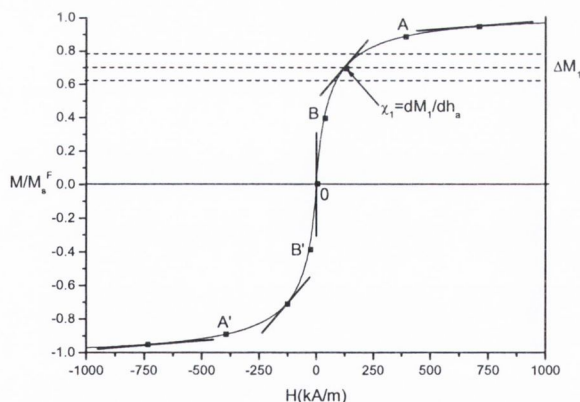


Figure 5.1 (a): Normalised magnetisation curve of a magnetite in water, ferrofluid. It shows the Langevin profile of the curve for various field strengths. The tangent value to a specific point of the curve determines the susceptibility.

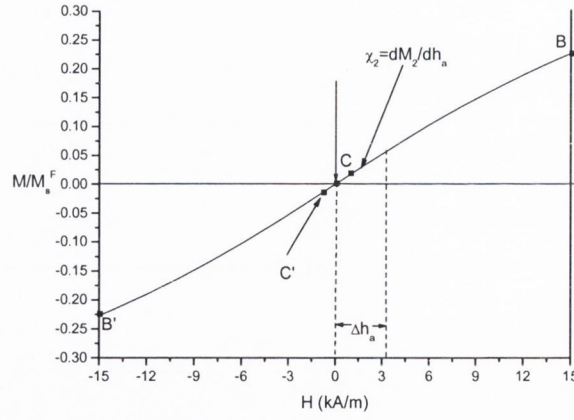


Figure 5.1 (b): Magnification of the magnetisation curve. The curvature is still significant for H above 1 kA/m indicated by the point C, (reflection C') and a relatively large oscillating field, h_a , can detect the nonlinearity.

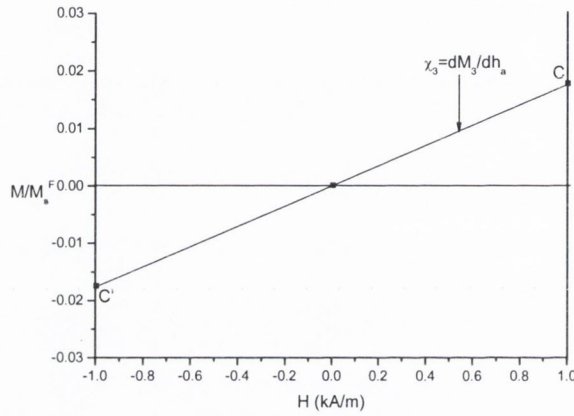


Figure 5.1 (c): The linear region of the magnetization curve. Here the detected susceptibility is independent of the value of the oscillating field h_a .

Coffey and Paranjape [1] derived a theory for nonlinear dielectric relaxation in dielectric systems which can be easily adapted for the case of ferrofluid magnetic systems. They extended the Debye theory of rotational diffusion of polar molecules to take account of the frequency and field dependence of the electric permittivity of a dielectric. The starting point for their treatment of the problem was the Smoluchowski equation (2.4.7). They considered the case of both a strong alternating electric field acting on its own (a), and the case of a strong d.c. electric field superimposed on a relatively weak alternating field (b). Only case (a) with alternating field $h_a = H_0 \cos(\omega t)$ shall be considered, resulting in a potential

$$V(\vartheta, t) = -\mu H_0 \cos(\omega t) \sin(\vartheta).$$

For each case they solved the Smoluchowski equation using spherical harmonics leading to an expression for the mean dipole moment, $\mu \langle P_l(\cos \vartheta) \rangle$.

$$\begin{aligned} \mu \langle P_1(\cos \vartheta) \rangle = & \frac{\mu^2 E_0}{3 \varepsilon_0 k_B T} \left\{ \left[1 - \frac{(27 - 13 \omega^2 \tau^2) \gamma_1^2}{540(1 + \omega^2 \tau^2)(1 + 4 \omega^2 \tau^2 / 9)} \right] \frac{\cos(\omega t)}{1 + \omega^2 \tau^2} + \right. \\ & \left[1 - \frac{(21 + \omega^2 \tau^2) \gamma_1^2}{270(1 + \omega^2 \tau^2)(1 + 4 \omega^2 \tau^2 / 9)} \right] \frac{\omega \tau \sin(\omega t)}{1 + \omega^2 \tau^2} - \quad (5.1.1) \\ & \left. \frac{\gamma_1^2}{180} \frac{[(3 - 17 \omega^2 \tau^2) \cos(3 \omega t) + \omega \tau (7 - 3 \omega^2 \tau^2) \sin(3 \omega t)]}{(1 + \omega^2 \tau^2)(1 + 4 \omega^2 \tau^2 / 9)(1 + 9 \omega^2 \tau^2)} \right\} \end{aligned}$$

where

$$\gamma_1 = \frac{\mu E_0}{k_B T}.$$

The terms independent of γ_1^2 in equation (5.1.1) correspond to those obtained by Debye in his discussion of dielectric relaxation under the influence of a weak alternating electric field, while the terms dependent on γ_1^2 represent relaxation due to the nonlinear behaviour of the dielectric. From equation (5.1.1) an equation for the polarisation of the dielectric may be written, by multiplying across both sides by the dipole number density, N , the number of dipoles per unit volume.

It can be seen from equation (5.1.1) that the polarisation will consist of two distinct components, one of angular frequency ω , the other of frequency 3ω . Adapting equation (5.1.1) to the magnetic case, N becomes the particle number density, E_0 becomes H_0 , μ becomes m the magnetic moment, and the free space permittivity ε_0 changes to the corresponding magnetic term, the free space permeability μ_0 .

Equation (5.1.1) may be written in terms of the complex magnetic susceptibilities in ω and 3ω respectively where,

$$\begin{aligned} \chi(\omega) = & \frac{Nm^2}{3\mu_0 k_B T} \left[\frac{1 + i\omega\tau}{1 + \omega^2\tau^2} - \gamma_1^2 \frac{27 - 13\omega^2\tau^2 + i\omega\tau(42 + 2\omega^2\tau^2)}{60(1 + \omega^2\tau^2)(9 + 4\omega^2\tau^2)} \right. \\ & \left. - 3 \frac{(3 - 17\omega^2\tau^2) + 2i\omega\tau(7 - 3\omega^2\tau^2)}{(1 + \omega^2\tau^2)(9 + 4\omega^2\tau^2)(1 + 9\omega^2\tau^2)} \right]. \quad (5.1.2) \end{aligned}$$

Multiplying the first term in (5.1.2) by

$$\frac{1 - i\omega\tau}{1 - i\omega\tau}$$

gives

$$\chi_1(\omega) = \frac{Nm^2}{3\mu_0 k_B T} \left[\frac{1}{1-i\omega\tau} - \gamma_1^2 \frac{27-13\omega^2\tau^2 + i\omega\tau(42+2\omega^2\tau^2)}{60(1+\omega^2\tau^2)(9+4\omega^2\tau^2)} \right], \quad (5.1.3)$$

and

$$\chi_3(\omega) = -3 \left[\frac{(3-17\omega^2\tau^2) + 2i\omega\tau(7-3\omega^2\tau^2)}{(1+\omega^2\tau^2)(9+4\omega^2\tau^2)(1+9\omega^2\tau^2)} \right]. \quad (5.1.4)$$

The first term in (5.1.3) above corresponds to the linear Debye equation, whilst the second term corresponds to the nonlinear magnetisation and is dependent on the square of the applied alternating field. The third harmonic of susceptibility has been separated from (5.1.3) and it is independent of the field parameter γ_1 . At present, with our measurement setup it is not possible to separate the 3rd harmonic of susceptibility from the overall measurement, hence the work done in this chapter will focus on $\chi_1(\omega)$ only.

The nonlinear increment $\Delta\chi_1(\omega)$ can be written as

$$\Delta\chi_1(\omega) = -\gamma_1^2 \left[\frac{27-13\omega^2\tau^2 + i\omega\tau(42+2\omega^2\tau^2)}{60(1+\omega^2\tau^2)(9+4\omega^2\tau^2)} \right], \quad (5.1.5)$$

where $\Delta\chi_1(\omega)$ is the difference between the susceptibility measured in the nonlinear and the linear regions.

Equation (5.1.3) may be rewritten as $\chi_1(\omega) = \chi_1'(\omega) - i\chi_1''(\omega)$

Giving

$$\chi_1'(\omega, H_0) = \frac{Nm^2}{3\mu_0 k_B T} \frac{1}{1+\omega^2\tau^2} \left[1 - \left(\frac{mH_0}{k_B T} \right)^2 \frac{(27-13\omega^2\tau^2)}{540(1+\omega^2\tau^2)(1+4\omega^2\tau^2/9)} \right], \quad (5.1.6)$$

and

$$\chi_1''(\omega, H_0) = \frac{Nm^2}{3\mu_0 k_B T} \frac{\omega\tau}{1+\omega^2\tau^2} \left[1 - \left(\frac{mH_0}{k_B T} \right)^2 \frac{(21+\omega^2\tau^2)}{270(1+\omega^2\tau^2)(1+4\omega^2\tau^2/9)} \right]. \quad (5.1.7)$$

$Nm^2/3\mu_0 k_B T = \chi_0$ is the zero frequency or static susceptibility.

The theory developed by Coffey and Paranjape is valid only in the case of a monodisperse system where variations in particle sizes are not taken into account. In reality all ferrofluid systems contain a distribution of particle shapes and sizes. Hence it is necessary to develop equations which take into account the polydispersity of the

ferrofluid samples and the high frequency susceptibility term χ_∞ . This can be done by applying the distribution functions mentioned earlier in section (2.5) to the equations of Coffey and Paranjape, or more desirably, the Cole-Cole parameter α can be used. To derive an equation containing the Cole-Cole parameter to describe the non linear effects in ferrofluid systems, it becomes necessary to solve the diffusion equation which describes anomalous diffusion in the case of a strong alternating field h_a . By extending the linear response solution originally given by Coffey et al [1] to the nonlinear case in the manner used by Coffey and Paranjape, Dejardin [2, 3] derived equations for the nonlinear susceptibility including a distribution parameter, for the cases of (a) a strong alternating field, and (b) a strong d.c. field superimposed on a weak alternating field. His equation is modified for the magnetic case, (including the static susceptibility term χ_0 , the high frequency susceptibility term χ_∞), and it should be noted that in our equations the Cole-Cole parameter α is represented by $(1-\alpha)$ with $\alpha=0$ corresponding to the monodisperse case. It should also be noted that in his derivation, Dejardin used the sign convention $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$ in comparison to the usual form of $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$. For the case of a strong alternating field that shall be focused on, Dejardin arrived at the following equation for the first harmonic of susceptibility $\chi_1(\omega, H_0)$.

$$\chi_1(\omega, H_0) = \frac{1}{1+(-i\omega\tau)^\alpha} - \frac{\gamma_1^2}{60} \frac{1}{[1+(-i\omega\tau)^\alpha]^2} * \left\{ \frac{2[1+(\omega\tau)^\alpha \cos(\pi\alpha/2)]}{1+(i\omega\tau)^\alpha} + \frac{3}{3+(-2i\omega\tau)^\alpha} \right\} \quad (5.1.8),$$

where γ_1^2 is as before.

Modifying the above equation for a real system of magnetic nanoparticles gives,

$$\chi_1(\omega, H_0) = \frac{\chi_0 - \chi_{\infty,1}}{1+(-i\omega\tau)^{(1-\alpha_1)}} - \frac{\gamma_1^2}{60} \frac{\chi_{0,2} - \chi_{\infty,2}}{[1+(-i\omega\tau)^{(1-\alpha_2)}]^2} * \left\{ \frac{2[1+(\omega\tau_2)^{(1-\alpha_2)} \cos(\pi(1-\alpha_2)/2)]}{1+(i\omega\tau)^{(1-\alpha_2)}} + \frac{3}{3+(-2i\omega\tau)^{(1-\alpha_2)}} \right\} + \chi_{\infty,1} + \chi_{\infty,2}, \quad (5.1.9)$$

where $\chi_{0,1}, \chi_{0,2}, \chi_{\infty,1}, \chi_{\infty,2}, \tau_1, \tau_2, \alpha_1, \alpha_2$ are the static susceptibilities, the high frequency susceptibilities, the effective relaxation times and the Cole-Cole parameters in the linear and non linear measurement regions respectively.

For $\alpha_1 = \alpha_2 = 0$, $\chi_0 = \chi_{0,2}$, $\chi_{\infty,1} = \chi_{\infty,2} = 0$, and $\tau_1 = \tau_2$ equation (5.1.9) reverts to the original equation of Coffey and Paranjape equation (5.1.3) as expected.

Evaluating for the case of the third harmonic of the susceptibility gives

$$\chi_3(\omega) = \frac{-1}{20} \left\{ \frac{\chi_{0,2} - \chi_{\text{inf},2}}{\left[1 + (-i\omega\tau)^{(1-\alpha_2)}\right] \left[3 + (-2i\omega\tau)^{(1-\alpha_2)}\right] \left[1 + (-3i\omega\tau)^{(1-\alpha_2)}\right]} \right\}. \quad (5.1.10)$$

Like the linear susceptibility, $\chi_3(\omega)$ is independent of the field parameter γ_1 .

The nonlinear increment is given as

$$\Delta\chi_1(\omega, H_0) = -\frac{\gamma_1^2}{60} \frac{\chi_{0,2} - \chi_{\infty,2}}{\left[1 + (-i\omega\tau)^{(1-\alpha_2)}\right]^2} * \left\{ \frac{2 \left[1 + (\omega\tau_2)^{(1-\alpha_2)} \cos\left(\frac{\pi(1-\alpha_2)}{2}\right)\right]}{1 + (i\omega\tau)^{(1-\alpha_2)}} + \frac{3}{3 + (-2i\omega\tau)^{(1-\alpha_2)}} \right\} + \chi_{\infty,1} + \chi_{\infty,2}. \quad (5.1.11)$$

Measurements of the nonlinear susceptibility have been presented in [4] for a 100 Gauss water-based ferrofluid comprising magnetite nanoparticles of mean radius 5nm. Figures 5.2 (a) to (k) show the results obtained for that particular fluid fitted against the theoretical equation. Figure 5.2 (a) shows the susceptibility fitted to the Cole-Cole equation for the linear measurement, whilst for the nonlinear measurements, figures 5.2 (a) and (b) show equations (5.1.9) and (5.1.11) fitted to the susceptibility and the increment of the susceptibility respectively.

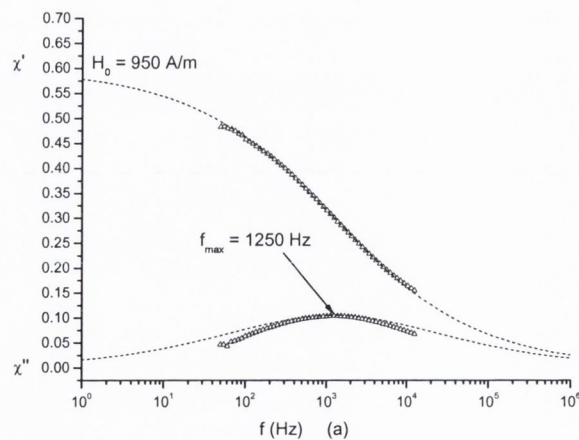


Figure 5.2 (a) : The susceptibility in the linear region fitted to the Debye equation.

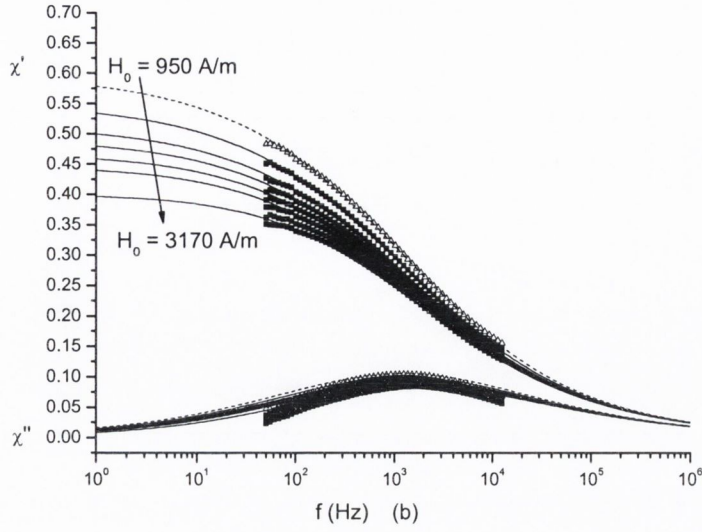


Figure 5.2 (b): Susceptibility data fitted to equation (5.1.9). The fit is represented by the dashed or solid lines. The open triangular symbols correspond to the susceptibility measured in the linear region ($H_0 < 1\text{ kA/m}$)

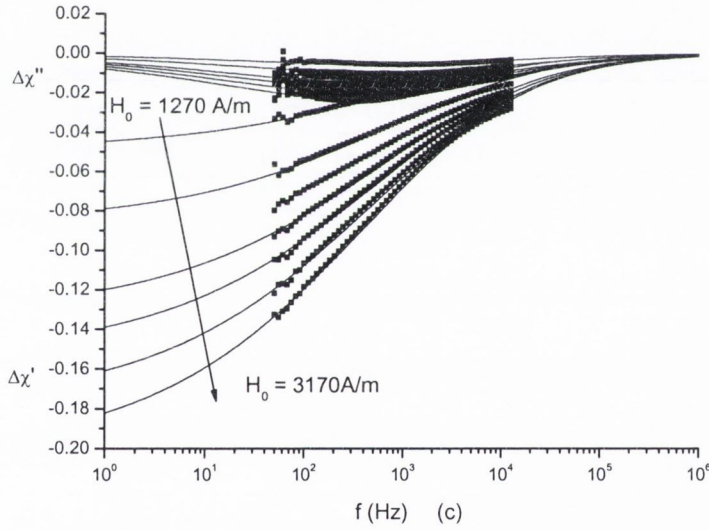


Figure 5.2 (c): The nonlinear increment of $\chi_1(\omega)$ and the corresponding fit from equation (5.1.11).

As can be seen from the figures above, equations (5.1.9) and (5.1.11) seem to provide a satisfactory fit over the frequency and field ranges measured. Figures 5.2 (d-k) shows the fits to $\chi_1(\omega)$ and $\Delta\chi_1(\omega)$ for selected values of H_0 .

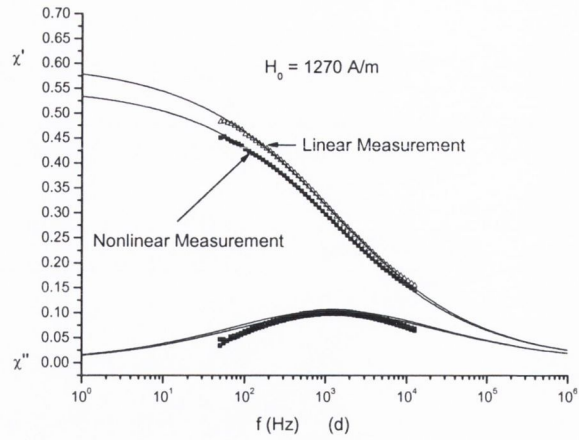


Figure 5.2 (d): Equation (5.1.9) fitted to the susceptibility data at $H_0 = 1270$ A/m. The continuous line corresponds to the fit.

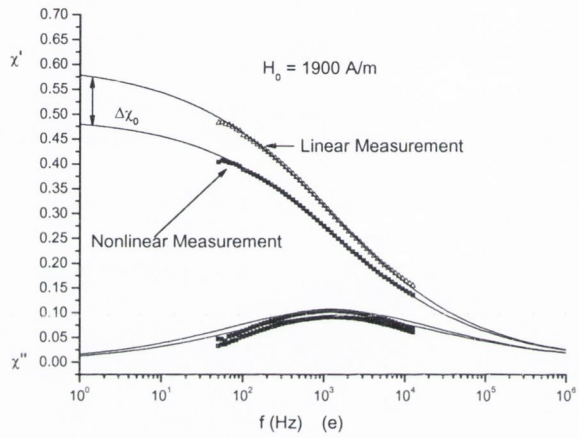


Figure 5.2 (e): Equation (5.1.9) fitted to the susceptibility data at $H_0 = 1900$ A/m. The continuous line corresponds to the fit.

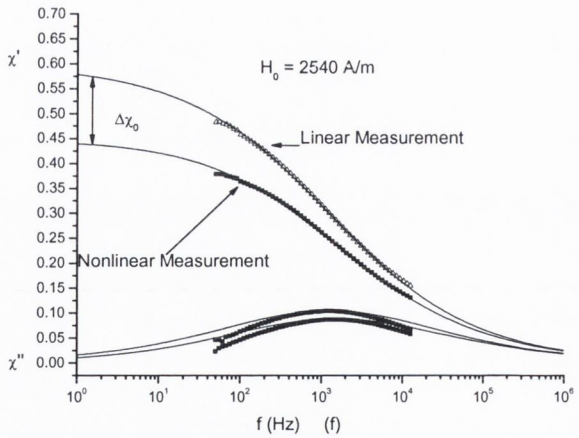


Figure 5.2 (f): Equation (5.1.9) fitted to the susceptibility data at $H_0 = 2540$ A/m. The continuous line corresponds to the fit.

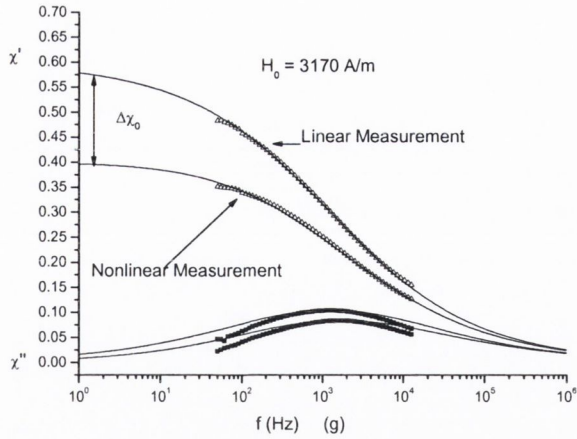


Figure 5.2 (g): Equation (5.1.9) fitted to the susceptibility data at $H_0 = 3170$ A/m. The continuous line corresponds to the fit.

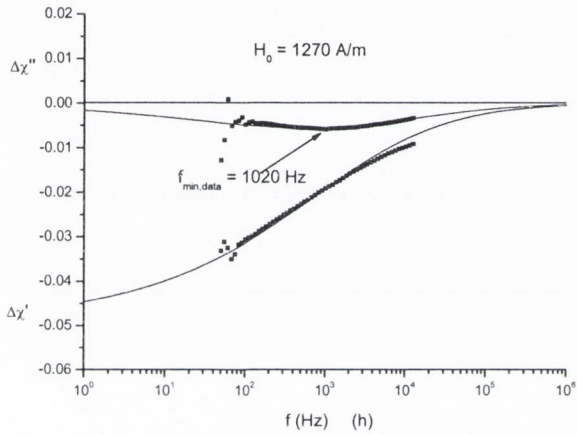


Figure 5.2 (h): Shows the increment of the susceptibility between the linear response (950 A/m) and the response at $H_0 = 1270$ A/m, and its fit to equation (5.1.11).

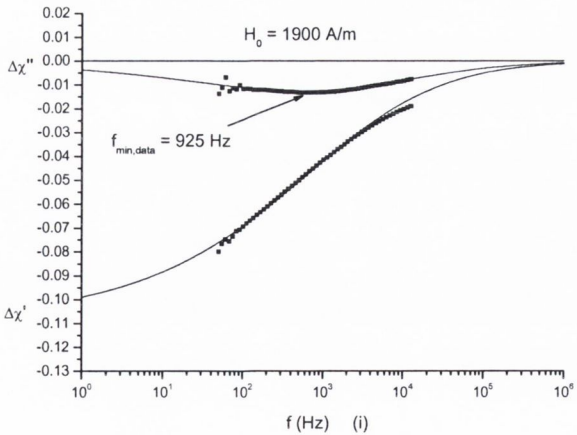


Figure 5.2 (i): Shows the increment of the susceptibility between the linear response (950 A/m) and the response at $H_0 = 1900$ A/m, and its fit to equation (5.1.11).

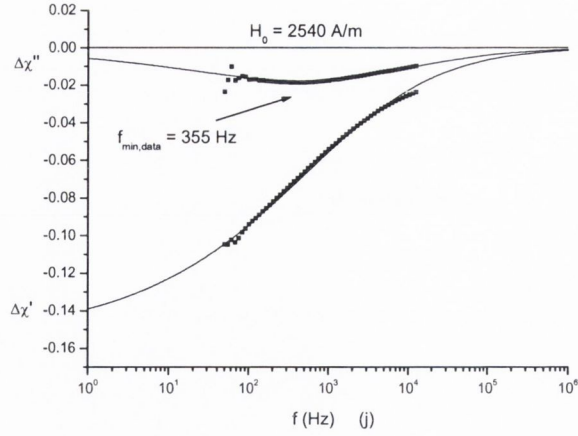


Figure 5.2 (j): Shows the increment of the susceptibility between the linear response (950 A/m) and the response at $H_0 = 2540$ A/m, and its fit to equation (5.1.11).

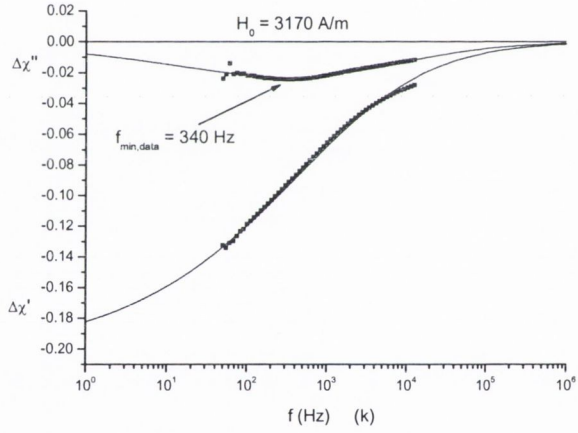


Figure 5.2 (k): Shows the increment of the susceptibility between the linear response (950 A/m) and the response at $H_0 = 3170$ A/m, and its fit to equation (5.1.11).

The nonlinear measurements were performed using the slit toroid technique as described previously in section (3.2), using toroid 2.

The fitting parameters used in the above figures are given in table 5.1. The term $\Delta\chi_0$ is evaluated by letting $\omega = 0$ in equation (5.1.11), giving

$$\Delta\chi_1(0, H_0) = -\frac{\gamma_1^2}{20} \chi_{0,2}. \quad (5.1.12)$$

Table 5.1:

Parameters used to fit equation (5.1.12) to the experimental data.

H_0	τ_2 (μs)	α_2	$\Delta\chi_0$
1270	28.94	0.652	0.0481
1590	28.94	0.652	0.0852
1900	30.61	0.652	0.1069
2220	34.6	0.655	0.1303
2540	37.89	0.655	0.1514
2850	41.88	0.655	0.1758
3170	48.23	0.655	0.1999

The values used for the linear portion of the fit using the Cole-Cole equation are, $\tau_1 = \tau_B = 12.73 \mu s$, $\alpha_1 = 0.57$, $m = 1 \times 10^{-24}$ and $\chi_{\infty,1} = 0.04$. The relaxation time of the linear measurement is assumed to be Brownian due to the low frequency at which the maximum of χ'' occurs. It is clear from equation (2.5.3) that aggregation has occurred in the sample. Clearly the increasing alternating field introduces a dependence of τ_2 on H_0 . It should be noted that if $\tau_2 = \tau_1 = \tau_B$, the quality of the fit to equations (5.1.9) and (5.1.11) diminishes considerably. Hence, to describe $\Delta\chi(\omega)$ accurately at low field strengths, it is necessary for $\tau_2 > \tau_B$.

Increasing H_0 leads to a corresponding increase in the relaxation time τ_2 and also to a decrease in the frequency of the minimum (f_{min}) at which $\Delta\chi''(\omega)$ occurs. Figures 5.3, 5.4 and 5.5 show the dependence of f_{min} , τ_{min} , and τ_2 on H_0 .

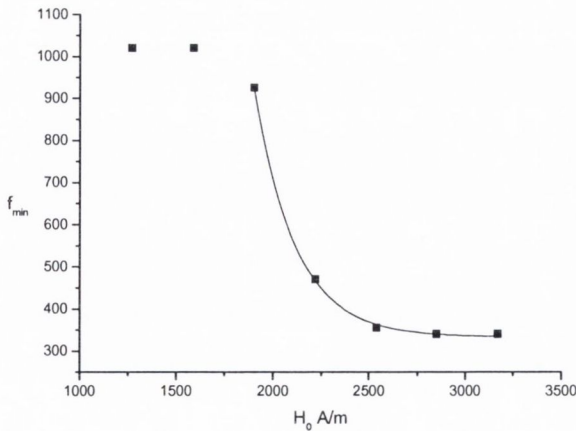


Figure 5.3: Dependence of f_{min} on amplitude of H_0 . The data points between $H_0 = 1900$ A/m and $H_0 = 3170$ A/m are fitted to an exponential decay.

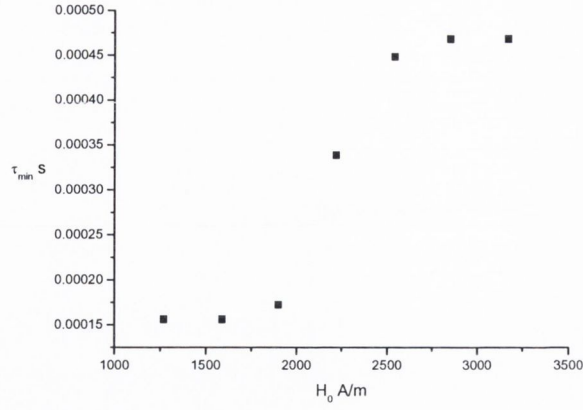


Figure 5.4: Dependence of τ_{min} on amplitude of H_0 .

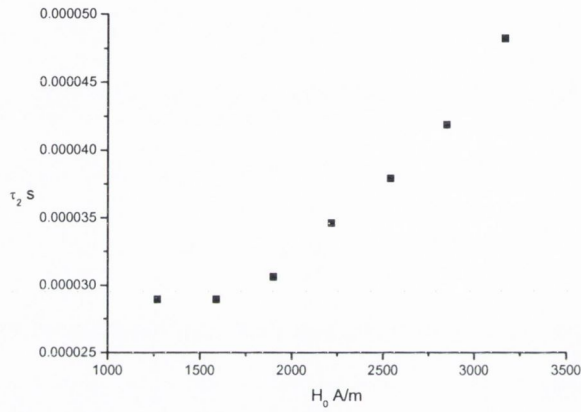


Figure 5.5: Dependence of τ_2 on amplitude of H_0 .

Figure 5.3 shows the dependence of f_{min} on H_0 . Initially f_{min} remains constant. As H_0 increases, and the magnetisation becomes more nonlinear, f_{min} begins to decrease exponentially until a constant value is reached close to $H_0 = 3$ kA/m.

Figures 5.4 and 5.5 show that both τ_{min} and τ_2 are increasing functions of H_0 . Initially, between $1270 \text{ A/m} \leq H_0 \leq 1600 \text{ A/m}$ both τ_{min} and τ_2 remain unchanged. In both cases, at approximately $H_0 = 1750 \text{ A/m}$, the relaxation time begins to increase. This change in relaxation time with applied field is similar to the relaxation of a ferrofluid under the influence of a large d.c. field as outlined in section 2.9. However, the equation given to describe the field dependence of the parallel relaxation time (equation 2.9.3) predicted a decrease in τ with increase in H_S , in contrast to the observed increase in τ shown here. The value of α_2 used throughout the fitting

remained approximately constant showing that the distribution of relaxation times did not change appreciably during the course of the measurement. As H_0 is increased, the difference in χ_0 between the linear and nonlinear measurement increases. This is reflected in the increase in $\Delta\chi_0$ in table 5.1.

It can be concluded that the equations of Coffey et al as modified by Dejardin, and adapted for the case of magnetic fluid, can be used to accurately describe the nonlinear susceptibility of a ferrofluid subject to a large alternating field H_0 .

5.2. Non Linear Loss Properties of Magnetic Fluids

Having established a satisfactory theoretical equation to describe the field dependence of the nonlinear susceptibility under a strong alternating field, it is now possible to extend this theory to take account of the effect of nonlinear magnetisation on the loss mechanisms in the ferrofluid. With recent advances in magneto electronics and the biotechnological applications of magnetic carriers [5] it becomes desirable to observe the losses generated by magnetic fluids. Because of the high a.c. fields [6, 7, 8] proposed for the generation of heat from magnetic fluids for the purpose of magnetic fluid hyperthermia, it becomes necessary to evaluate the effects of operating in the non linear region of magnetisation on the losses generated by the fluid.

One convenient method for doing so is by plotting the frequency dependent loss factor, $\tan\delta$ [9]. This property can be investigated via the permeability of the magnetic fluid, $\mu(\omega) = \mu'(\omega) - i\mu''(\omega)$, which is related to the complex susceptibility. The imaginary component of the permeability, $\mu''(\omega) = \chi''(\omega)$, describes the losses in the magnetic fluid which are usually dissipated in the form of heat. Assuming superparamagnetism and hence the absence of hysteresis losses, the losses arise due to relaxational effects in the ferrofluid, where the magnetic nanoparticles undergo Brownian and or Néel relaxation. The loss mechanisms cause the flux density, B , to lag behind the applied alternating field, H , by a phase angle, δ . We can write a relationship between the phase angle and the complex susceptibility where,

$$\tan(\delta) = \frac{\chi''(\omega)}{1 + \chi'(\omega)}. \quad (5.2.1)$$

The losses arising from the superimposition of a weak alternating field and a strong d.c. field have been studied in detail by Fannin et al [9] and an expression for the loss tangent in the context of the theoretical nonlinear susceptibility has been provided by Coffey and Paranjape [2]. Here, using the original expressions given by Dejardin and modified for the case of a magnetic fluid, results are presented for the loss tangent of a magnetic fluid under the effect of various strong alternating fields some of which operate in the nonlinear region.

The formulism of the previous section used to define the increment of the nonlinear susceptibility, can be extended to define the nonlinear increment of the loss tangent with

$$\Delta \tan \delta = \frac{\Delta \chi''}{1 + \Delta \chi'} \quad (5.2.2)$$

where $\Delta \chi''$ and $\Delta \chi'$ are the real and imaginary components of equation (5.1.11).

The field dependence of the loss tangent has been documented in [10] where analytical formulae have been given for $\tan \delta$ in the context of the Langevin equation, and this has been demonstrated by Fannin et al [9].

To evaluate the loss tangent in the nonlinear region it is necessary to substitute the real and imaginary components of equations (5.1.9) into (5.2.1). Using the same values given in table 5.1 for the fit, $\tan \delta$ is plotted against the experimental susceptibility data.

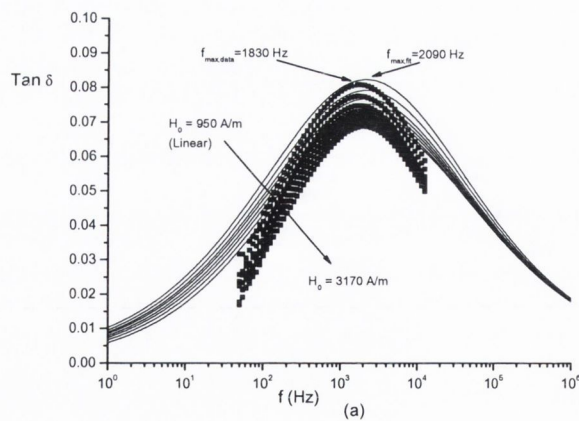


figure 5.6 (a): Fit of equation (5.2.1) using values from table 5.1 to experimental $\tan \delta$. The top most data points correspond to the loss tangent in the linear region. The fit is the solid line, and the data points are the square symbols.

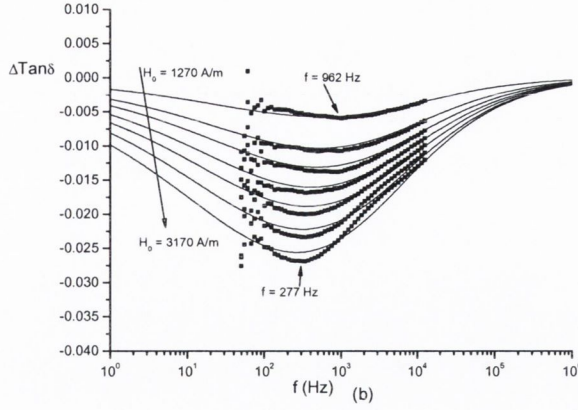


figure 5.6 (b): Fit of equation (5.2.2) using values from (5.1.11) to experimental $\Delta \tan \delta$. The fit is the solid line, and the data points are the square symbols.

In figure 5.6 (a) the frequency and field dependence of $\tan \delta$ is shown. With increasing H_0 the magnitude of $\tan \delta$ decreases, with a corresponding shift to higher frequencies of the maximum value. These findings echo the case of superimposed a.c. and d.c. fields. Figure 5.6 (b) shows the component of the losses which are due to the nonlinear response of the ferrofluid.

5.2.1: Calculation of the Heat losses due to the nonlinear response

In ferrofluids, assuming superparamagnetic behaviour where hysteresis losses do not occur, the primary loss mechanism is by heat lost to the surroundings. Rosensweig [11] derived formulae to describe the heating loss of a ferrofluid due to relaxation losses. He gave an equation to describe the volumetric power dissipation in a ferrofluid over the course of one cycle as

$$P = \delta U_{heat} = \mu_0 \pi \chi'' H_0^2. \quad (5.2.1.1)$$

Again it is possible to extend the formulism of the nonlinear increment to define the nonlinear increment of heating rate, ΔU_{heat} as

$$\Delta U_{heat} = \delta U_{heatNL} - \delta U_{heatLinear} = \pi \mu_0 \{ \chi''_T(\omega) H_{acNL}^2 - \chi''_{Lin}(\omega) H_{acLin}^2 \}. \quad (5.2.1.2)$$

Despite the fact that $\chi''_1(\omega)$ is a decreasing function of H_0 , figure 5.7 (a) shows U_{heat} as an increasing function of H_0 . This is due to the strong field dependence of U_{heat} which varies with the square of the alternating field. The maximum amount of heat

generated will occur at the frequency where $\chi''_1(\omega)$ is a maximum. Figure 5.7 (b) shows a nine fold increase in the peak heat generation of the ferrofluid with increasing field, with a jump from 0.37 J/m^3 to 3.34 J/m^3 .

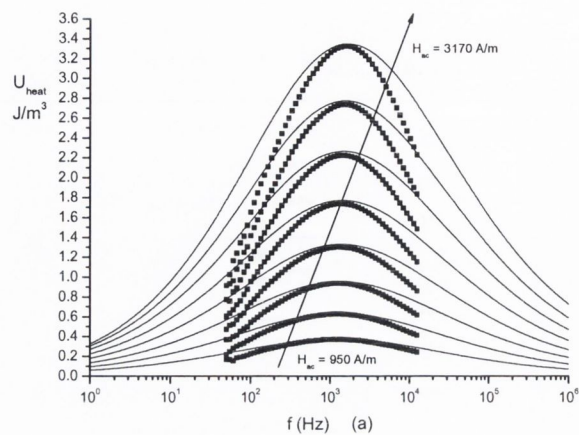


figure 5.7 (a): Fit of the heat losses for the first harmonic of susceptibility to the experimental data as per equation (5.2.1.1)

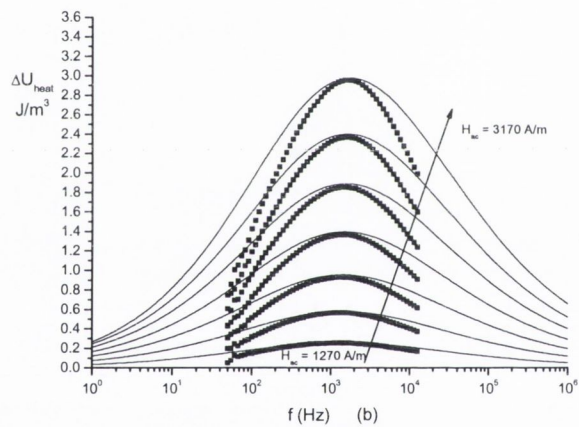


figure 5.7 (b): Fit of the heat losses for the first harmonic of susceptibility to the increment of the experimental data as per equation (5.2.1.2)

In contrast to the increments of susceptibility and loss tangent, the increment of heating rate is a positive increasing function of applied field. This is due again, to the strong dependence on H_0^2 . To evaluate how much of the total heating is caused by the nonlinear response, the value of the maximum value of ΔU_{heat} evaluated as a percentage of the maximum value of δU_{heat} can be plotted (figure 5.8 (a) and (b))

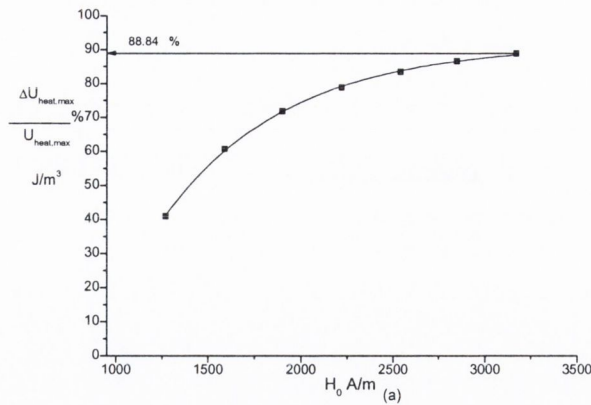


figure 5.8 (a): Increment of heating rate expressed as a percentage of maximum heating rate vs. applied field. In this graph the experimental data points are fitted to an asymptotic equation, $y = A - B \cdot C^x$.

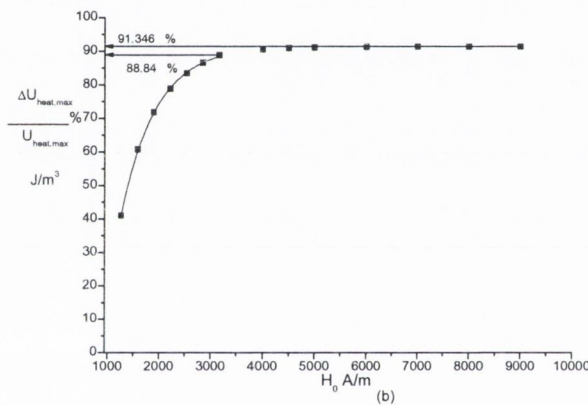


figure 5.8 (b): Increment of heating rate expressed as a percentage of maximum heating rate vs. applied field. In this graph the experimental data points are extrapolated forward to higher values of H_0 (star symbols) using the equation for the asymptotic fit.

Figure 5.8 (a) shows that at 1250 A/m the increment of heating rate is approximately 41 percent of the maximum heating rate, that is to say that the heating due to the nonlinear response accounts for 41 percent of the maximum heat generated. Moving further into the nonlinear region the percentage increases until a maximum value of 88.84 % is reached at the maximum field value.

Fitting an asymptotic equation to the data and extrapolating (figure 5.8 (b)) for field values of 4000, 4500, 5000, 6000, 7000, 8000, and 10,000 A/m shows that the percentages of maximum heating rate levels out at higher values of H_0 , to a value of 91.346 %. This would suggest that the heating due to the nonlinear response of the

magnetisation of a ferrofluid, tapers off at a certain value of applied alternating magnetic field, and that its contribution to the overall heating effect does not increase significantly after this point. Evaluating for $H_0 = 100$ kA/m returns the same value as for $H_0 = 10,000$ A/m thus demonstrating that a dramatic rise in the alternating field amplitude has little or no increased effect on the heat generation arising from the contribution of the nonlinear magnetisation.

5.3. Conclusions

We conclude that the model for the non linear susceptibility first proposed by Coffey and Paranjape, and modified by Dejardin, can be used to describe the nonlinear susceptibility of ferrofluids subject to large alternating magnetic fields, with suitable modifications. The model is shown to be suitable for modelling the loss processes in a magnetic fluid subject to a large alternating field. It is shown that the contribution of the nonlinear susceptibility to the total heat generated, reaches a maximum for values of H_0 in excess of 9 kA/m. This result could have important implications in applications of magnetic fluids, such as magnetic fluid hyperthermia, that seek to maximise the heat loss capabilities of a ferrofluid under large alternating fields.

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Chapter 6: Conclusions

6.1. Conclusions

This thesis has analysed the magnetic properties of ferrofluid, using the frequency and field dependent complex susceptibility data, $(\chi(\omega, H))$, as obtained from impedance measurement techniques. Measurements were performed in two frequency ranges spanning 10 Hz to 10 MHz (low frequency region), and 20 MHz to 16 GHz (high frequency region). In the low frequency region measurements were performed using the slit toroid technique, whilst at high frequencies, the transmission line technique was used. Both techniques have been described in detail in chapter 3.

Analysis was performed on 9 ferrofluids of varying composition over the frequency ranges. The first section of the investigation in the low frequency range focused on the effect of applying a strong polarising field, H_S , to a ferrofluid. For fluids 1 and 3, H_S was applied in the forward and reverse directions, i.e. H_S was increased from 0 to its maximum value and then decreased back to zero again. The relevant $\chi(\omega, H)$ data was then plotted for the forward and reverse direction against frequency. The plots revealed that both forward and reverse measurements had almost equal magnitudes over the frequency range measured. Hence it was determined that the variation of H_S induced no permanent hysteresis into the fluid.

The analysis was extended further to investigate the isotropic properties of a ferrofluid. The fluid is isotropic in H , if the measurement of $\chi(\omega, H)$ is independent of the direction of H . The test applied to determine the isotropy of the fluid, was to plot $\chi(\omega, H)$ at a specific value of ω against H_S . If the plot is symmetrical about the vertical axis, then the fluid is deemed isotropic in H_S . The Weierstrass hypothesis was used as an aid in judging the symmetry of the plots. If the odd coefficients of a polynomial fitted to the plots were zero or close to zero, the plot was then deemed symmetric, and hence the fluid isotropic. To demonstrate this, cycled measurements of $\chi(\omega, H)$, where H_S is varied between 0 and ± 13.6 kA/m, were performed on fluid 4. The plots of $\chi(\omega, H)$ at various values of ω were indeed symmetric about the vertical axis, and the fluid was proved to be isotropic in H_S . The symmetry was further emphasised using the polynomial fits, and by fitting a Gaussian curve to the data.

The second area of interest in the low frequency range was the measurement of $\chi(\omega, H)$ for a suspension of magnetic microspheres (fluids 5, 6). The measurements revealed an unusual trend of increasing $\chi'(\omega, H)$ and $\chi''(\omega, H)$ with increasing H_S . The increase in $\chi''(\omega, H)$ was explained in the context of the relaxation of the maghemite nanoparticles inside the microspheres. It was found that the maghemite particles were undergoing Néel relaxation, and that as H_S increased, the number of particles aligned with the field would also increase, leading to an overall increase of the magnetic moments of the individual microspheres. Once all the nanoparticles inside a microsphere were aligned with H_S , the spheres began to form individual chains. The effective moment of the chain which was given as the sum of all the individual sphere moments, was found to also increase with H_S , leading to the observed increase in $\chi'(\omega, H)$. Hysteresis measurements were also performed to see whether the applied field had any lasting effect on the structure of the fluid. It was found that $H_S = 4.5$ kA/m was a critical point whereby, the chain formation would begin or stop. As H_S was reduced below this point to zero $\chi'(\omega, H)$ behaved normally as described by the equation for the field dependence given in chapter 2. The final value of $\chi(\omega, H)$ was found to be very close to its initial value, indicating that no appreciable hysteresis had been introduced into the fluid.

Finally the nonlinear properties of a water based magnetite ferrofluid (fluid 9) subject to a large alternating magnetic field, $h_a = H_0 \cos(\omega t)$, were investigated. The equations of Dejardin for the nonlinear susceptibility of a dielectric under the influence of a large alternating electric field were modified for the magnetic case, and were found to be in good agreement with the measured data. Having verified the suitability of the equation to describe the nonlinear magnetisation, the analysis was extended to take account of the nonlinear losses in a ferrofluid. The loss tangent, $\tan \delta$, and the heat rate energy density, U_{heat} , were the quantities used to investigate the losses generated by the nonlinear magnetisation. Equations for $\Delta \tan \delta$ and ΔU_{heat} were given in terms of the previously fitted equations for the nonlinear susceptibility, and were found to be a good fit to the measured data. It was determined that the contribution of the nonlinear magnetisation to the heat losses reached a theoretical maximum at $H_0 = 9$ kA/m, and did not increase after this point.

In the high frequency region, a comparison was performed on the susceptibility data generated by measuring with the transmission line terminated in a

short circuit, and between the data generated when the line was terminated in both open and short circuits. Fluids 4 and 9 were measured. The accuracy of the short circuit only measurement was shown to diminish at the higher frequencies of the measurement range where the wavelength of the radiation in the line becomes comparable to the cell depth. The combined open and short circuited measurement was shown to be accurate across all frequency in the range measured.

Using the equations of Landau and Lifshitz as modified by Raikher and Shliomis, the susceptibility data was fitted in Cole-Cole format. This fitting technique yielded values for the anisotropy constant, K , the precessional decay time, τ_0 and the gyromagnetic ratio, γ . The values obtained compared favourably to values obtained from a different method where the dependence of the resonant frequency, f_{res} , was plotted against H_S , thus verifying the usefulness of the fitting method.

Appendix A

Calculation of the susceptibility by means of the slit toroid technique.

To measure the permeability and hence the susceptibility of a ferrofluid with the slit toroid technique, it is necessary to perform two measurements. The first measurement is with the slit empty, the second with the slit full of ferrofluid. The following treatment will derive equations for the calculation of μ in terms of the geometrical characteristics of the toroid and impedance measurements with the toroid empty and full. The geometry of the toroid shown in figure 3.1 shall be used for the course of this derivation. The toroid had the following dimensions:

A	cross sectional area, m^2
r_2	mean radius, m
L_1	Slit length, m
L_2	mean magnetic path length in toroid, m
μ_0	free space permeability, Hm^{-1}
μ_{eff}	effective permeability of cut toroid, Hm^{-1}
μ_r	relative permeability of cut toroid

If the toroid has N turns and $I(t)$ is the alternating current in the winding, the current produces a magnetizing force, H , of

$$H = \frac{NI(t)}{L_1 + L_2}, \text{ (A/m)} \quad (\text{A.1})$$

If Φ_B is the flux in webers then

$$\Phi_B = B_{toroid} A = B_{gap} A = \mu_0 H_{gap} A \quad (\text{A.2})$$

since the flux is the same throughout the core.

Hence

$$B_{toroid} = \mu_r \mu_0 H_{toroid} = \mu_0 H_{gap} \quad (\text{A.3})$$

$H(L_1 + L_2) = NI(t)$ (ampere-turns) is always the same across the core and the slit.

Therefore,

$$H(L_1 + L_2) = NI(t) = H_{gap} L_1 + H_{toroid} L_2 = H_{gap} (L_1 + L_2 / \mu_r) \quad (\text{A.4})$$

The flux density across the toroid is given as,

$$B = \frac{\Phi_B}{A} = \mu_{eff} \mu_0 \frac{NI(t)}{L_1 + L_2} = \mu_0 \frac{NI(t)}{(L_1 + L_2 / \mu_r)} \quad (A.5)$$

Consequently the effective relative permeability is equal to,

$$\mu_{eff} = \frac{1 + (L_1 / L_2)}{1 / \mu_r + (L_1 / L_2)} \quad (A.6)$$

If $L_1/L_2 \ll 1$ the latter equation is simplified to,

$$\mu_{eff} = \frac{1}{1 / \mu_r + (L_1 / L_2)} \quad (A.7)$$

Let L_0 be the inductance of the excitation winding without any material in the toroid, that is, the inductance of N turns uniformly around the periphery of the toroid, then

$$L_0 = \frac{\mu_0 N^2 A}{L_1 + L_2} \cong \frac{\mu_0 N^2 A}{L_2} \quad (A.8)$$

Let L_{nocut} be the inductance of the toroid without a cut, then

$$L_{nocut} = \frac{\mu_0 \mu_r N^2 A}{L_1 + L_2} \cong \frac{\mu_0 \mu_r N^2 A}{L_2} \quad (A.9)$$

If L_{cut}^{empty} denotes the inductance of the toroid with an empty cut, and by using equations (A.7), and (A.9),

$$L_{cut}^{empty} = \frac{\mu_0 \mu_{eff} N^2 A}{L_1 + L_2} \approx \frac{\mu_0 \mu_r N^2 A}{(1 + \mu_r L_1 / L_2)(L_1 + L_2)} = \frac{L_{nocut}}{1 + \mu_r L_1 / L_2} \quad (A.10)$$

Therefore the inductance with a cut = $\frac{\text{inductance without a cut}}{1 + \mu_r L_1 / L_2}$

From (A.9) and (A.8)

$$L_{cut}^{empty} = \frac{L_0}{1 / \mu_r + L_1 / L_2} \quad (A.11)$$

Therefore the impedance of the coil on the core with a cut is

$$Z_e = R_w + i\omega L_{cut}^{empty} = R_w + \frac{i\omega L_0}{\left(\frac{1}{\mu'_r - i\mu''_r} + \frac{L_1}{L_2} \right)} \quad (A.12)$$

where R_w is the dc resistance of the wire.

Therefore

$$Z_e = R_w + \frac{i\omega L_0(\mu'_r - i\mu''_r)}{1 + \gamma_g(\mu'_r - i\mu''_r)}, \quad (\text{A.13})$$

where $\gamma_g = L_1 / L_2 \ll 1$.

Insertion of a ferrofluid of relative permeability μ_l into the slit gives

$$L_{cut}^{full} = \frac{\mu_0 N^2 A}{[L_1/\mu_l + L_2/\mu_r]} = \frac{\mu_0 N^2 A}{(L_2/\mu_r)(1 + L_1\mu_r/L_2\mu_l)} = \frac{L_0(\mu'_r - i\mu''_r)}{1 + L_1(\mu'_r - i\mu''_r)/L_2(\mu'_l - i\mu''_l)} \quad (\text{A.14})$$

The impedance of the toroid with the slit full of ferrofluid is given by

$$Z_f = R_w + i\omega L_{cut}^{full} = R_w + \frac{i\omega L_0(\mu'_r - i\mu''_r)}{1 + L_1(\mu'_r - i\mu''_r)/L_2(\mu'_l - i\mu''_l)} = R_w + \frac{i\omega L_0(\mu'_r - i\mu''_r)}{1 + \gamma_g \frac{(\mu'_r - i\mu''_r)}{(\mu'_l - i\mu''_l)}} \quad (\text{A.15})$$

Equation (A.13) can be rewritten as

$$Z_e - R_w [1 + \gamma_g(\mu'_r - i\mu''_r)] = i\omega L_0(\mu'_r - i\mu''_r). \quad (\text{A.16})$$

It is possible to write equation (A.15) in the same manner giving

$$Z_f - R_w = \frac{i\omega L_0(\mu'_r - i\mu''_r)}{1 + \gamma_g \frac{\mu'_r - i\mu''_r}{\mu'_l - i\mu''_l}}. \quad (\text{A.17})$$

After some manipulation and letting $Z = \left(\frac{Z_f - R_w}{Z_e - R_w} \right)^{-1}$ it is possible to write

$$\frac{(\mu'_l - i\mu''_l) + \gamma_g(\mu'_r - i\mu''_r)}{\mu'_l - i\mu''_l} = Z[1 + \gamma_g(\mu'_r - i\mu''_r)]. \quad (\text{A.18})$$

Cross multiplying gives

$$(\mu'_l - i\mu''_l) + \gamma_g(\mu'_r - i\mu''_r) = Z(\mu'_l - i\mu''_l)[1 + \gamma_g(\mu'_r - i\mu''_r)]. \quad (\text{A.19})$$

Solving for $\mu'_l - i\mu''_l$ we obtain

$$\mu'_l - i\mu''_l = \frac{-\gamma_g(\mu'_r - i\mu''_r)}{1 - Z[1 + \gamma_g(\mu'_r - i\mu''_r)]}. \quad (\text{A.20})$$

Solving equation (A.13) for $\mu'_r - i\mu''_r$, we get

$$\mu'_r - i\mu''_r = \frac{Z_e - R_w}{i\omega L_0 + \gamma_g R_w - \gamma_g Z_e}. \quad (\text{A.21})$$

Consequently

$$\mu'_1 - i\mu''_1 = \frac{-\gamma_g \left(\frac{Z_e - R_w}{i\omega L_0 + \gamma_g R_w - \gamma_g Z_e} \right)}{1 - Z \left[1 + \gamma_g \left(\frac{Z_e - R_w}{i\omega L_0 + \gamma_g R_w - \gamma_g Z_e} \right) \right]} = \frac{-\gamma_g [Z_e - R_w]}{i\omega L_0 + \gamma_g R_w - \gamma_g Z_e - Zi\omega L_0}. \quad (\text{A.22})$$

Substituting for Z yields

$$\mu'_1 - i\mu''_1 = \frac{-\gamma_g (Z_e - R_w)(Z_f - R_w)}{(Z_f - R_w)(i\omega L_0 + \gamma_g R_w - \gamma_g Z_e) - (Z_e - R_w)i\omega L_0}. \quad (\text{A.23})$$

Considering the denominator of equation (A.23) with

$$Z_f = R_f - iX_f, \text{ and } Z_e = R_e - iX_e$$

then

$$\begin{aligned} & (Z_f - R_w)(i\omega L_0 + \gamma_g R_w - \gamma_g Z_e) - (Z_e - R_w)i\omega L_0 \\ &= (R_f - R_w - iX_f)(i\omega L_0 + \gamma_g R_w - \gamma_g R_e - i\gamma_g X_e) - (R_e - R_w - iX_e)i\omega L_0 \end{aligned} \quad (\text{A.24})$$

The real part of (A.24) is equal to

$$-\omega L_0 X_f + \gamma_g R_w R_f - \gamma_g R_w^2 - \gamma_g R_e R_f + \gamma_g R_w R_e + \gamma_g X_e X_f + \omega L_0 X_e, \quad (\text{A.25})$$

and the imaginary part is equal to

$$i\gamma_g R_w X_f - i\gamma_g R_e X_f - i\gamma_g R_f X_e + i\gamma_g R_w X_e + i\omega L_0 R_f - i\omega L_0 R_e \quad (\text{A.26})$$

Let

$$\tilde{A} = \gamma_g (R_e R_f + R_w^2 - R_w R_f - R_w R_e - X_e X_f) \quad (\text{A.27})$$

$$\tilde{B} = \gamma_g (-R_w X_e - R_w X_f + R_f X_e + R_e X_f) \quad (\text{A.28})$$

$$\tilde{U} = \gamma_g R_w R_f + \gamma_g R_w R_e + \gamma_g X_f X_e - \gamma_g R_w^2 - \gamma_g R_f R_e + \omega L_0 (X_e - X_f) \quad (\text{A.29})$$

$$\tilde{V} = \gamma_g R_w X_f - \gamma_g R_e X_f - \gamma_g R_f X_e + \gamma_g R_w R_e + \omega L_0 (-R_e + R_f) \quad (\text{A.30})$$

Clearly $\tilde{A}$, $\tilde{B}$, $\tilde{U}$, $\tilde{V}$ can be evaluated by measuring R_f, R_e, X_f, X_e . γ_g and L_0 are given by the geometrical characteristics of the toroid, i.e. L_1, L_2, N , and A . Finally, the permeability can be written in terms of $\tilde{A}$, $\tilde{B}$, $\tilde{U}$, $\tilde{V}$ as

$$\mu'_1 - i\mu''_1 = \frac{(-\tilde{A} - i\tilde{B})(\tilde{U} - i\tilde{V})}{\tilde{U}^2 + \tilde{V}^2} = -\frac{(\tilde{A}\tilde{U} + \tilde{B}\tilde{V}) - i(\tilde{B}\tilde{U} - \tilde{A}\tilde{V})}{\tilde{U}^2 + \tilde{V}^2}. \quad (\text{A.31})$$

Therefore,

$$\mu'_1 = -\frac{(\tilde{A}\tilde{U} + \tilde{B}\tilde{V})}{\tilde{U}^2 + \tilde{V}^2}, \quad \mu''_1 = \frac{(\tilde{B}\tilde{U} - \tilde{A}\tilde{V})}{\tilde{U}^2 + \tilde{V}^2} \quad (\text{A.32})$$

The susceptibility will be given, then, as

$$\chi' = \mu'_1 - 1 = -\frac{\tilde{A}\tilde{U} + \tilde{B}\tilde{V}}{\tilde{U}^2 + \tilde{V}^2} - 1, \quad (\text{A.33})$$

$$\chi'' = \mu''_1 = \frac{\tilde{B}\tilde{U} - \tilde{A}\tilde{V}}{\tilde{U}^2 + \tilde{V}^2} \quad (\text{A.34})$$

It is then possible to compute the susceptibility by importing the measured impedance data, both empty and full into a computer program, and evaluating the above equations.