

## CHAPTER 2

# BASIC CONCEPTS OF MAGNETIC LIQUIDS

### 1. INTRODUCTORY CONCEPTS OF MAGNETISM

Ferromagnetic fluids, or ferrofluids as they are often called, are suspensions of magnetic particles that behave like magnetic liquids. Before defining and describing ferrofluids, however, it may be necessary to explain certain terms used in magnetism.

Magnetic moments may arise from the orbital motion of electrons in atoms. Electrons also have an intrinsic angular momentum referred to as spin, which causes the electrons to behave as though they had magnetic moments of their own. Application of an external magnetic field to an atom may influence the alignment of these moments. [1, 2]

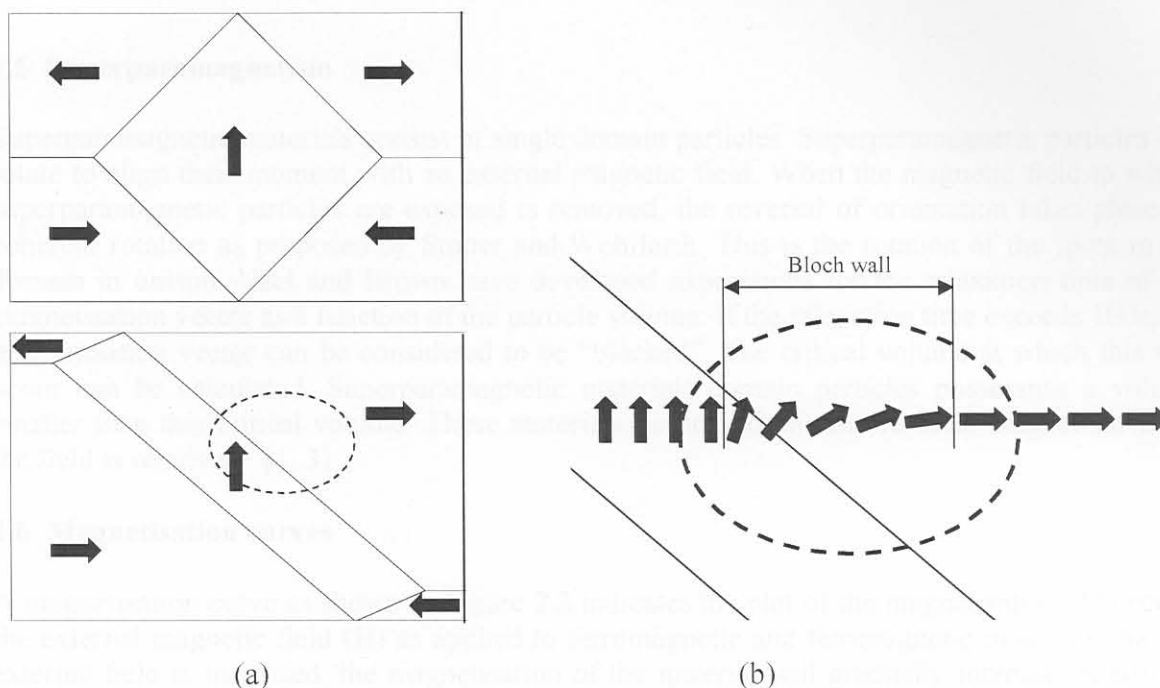
#### 1.1 Ferromagnetism

When an external magnetic field is applied to a ferromagnetic material, the alignment of moments is parallel to the field. French physicist Pierre-Ernest Weiss proposed that ferromagnetic materials are subdivided into areas known as domains. [1] In an unmagnetised sample, the moments of the domains are randomly orientated. When a magnetic field is applied to the sample, the moments of the domains tend to orient themselves in the direction of the field. This phenomenon occurs below a certain temperature known as the Curie temperature (above the Curie temperature, the ferromagnetic property disappears as a result of thermal agitation). Figure 2.1 (a) gives a schematic representation of this phenomenon. In the top picture of Figure 2.1 (a), there is no applied field. In the bottom picture, there is a strong field applied to the right causing the moments of the domains to orientate themselves in the direction of the applied field. [1, 2] The transition of moments between domains is gradual. The region over which the transition occurs is known as the Bloch wall. This is shown in Figure 2.1 (b) for the area circled in Figure 2.1 (a). [3]

In ferromagnetic material, some of the moments of the domains are orientated in the direction of the field whilst other moments are orientated in the opposite direction to the field. For a net magnetic moment to be produced, the number or size of the moments aligned in the direction of the field is greater than that in the opposite direction to the field, resulting in a net magnetic moment. The net magnetic moment for ferromagnetic materials is smaller than that for paramagnetic materials. [1, 4, 5]

#### 1.2 Paramagnetism

A paramagnetic material is a material containing atoms with permanent magnetic dipole moments in the absence of an external magnetic field. The moments point in random directions. When placed in a magnetic field, the moments tend to align with the magnetic field as a result of the field exerting a torque on these moments. The atoms align in such positions of minimum potential energy. The alignment, however, is not complete, due to the disruptive effect of thermal agitation. Paramagnetic substances are therefore weakly attracted by a magnet. [1, 2]



**Figure 2.1** (a) Domains with no field (top) and applied field directed to the right (bottom) and (b) schematic of Bloch wall

## 1.2 Antiferromagnetism

Antiferromagnetic materials consist of sublattices possessing antiparallel moments. These moments are of the same size and result in no net magnetic moment. [1]

## 1.3 Ferrimagnetism

Ferrimagnetic materials also consist of interpenetrating sublattices. When a magnetic field is applied to a ferrimagnetic material, some of the moments of the domains are orientated in the direction of the field whilst other moments are aligned in the opposite direction to the field. Either the number or size of the moments aligned in the direction of the field is greater than that in the opposite direction to the field resulting in a net magnetic moment. The net magnetic moment for ferrimagnetic materials is smaller than that for ferromagnetic materials. [1, 4, 5]

## 1.4 Paramagnetism

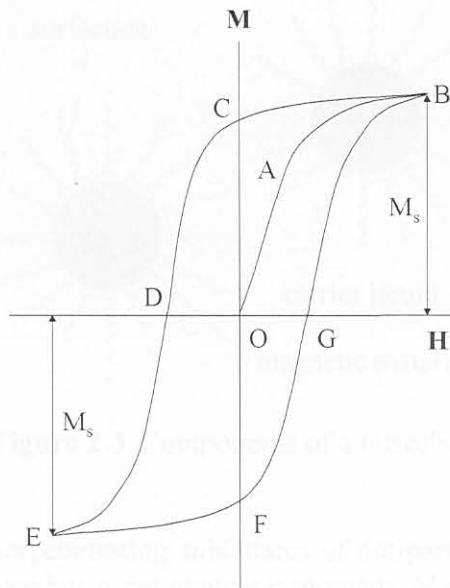
A paramagnetic material is a material containing atoms with permanent magnetic dipole moments. In the absence of an external magnetic field, the moments point in random directions. When placed in a magnetic field, the moments tend to align with the magnetic field as a result of the field exerting a torque on these moments. The atoms align in their position of minimum potential energy. The alignment, however, is not complete, due to the disruptive effect of thermal vibrations. Paramagnetic substances are therefore only weakly attracted by a magnet. [1, 2]

## 1.5 Superparamagnetism

Superparamagnetic materials consist of single domain particles. Superparamagnetic particles can rotate to align their moment with an external magnetic field. When the magnetic field to which superparamagnetic particles are exposed is removed, the reversal of orientation takes place by coherent rotation as proposed by Stoner and Wohlfarth. This is the rotation of the spins in the domain in unison. Néel and Brown have developed expressions for the relaxation time of the magnetisation vector as a function of the particle volume. If the relaxation time exceeds 100s, the magnetisation vector can be considered to be “blocked”. The critical volume at which this will occur can be calculated. Superparamagnetic materials contain particles possessing a volume smaller than this critical volume. These materials do not exhibit any residual magnetism when the field is removed. [1, 3]

## 1.6 Magnetisation curves

A magnetisation curve as shown in Figure 2.2 indicates the plot of the magnetisation ( $M$ ) versus the external magnetic field ( $H$ ) as applied to ferromagnetic and ferrimagnetic materials. As this external field is increased, the magnetisation of the material will gradually increase. A point is reached where the magnetisation is constant and no further magnetisation can take place (B in Figure 2.2), however strong the field. This condition is called the saturation magnetisation ( $M_s$ ). If the field is decreased, the magnetisation does not retrace the original curve B-A-O. When the field is decreased to zero, the magnetisation has a non-zero value (C). The magnetisation now increases in the direction in which the field is applied. When the field is sufficiently large applied in the opposite direction, the magnetisation passes through zero (D) and begins to increase in the direction in which the field is applied until the magnetisation reaches the saturation magnetisation value again (E). If the field is decreased again, the magnetisation follows the curve through F and G to the saturation magnetisation (B) again. If the field is continuously varied in this manner, the magnetisation will vary repeatedly along the closed loop B-C-D-E-F-G-B. This loop is called the hysteresis loop. Curve O-A-B is called the initial magnetisation curve. [1]



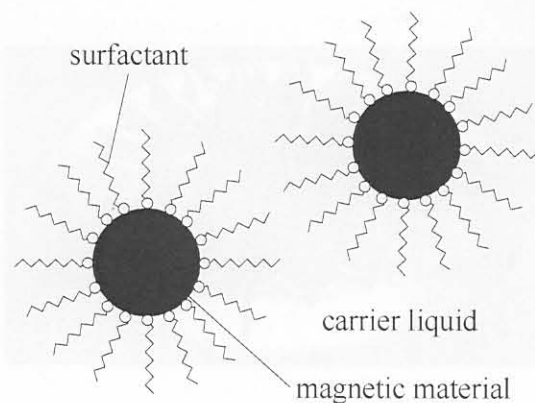
**Figure 2.2** Magnetisation curve showing hysteresis loop

## 2. DEFINITION AND DESCRIPTION OF FERROFLUID

### 2.1 Structure of magnetic liquids

The existence of intrinsic ferromagnetism in the liquid state is not known to exist. There is no mathematical reason for this state not to exist and it is therefore suggested that other factors which make its existence impossible or unlikely have not been considered. [6] Reports of ferromagnetism in the liquid state probably refer to liquids containing ferromagnetic particles. The ferromagnetic liquid or ferrofluid as discussed in this dissertation refers to a stable colloidal dispersion or suspension of single domain ferrimagnetic particles in a carrier liquid. [7] The suspension of particles is coated with a surfactant and is suspended in a carrier liquid. In this dissertation, magnetite ( $\text{Fe}_3\text{O}_4$ ) is the ferrimagnetic material coated with oleic acid as the surfactant and suspended in kerosene as the carrier liquid.

The components of a ferrofluid are indicated schematically in Figure 2.3.



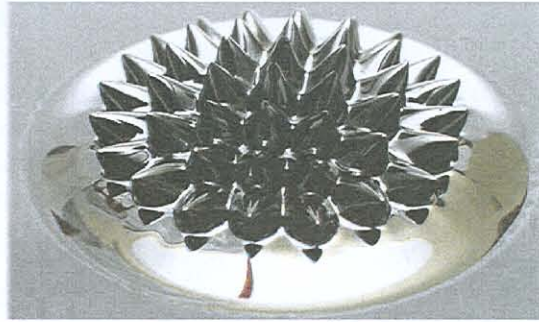
**Figure 2.3** Components of a ferrofluid

Magnetite consists of two interpenetrating sublattices of antiparallel spins. These moments are unequal and magnetite therefore has a net magnetic moment. Magnetite is an iron (II)-iron (III) ion mixed oxide possessing an inverse spinel structure. This means that the two cations of different valence ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) share octahedral sites. [8] This can have an important influence on the magnetic and electrical properties of the compound.

Other magnetic particles that are often used in ferrofluids are  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite), Fe, Co or Ni. [9] Carrier liquids could be, for example, different types of oils, fluorocarbons or even water. (Water-based fluids usually exhibit a lower saturation magnetisation as it is more difficult to stabilise a concentrated water-based fluid.)

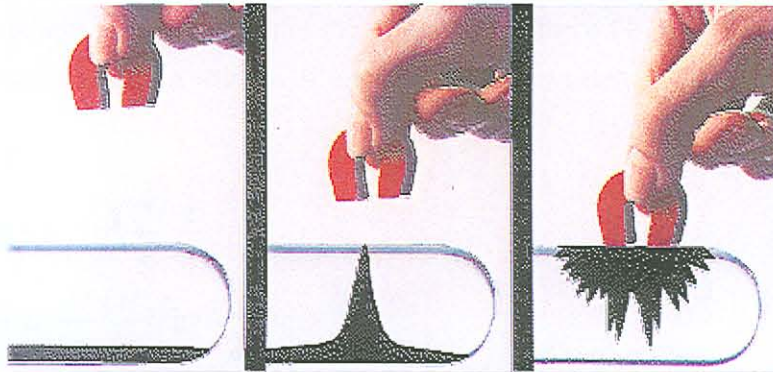
The magnetite particle size, which is important for stability, is approximately 10 nm. This particle size is small enough to ensure that the kinetic energy imparted to the particle by the motion of solvent molecules (Brownian motion) is sufficient to overcome both magnetic interactions and the effects of gravity thereby preventing agglomeration and settling. [7] This property is discussed further in Section 4. The stability of the ferrofluid also arises from the fact that each magnetite particle is coated with a monolayer of surfactant. This surfactant inhibits the agglomeration of particles which could occur as a result of Van der Waals interactions. This property is discussed further in Section 4 and in Chapter 6.

Each magnetite particle in the ferrofluid behaves like a spherical permanent magnet. In the absence of a magnetic field, the particles exhibit a random distribution of magnetic moments and the fluid has no net magnetisation. In an applied field, the moments experience a torque and align in the direction of the field. The critical volume for single domain particles for magnetite, is calculated to be approximately 50 nm, however, superparamagnetism is often only displayed at room temperature when the particle size is in the region of 10 nm. [3] Seeing as ferrofluid exhibits superparamagnetic properties, the fluid does not retain any residual magnetisation once the magnetic field is removed and the particles randomise quickly. The fluid shows no hysteresis in its magnetisation curve. [9] Figure 2.4 shows a magnetic fluid exposed to a magnetic field. The ferrofluid forms spikes as the fluid aligns itself with the external magnetic field gradient.



**Figure 2.4** Magnetic fluid exposed to a magnetic field [10]

Figure 2.5 shows a permanent magnet being brought close to a vessel containing ferrofluid and water. The ferrofluid is pulled towards the magnet.



**Figure 2.5** Effect of a magnetic field on a magnetic fluid exposed to the field [11]

## 2.2 The history of ferrofluids

The history of ferrofluids dates back to the 1700s when Gowan Knight in 1779 attempted to disperse iron filings in water. He obtained a suspension of small particles after several hours of mixing, but the fluid was not stable over long periods of time. In 1932, Bitter produced a suspension of magnetite of particle size  $10^3$  nm in water. Elmore (in 1938) as well as Craik and Griffiths (in 1958) produced suspensions containing smaller particles (20 nm) which closely resembled ferrofluids. Ultrastable ferrofluids containing ferrite particles in a non-conducting liquid carrier were first prepared by Papell at NASA in the 1960s. [6, 9]

Magnetic suspensions were first used to detect microscopic-magnetic patterns on ferromagnetic tools (through deposition of the fluid on the surface and evaporation of the carrier liquid) and later for the identification of flux change on magnetic tapes. NASA manufactured ferrofluids for investigations into its use as a pumpable rocket propellant in microgravity conditions (controlling

fuel flow under conditions of weightlessness). Ferrofluids can be manipulated to flow or remain immobilized via application of an external magnetic field. One of the most common applications is the use of ferrofluid in the voice coils of loudspeakers. In this case, the ferrofluid functions as a coolant and damping medium and keeps the voice coil concentric with the magnet. Ferrofluid has also been used to form airtight seals in rotating machinery. The performance of such a seal is impressive: the seal is able to withstand a differential pressure of greater than 4 MPa at 10 000 rpm or 100 000 rpm for a shorter period of time. Most conventional O-ring seals function at approximately 300 rpm. [6, 12]

The use of ferrofluid has been investigated as a variable density fluid for the separation of scrap metals. Magnetic paints have been developed and magnetisable liquids have found application in the fields of biology and medicine (e.g. enzyme fixing, immunoanalysis, cell separation of bacteria cultures and drug delivery to specific points in the body by application of a magnetic field). [9, 12]

### 2.3 Forces acting on a volume of ferrofluid and on a particle suspended in the ferrofluid

Two fundamental forces act on a given volume ( $V$ , in  $\text{m}^3$ ) of ferrofluid when it is placed in a magnetic field gradient. These forces are the gravitational force ( $\mathbf{F}_g$ ) and the magnetic traction force ( $\mathbf{F}_m$ ). The total force on a volume of ferrofluid can be written as: [13]

$$\begin{aligned}\mathbf{F} &= \mathbf{F}_g + \mathbf{F}_m \\ &= \rho_f V \mathbf{g} + \mu_0 M V \frac{\partial H}{\partial z} \frac{\mathbf{g}}{g} \\ &= (\rho_f + \mu_0 \frac{M}{g} \frac{\partial H}{\partial z}) V \mathbf{g}\end{aligned}\tag{2.1}$$

where  $\rho_f$  is the density of the ferrofluid ( $\text{kg}/\text{m}^3$ ),  $\mu_0$  is the magnetic permeability of a vacuum ( $4\pi \cdot 10^{-7} \text{ Tm}/\text{A}$ ),  $M$  is the magnetisation of the fluid ( $\text{A}/\text{m}$ ),  $H$  is the magnetic field strength ( $\text{A}/\text{m}$ ),  $\frac{\partial H}{\partial z}$  is the vertical magnetic field gradient ( $\text{A}/\text{m}^2$ ) and  $g$  is the gravitational acceleration ( $\text{m}/\text{s}^2$ ).

$$(1 \text{ T} = 1 \text{ N}/\text{A m})$$

The expression in parenthesis in eq. (2.1) can be viewed as the apparent density ( $\rho_a$ , in  $\text{kg}/\text{m}^3$ ) of the fluid if it is assumed that the magnetic field gradient is parallel to gravity and of the same sense. [13]

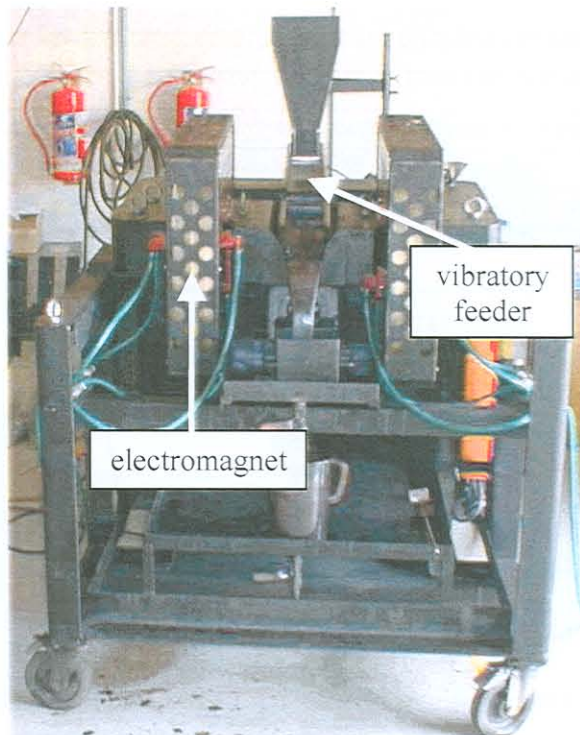
$$\rho_a = \rho_f + \frac{\mu_0 M}{g} \frac{\partial H}{\partial z}\tag{2.2}$$

When the field gradient makes an angle with gravity, eq. (2.2) can be written as: [13]

$$\rho_a = \rho_f + \frac{\mu_0 M}{g} \frac{\partial H}{\partial z} \cos\left(\mathbf{g} \frac{\partial \mathbf{H}}{\partial z}\right) \quad (2.3)$$

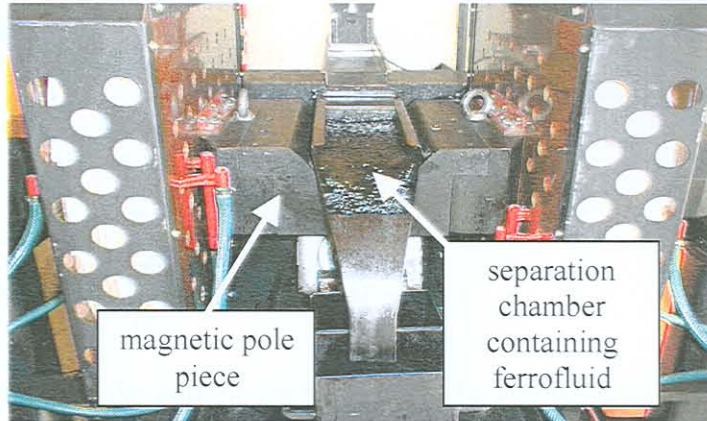
As can be seen from eq. 2.2, it is possible to control the apparent density of the magnetic fluid by changing the magnetic field gradient to which the fluid is exposed.

The production of ferrofluid has become increasingly important in the diamond industry as a result of developments in ferrohydrostatic separation (FHS). FHS making use of a ferrohydrostatic separator is used for the recovery of diamonds. The ferrohydrostatic separator consists of an electromagnet and a separation chamber in which a pool of ferrofluid is held. Material is introduced into the separation chamber via a vibratory feeder. A photograph of such a separator is shown in Figure 2.6 with a close-up of the separation chamber shown in Figure 2.7.



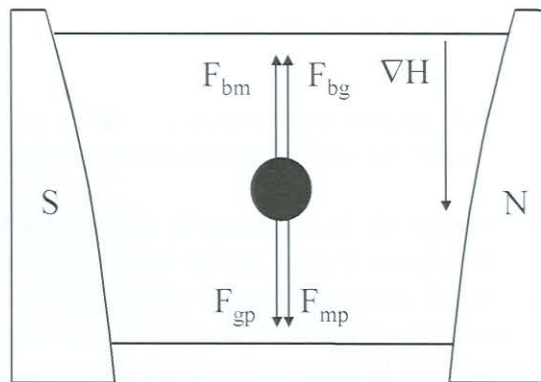
**Figure 2.6** Ferrohydrostatic separator





**Figure 2.7** Ferrohydrostatic separator chamber

A particle entering the ferrohydrostatic separator chamber is suspended in ferrofluid and is acted upon by the gravitational force ( $\mathbf{F}_{gp}$ ), the magnetic traction force ( $\mathbf{F}_{mp}$ ), a gravity-related buoyancy force ( $\mathbf{F}_{bg}$ ) and a magnetically induced buoyancy force ( $\mathbf{F}_{bm}$ ). This is shown schematically in Figure 2.8. [14]



**Figure 2.8** Forces acting on a particle in a separation chamber

These forces acting on the particle are given in eqs (2.4) to (2.7) with the net vertical force on the particle given in (2.8) (in cgs units). [13]

$$\mathbf{F}_{gp} = \rho_p V_p \mathbf{g} \quad (2.4)$$

$$\mathbf{F}_{mp} = V_p \chi_p H \frac{\partial \mathbf{H}}{\partial z} \quad (2.5)$$

$$\mathbf{F}_{bg} = \rho_f V_p \mathbf{g} \quad (2.6)$$

$$\mathbf{F}_{bm} = V_p M \frac{\partial \mathbf{H}}{\partial z} \quad (2.7)$$

$$\begin{aligned} \mathbf{F} &= \mathbf{F}_{gp} + \mathbf{F}_{mp} + \mathbf{F}_{bg} + \mathbf{F}_{bm} \\ &= \rho_p V_p \mathbf{g} + V_p \chi_p H \frac{\partial \mathbf{H}}{\partial z} - \rho_f V_p \mathbf{g} - V_p M \frac{\partial \mathbf{H}}{\partial z} \end{aligned} \quad (2.8)$$

where  $\rho_p$  is the density of the particle ( $\text{kg/m}^3$ ),  $V_p$  is the volume of the particle ( $\text{m}^3$ ) and  $\chi_p$  is the volume magnetic susceptibility of the particle.

When the resultant force acting on a particle is zero, eq. (2.8) reduces to eq. (2.9) to where  $\rho_{sp}$  is defined as the effective cut point density of separation.

$$\rho_{sp} = \rho_f + \frac{1}{g} \left[ M \frac{\partial \mathbf{H}}{\partial z} - \chi_p H \frac{\partial \mathbf{H}}{\partial z} \right] \quad (2.9)$$

For non-magnetic particles,  $\chi_p = 0$  and (2.9) reduces to (in SI units):

$$\rho_{sp} = \rho_f + \frac{\mu_0 M}{g} \frac{\partial H}{\partial z} \quad (2.10)$$

Eq. (2.10) is equivalent to eq. (2.2). It can therefore be seen that for non-magnetic particles, the density cut point is equal to the apparent density of the ferrofluid.

These equations describe the principle of operation of the ferrohydrostatic separators. If the sum of the forces exerted on a particle fed to the separation chamber is such that the sum of the magnetic buoyancy force and the gravity-related buoyancy force is greater than the gravitational and magnetic forces, the particle will float. (The particle will float when its density is lower than the apparent density of the magnetic fluid.) If the sum of the forces exerted on a particle is such that the sum of the magnetic buoyancy force and the gravity-related buoyancy force is less than the gravitational and magnetic forces, the particle will sink. (The particle will sink when its density is higher than the apparent density of the magnetic fluid.) [15]

## 1.2 Separation

### 3. MANUFACTURE OF FERROFLUIDS

The production of ferrofluid can be according to a variety of methods. The magnetic liquids can contain either a suspension of fine metal particles or fine particles of ferrites. The early magnetic fluids were unstable owing to their large particle size and inadequate surfactant stabilisation. [9]

Metal particles of diameter less than  $10^3$  nm have been produced by evaporation of the metal in the presence of an inert gas. Single domain ferromagnetic metal particles have also been

produced by electrodeposition techniques. This involves using the salts of the ferromagnetic metals dissolved in water or alcohol and the metal carrier liquid as the cathode. Papell and Rosensweig investigated the method of grinding ferrites in a ball mill and then suspending the particles in a carrier liquid. [6] One of the preferred methods for the economic production of magnetite-based ferrofluid is to obtain the magnetite colloids by precipitation of magnetite from a solution of ferric and ferrous ions using an excess of an alkali hydroxide.

The ferrofluid as referred to in this dissertation is produced in three main stages: oxide precipitation and magnetite formation, saponification of the surfactant and peptization of the coated particles.

### 3.1 Oxide precipitation and magnetite formation

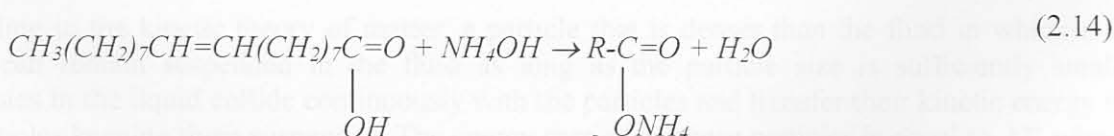
A solution of ferric and ferrous ions (from ferric chloride ( $\text{FeCl}_3$ ) and ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) respectively) is reacted with ammonium hydroxide solution ( $\text{NH}_4\text{OH}$ ) to form magnetite. An ammonium chloride and ammonium sulphate solution forms as a result of the precipitation reactions. A very simplified representation of this process is given by eqs (2.11) to (2.13). [12]



A volumetric packing fraction (volume of magnetite per volume of ferrofluid) of approximately 0.1 is commonly selected for ferrofluid production. According to the stoichiometry of the reactions (eqs (2.11) to (2.13)), a ratio of 2:1 of iron (II):iron (III) ions is required. However, to compensate for the oxidation of iron (II) to iron (III) ions during oxide formation, a ratio of 3:2 (iron (II):iron (III) ions) is used. The ammonium hydroxide should be added rapidly to the iron solution with good mixing to result in the precipitation of the required precursors for the formation of magnetite. If the alkali hydroxide is added slowly with poor mixing, it may lead to local pH gradients and the subsequent variation in hydrolysed species. An excess of ammonium hydroxide is used so that low values of pH are avoided at the end of the reaction and to provide ammonium hydroxide for the saponification reaction. [16]

### 3.2 Saponification

The excess ammonium hydroxide reacts with oleic acid to form an ammonium oleate soap.



### 3.3 Peptization

This ammonium oleate soap can bond to the magnetite particle through covalent bonding to iron ions on the surface. This results in a coated particle that still retains an affinity for water due to the polar nature of the oleate coating. The ammonium oleate coating is transformed upon heating into oleic acid and ammonia gas without becoming detached from the magnetite surface. The coated particles are now reasonably non-polar and would be more stable in a non-polar liquid like kerosene. A migration therefore takes place to the kerosene phase where they form a stable colloidal suspension.



## 4. STABILITY REQUIREMENTS FOR FERROFLUIDS AS DICTATED BY MAGNETITE PARTICLE SIZE

The mechanism by which the single domain particles are produced for use in magnetic liquids leads to particle size distributions which influence the magnetic properties of the liquid. A number of different factors come into play when determining the stability against settling of a magnetic liquid. For example, the particles must be sufficiently small so that Brownian motion opposes particle agglomeration. Particle interactions arising from London-type Van der Waals forces may cause particle agglomeration which can destroy the desirable characteristics of the fluid. [6] These and other factors are discussed in more detail in Sections 4.1 to 4.4.

### 4.1 Stability in a magnetic field gradient

Magnetic particles exposed to a magnetic field are attracted to the higher intensity regions of the magnetic field. The magnetic energy (see eq. (2.16)) is the work required to move a magnetised particle from a point in the fluid where the field strength is  $H$  to a point outside the field where the field is equal to 0 [7]. In eq. (2.16)  $M_s$  is the saturation magnetisation of magnetite (480000 A/m) and  $V$  is the volume. In eq. (2.16),  $\nabla H$ , the field gradient is equal to  $(0-H)$  or  $-H$  and therefore, the value for the field strength,  $H$  (in the range of 100 to 200 kA/m for ferrohydrostatic separators) can be used.

$$W = -\int_H^0 (\mu_0 M \frac{dH}{ds} V) ds \approx \mu_0 M_s H V \quad (2.16)$$

According to the kinetic theory of matter, a particle that is denser than the fluid in which it is found can remain suspended in the fluid as long as the particle size is sufficiently small. Molecules in the liquid collide continuously with the particles and transfer their kinetic energy to the particles keeping them suspended. The energy carried by these particles is equal to  $kT$  where  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K) and  $T$  is the temperature (K). For a particle in a

magnetic field to remain in suspension, the ratio of the thermal energy ( $kT$ ) to the magnetic energy must be greater than or equal to 1. [17]

$$\frac{\text{thermal energy}}{\text{magnetic energy}} = \frac{kT}{\mu_0 M_s H V} \geq 1 \quad (2.17)$$

If the volume of a sphere is substituted in eq. (2.17), the maximum particle size can be determined. [7]

$$\frac{kT}{\mu_0 M_s H} \frac{6}{\pi d^3} \geq 1 \quad (2.18)$$

$$\therefore d \leq (6kT / \pi \mu_0 M_s H)^{1/3}$$

At ambient temperature (298 K) the particle size is calculated as follows:

$$d \leq \left[ \frac{6(1.38 * 10^{-23} \text{ J / K})(298 \text{ K})}{\pi(4\pi * 10^{-7} \text{ Tm / A})(480000 \text{ A / m})(100000 \text{ A / m})} \right]^{1/3} * \frac{1 \text{ nm}}{1 * 10^{-9} \text{ m}} = 5.1 \text{ nm} \quad (2.19)$$

The particle size is found to be smaller than or equal to 5.1 nm. This value is used as a guideline for the particle size. Other effects in the environment in which the fluid is located will also influence the allowable particle size perhaps resulting in the allowable particle being larger. Such a small particle size may be detrimental to the fluid. It is thought that particles of too small a size may possess a lower saturation magnetisation and would thus be less effective for use in ferrohydrostatic separators. [18]

## 4.2 Stability in a gravitational field

The relative effect of the gravitational to the magnetic energy can be calculated to determine whether this force is significant or not.

$$\frac{\text{gravitational energy}}{\text{magnetic energy}} = \frac{\Delta \rho V g L}{\mu_0 M_s H V} = \frac{\Delta \rho g L}{\mu_0 M_s H} \quad (2.20)$$

Typical values for the ferrofluid are substituted into eq. (2.20) with  $L$  equal to 0.1 m (as the approximate height in a magnetic separation chamber), and the difference in density between the solid and liquid equal to  $4400 \text{ kg/m}^3$  (with magnetite density equal to  $5180 \text{ kg/m}^3$  and kerosene density equal to  $780 \text{ kg/m}^3$ ) to give:

$$\frac{\text{gravitational energy}}{\text{magnetic energy}} = \frac{(4400 \text{ kg / m}^3)(9.81 \text{ m / s}^2)(0.1 \text{ m})}{(4\pi * 10^{-7} \text{ Tm / A})(480000 \text{ A / m})(100000 \text{ A / m})} = 0.072 \quad (2.21)$$

Gravity is therefore less of a threat than the magnetic energy to the settling out of particles in ferrofluid. [7] This is further confirmed by checking what the size of a magnetite particle can be

to prevent settling in a gravitational field. For a particle in a gravitational field to remain in suspension, the ratio of the thermal energy ( $kT$ ) to the gravitational energy must be greater than or equal to 1:

$$\frac{\text{thermal energy}}{\text{gravitational energy}} = \frac{kT}{\Delta\rho VgL} \geq 1 \quad (2.22)$$

If the volume of a sphere is substituted in eq. (2.22), the maximum particle size can be determined.

$$\frac{kT}{\Delta\rho gL} \frac{6}{\pi d^3} \geq 1 \quad (2.23)$$

$$\therefore d \leq (6kT / \pi\Delta\rho gL)^{1/3}$$

At ambient temperature (298 K) the particle size is calculated as follows:

$$d \leq \left[ \frac{6(1.38 * 10^{-23} \text{ J / K})(298 \text{ K})(1 \text{ nm})}{\pi(5180 \text{ kg / m}^3)(9.81 \text{ m / s}^2)(0.1 \text{ m})} \right]^{1/3} * \frac{1 \text{ nm}}{1 * 10^{-9} \text{ m}} = 11.56 \text{ nm} \quad (2.24)$$

For the ratio of the thermal to the gravitational energy to be greater than or equal to one, the particle size should be smaller than or equal to 11.56 nm. The magnetic field gradient is of more of a threat to the settling out of particles than the gravitational energy as the gravitational energy allows for a larger particle size before settling will take place. The magnetic field gradient allowed for a maximum particle size of 5.1 nm.

### 4.3 Stability against magnetic agglomeration

Collisions between particles are frequent in a typical colloidal magnetic fluid as such a fluid contains in the order of  $10^{23}$  particles per cubic metre. A magnetic attractive force can exist between two particles that approach one another. Each particle will be treated as a magnetic dipole which generates a magnetic field. The magnetic-dipole magnetic-dipole interaction energy between the particles is given by eq. (2.25). [7]

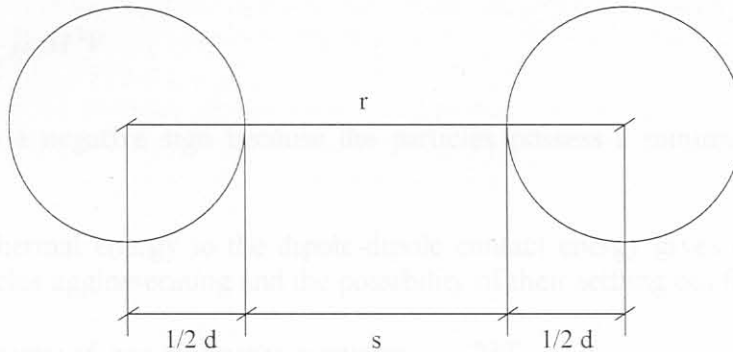
$$E_{dd} = \frac{1}{4\pi\mu_0} \left[ \frac{\mathbf{m}_1 \cdot \mathbf{m}_2}{r^3} - \frac{3}{r^5} (\mathbf{m}_1 \cdot \mathbf{r})(\mathbf{m}_2 \cdot \mathbf{r}) \right] \quad (2.25)$$

where  $\mathbf{m}$  is a dipole moment and  $r$  is the distance between the centres of two particles.

It is assumed that the particles are single domain, spherical and of the same dimensions. If the particles are below the Curie temperature, they will be saturated and it can be assumed that their moments are equal ( $\mathbf{m}_1 = \mathbf{m}_2 = \mathbf{m}$ ). When these moments are aligned,  $\mathbf{m}_1 = \mathbf{m}_2 = m^2$  (dot product of parallel vectors) and  $(\mathbf{m}_1 \cdot \mathbf{r})(\mathbf{m}_2 \cdot \mathbf{r}) = m^2 r^2$ . According to [7], the moment of the particle is given by:

$$m = \frac{\mu_o M \pi d^3}{6} \quad (2.26)$$

$s$  is the distance between the surfaces of the particles) and  $d$  is the diameter of a particle as shown in Figure 2.9.



**Figure 2.9** Representation of distances between particles

Eq (2.26) is substituted into (2.25) to give:

$$\begin{aligned} E_{dd} &= \frac{1}{4\pi\mu_o} \left[ \frac{m^2}{r^3} - \frac{3}{r^5} m^2 r^2 \right] \\ &= \frac{m^2}{4\pi\mu_o} \left[ -\frac{2}{r^3} \right] \\ &= \frac{\mu_o^2 M^2 \pi^2 d^6}{36(4\pi\mu_o)} \left[ -\frac{2}{r^3} \right] \\ &= -\frac{\mu_o M^2 \pi d^6}{72} \left[ \frac{1}{(s+d)^3} \right] \end{aligned} \quad (2.27)$$

When the particles are in contact i.e.  $s = 0$ , and the diameter of the sphere is replaced in terms of its volume, eq. (2.27) reduces to:

#### 4.4 London-type Van der Waals attractive forces

Particles in a fluid may be attracted to each other by London-type Van Der Waals attractive forces. Fluctuating orbital electrons in one particle may induce dipoles in another and result in Van der Waals forces arising between the particles. According to Fritz London, the energy required to overcome Van Der Waals forces between two particles is inversely proportional to the sixth power of the distance between their centres. For spheres of equal size the Van

$$\begin{aligned}
E_{dd} &= -\frac{\mu_o M^2 \pi d^6}{72} \left[ \frac{1}{(0+d)^3} \right] \\
&= -\frac{\mu_o M^2 \pi d^3}{72} \\
&= -\frac{\mu_o M^2 \pi \frac{6V}{\pi}}{72} \\
&= -\frac{1}{12} \mu_o M^2 V
\end{aligned} \tag{2.28}$$

This equation has a negative sign because the particles possess a minimum potential energy when they touch.

The ratio of the thermal energy to the dipole-dipole contact energy gives an indication of the likelihood of particles agglomerating and the possibility of their settling out from suspension.

$$\frac{\text{thermal energy of two magnetite particles}}{\text{dipole - dipole contact energy}} = \frac{2kT}{\frac{\mu_o M^2 V}{12}} \tag{2.29}$$

Solving for  $d$ , again with the substitution for the volume of a sphere, gives

$$\begin{aligned}
\frac{24kT}{\mu_o M^2} \frac{6}{\pi d^3} &\geq 1 \\
d &\leq (144kT / \pi \mu_o M^2)^{1/3}
\end{aligned} \tag{2.30}$$

For magnetite particles at room temperature:

$$d \leq \left[ \frac{144(1.38 * 10^{-3} \text{ J/k})(298 \text{ K})(1 \text{ nm})}{\pi(4\pi * 10^{-7} \text{ Tm/A})(480000 \text{ A/m})^2 (1 * 10^{-9} \text{ m})} \right]^{1/3} = 8.7 \text{ nm} \tag{2.31}$$

Particles of the order of 9 nm are therefore not likely to experience magnetically induced agglomeration and the subsequent settling of agglomerates is not expected from ferrofluids with particles of diameter of the order of 10 nm.

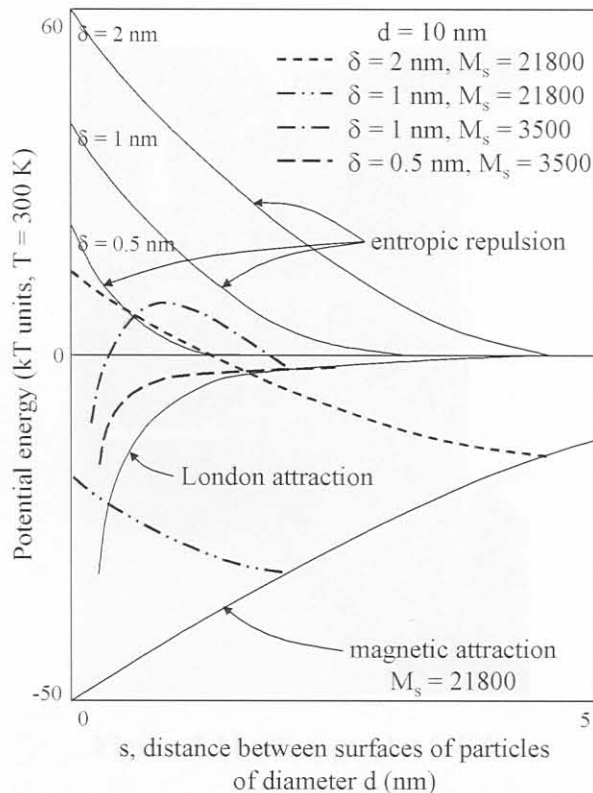
#### 4.4 London-type Van der Waals attractive forces

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Waals energy is equal to the thermal energy  $kT$ , when two spheres are separated by a distance approximately equal to their radius. To avoid agglomeration, the particles must be kept apart or, as is done in the case of ferrofluids, the particles are coated with a surfactant which then acts as an elastic cushion and provides some sort of “entropic repulsion”. [6, 7]

Figure 2.10 shows a plot of the potential energy versus distance between coated particles. [6] As can be seen from Figure 2.10, particles of any size will experience London-type interactions and have a large potential energy when in contact. A repulsive force is required to overcome these interactions. The entropic repulsion is introduced by coating the particles so that, when particles are close together, the repulsion due to steric hindrance overcomes the attractive interaction. For example, the resultant potential energy plots (from entropic repulsion, London attraction and magnetic attraction) for particles of diameter 10 nm are given for particles that are coated to a thickness ( $\delta$ ) of between 0.5 and 2 nm. Through coating of particles, the repulsion owing to steric hindrance of the surfactant long chain molecules is sufficient to overcome the attractive energy. [6]



**Figure 2.10** Example of a plot of potential energy versus distance between particles for coated particles

In conclusion then, to ensure a ferrofluid remains stable, the particles must be small enough so that thermal agitation can overcome the effect of the magnetic field gradient and gravitational

field and overcome magnetic agglomeration. In addition, a short range repulsive force in the form of coated particles must be present so that the London-type Van der Waals attractive repulsive interaction can be overcome.

## 5. FERROFLUID QUALIFICATION

A simple method to determine the quality of a ferrofluid that is produced, is by recording a magnetisation curve of the fluid and measuring its saturation magnetisation.

The saturation magnetisation is measured at room temperature using a Vibrating Sample Magnetometer (VSM). A small sample is vibrated in a magnetic field at a constant frequency. The sample is suspended between two coils. When a magnetic field is applied, oscillating magnetic flux lines from the sample induce an oscillating voltage in the coils which are in close proximity to the sample. Using this data, a hysteresis curve can be generated. A photograph of a VSM is shown in Figure 2.11. [19]



**Figure 2.11** Photograph of VSM

An approximation of the magnetite particle size can be determined indirectly from the saturation magnetisation measurements. There is evidence that the distribution of particle size  $f(y)$  where  $y$  is the reduced diameter  $\frac{D}{D_v}$  ( $D$  is the particle diameter  $D_v$  and is the median diameter of the distribution) is given by a log normal distribution.

$$f(y) = \frac{1}{y\sigma\sqrt{2\pi}} \exp\left(\frac{-(\ln(y))^2}{2\sigma^2}\right) \quad (2.32)$$

Ferrofluids usually contain a distribution of particle size and this modifies the magnetic properties of the system. In this case, the total magnetisation is given by the sum of the contribution from each particle size weighted using the distribution function. Chantrell *et al.* have derived formulae for the median diameter of the log normal distribution ( $D_v$ ) and the standard deviation ( $\sigma$ ) of the log normal distribution. [20]

$$D_v = \left[ \frac{18kT}{\pi I_s'} \sqrt{\frac{\chi_i}{3 \varepsilon I_s' H_o}} \right]^{\frac{1}{3}} \quad (2.33)$$

$$\sigma = \frac{\sqrt{\ln\left(\frac{3\chi_i}{\varepsilon I_s' H_o}\right)}}{3} \quad (2.34)$$

$I_s'$  (G) is the saturation magnetisation for the bulk magnetic particles,  $\varepsilon$  is the volumetric particle packing fraction ( $\varepsilon I_s'$  is the saturation magnetisation of the ferrofluid),  $\chi_i$  is the initial susceptibility and  $\frac{1}{H_o}$  (Oe<sup>-1</sup>) is the reciprocal field at  $I=0$ . [20] (1 Oe = 1000/4 $\pi$  A/m)

A spreadsheet is used to calculate  $D_v$  and  $\sigma$  using the constants  $k$ ,  $T$ ,  $I_s'$  and  $\pi$ .  $\chi_i$  and  $\varepsilon I_s'$  can be calculated from the parameters read off from the magnetisation curve (from the initial slope and the saturation magnetisation). The linear behaviour between  $H_1=7000$  Oe and  $H_2=H_{\max}$  has been determined.  $\frac{1}{H_o}$  is determined from inputting  $H_1$ ,  $H_2$  and the corresponding values of magnetisation. [20]

This method of particle size determination should be considered as an approximate one. The accuracy of the method has been tested against electron microscope measurements and results indicate that the  $D_v$  values calculated from the magnetisation curve are lower than the measured ones (17% for the petroleum based ferrofluids). The discrepancy could arise from the assumptions in terms of the validity of the log normal distribution of particle sizes. [20]