Magnetophoretic Focusing of Submicron Particles Dispersed in a Polymer-Stabilized Magnetic Fluid

by

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Submitted to the Department of Chemical Engineering
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Abstract

Magnetophoresis is the migration of particles upon the application of an inhomogeneous magnetic field. The overall goal of this work was to investigate the magnetophoretic focusing of non-magnetic particles suspended in magnetic fluids, which are colloidal suspensions of nano-sized magnetic particles. With the magnetic fluid as the solvent, dispersed non-magnetic particles behave as if they were diamagnetic due to the difference in magnetic susceptibility between them and the surrounding magnetic continuum. When an inhomogeneous magnetic force is applied, a magnetic force acts on the colloidal particles, the magnitude of which is linearly proportional to the volume of the particles, the difference in the magnetic susceptibilities of the particles and the surrounding magnetic fluid, and the gradient of the square of the magnetic field. One potential application for this phenomenon is in the separation of submicron biological particles such as viruses, cell fragments, DNA and inclusion bodies.

Magnetic fluids have several characteristics that make them attractive for use in separation. For example, they can be tailored to the separation needs at hand, manipulated using external magnetic fields, and completely removed through magnetic filtration. Since the scope of the work was to use physical forces for attaining the desired separations, the magnetic particles were designed and synthesized without any chemical affinity to the solute to be separated. They were prepared by coprecipitation of iron (II) and (III) ions to form magnetite, which is coated by a comb copolymer that serves two purposes: to limit growth of magnetite to about 10 nm and to stabilize the particles against aggregation. The polymer was prepared by a reaction between amine-terminated polyethylene oxide and polyacrylic acid. Characterization of the particles was done experimentally and theoretically. Dynamic light scattering was used to measure the diffusion coefficient and the hydrodynamic diameter of the particles, while transmission electron microscopy was used to measure the diameter of the magnetic core.

Since the structure of the magnetic fluid is an important parameter in its application in any magnetophoretic separation, we characterized the aggregation behavior
of the magnetic fluids using different theoretical techniques. Monte Carlo simulation was used to understand the clustering in sterically-stabilized magnetic fluids. Simulation results agree favorably with the scattering experiments with regards to the cluster sizes and fractal dimensions. The characterization of a closely related system, a charge stabilized magnetic fluid, was also performed to explain the finite cluster size observed experimentally.

Next, we investigated magnetophoretic focusing in the synthesized magnetic fluid, as a means to separate submicron colloidal particles based on size. The magnetophoresis concepts were validated experimentally by monitoring the dynamic evolution of the concentration profile of fluorescently-tagged polymer beads of various sizes in a magnetic fluid upon the application of an inhomogeneous magnetic field. Polymer beads larger than 0.2 μm focused at the point of zero force, and the effect of the magnetic field on the particles was correlated with their size. A transport model was developed to provide a priori predictions of the dynamic concentration profile, which were in good agreement with the experimental results. This model was based on the Stefan-Maxwell multicomponent diffusion approach and it included the effect of the magnetophoretic forces as well as the non-ideal component of the chemical potential due to the electrostatic repulsion, which were shown to be the dominant terms for the size range of interest. The model was used to study the effect of the concentration of the polymer beads and the magnetic fluid on the concentration profile and the bead mobility. Results indicate that there is a potential for using the dynamic response of different size particles to attain their separation. The model was used to design and a simple device that showed the feasibility of separating 0.2 μm particles from 0.51 μm particles based on the ideas developed in this thesis.

Thesis Supervisor: T. Alan Hatton
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Contents

1 Introduction and Overview of Magnetic Separations 19
   1.1 Magnetic separation ..................................... 19
   1.1.1 Magnetic and nonmagnetic particles .................. 20
   1.1.2 Forces acting on a particle .......................... 20
   1.1.3 Types of magnetic separation ......................... 22
   1.2 Examples of magnetic separation devices ............... 23
      1.2.1 High gradient magnetic separation .................. 23
      1.2.2 Separation in magnetic fluids ...................... 24
      1.2.3 Nanoparticles magnetic separation ................. 26
   1.3 Examples of applications .................................. 26
      1.3.1 Biological applications ............................ 27
      1.3.2 Water treatment ................................ 27
      1.3.3 Mineral separations ................................ 28
      1.3.4 Coal treatment ................................... 28
      1.3.5 Heavy metals removal .............................. 29
  1.4 Summary and conclusions .................................. 29

2 Synthesis and Characterization of a Polymer-Based Magnetic Fluid 39
   2.1 Overview of magnetic fluids ............................... 40
      2.1.1 Synthesis ......................................... 40
      2.1.2 Applications .................................... 41
   2.2 Experimental ............................................ 41
      2.2.1 Desired characteristics of a magnetic fluid .... 41
2.2.2 Synthesis of PAA-PEO graft copolymer           42
2.2.3 Synthesis of a polymer-based magnetic fluid      44
2.2.4 Characterization of the magnetic fluid            44
2.3 Results                                            46
2.4 Summary                                            48

3 Monte Carlo Simulation of Sterically-Stabilized Magnetic Fluids  55
3.1 Procedure                                          56
3.2 Force field description                           59
3.3 Simulation parameters                             65
3.4 Structural properties                             66
3.5 Equilibration                                     67
3.6 Results and discussion                            68
    3.6.1 Importance of autocorrelation function       69
    3.6.2 Validity of algorithm                        70
    3.6.3 Cluster size distribution                    71
    3.6.4 Fractal dimension                            72
    3.6.5 Importance of van der Waals interactions     77
    3.6.6 Effect of magnetic field                     78
    3.6.7 Cluster net magnetic moment                  80
    3.6.8 Structure factor and comparison with experiments  81
3.7 Conclusions                                       82
3.8 Appendix: The rejection method                    83

4 On the Finite Cluster Sizes of Aqueous-Based Magnetic Fluids  91
4.1 Equivalent-sphere cluster model                    93
4.2 Full particle-cluster interaction model            96
4.3 Cluster configurations                             98
4.4 Results and discussion                             100
4.5 Conclusion                                         103
5 Magnetophoresis in Magnetic Fluids

5.1 Fluorescent measurements experiments ........................................ 109
  5.1.1 Materials ................................................................. 109
  5.1.2 Experimental ............................................................ 110
  5.1.3 Data gathering and reduction .......................................... 114
  5.1.4 Results and discussion ................................................ 116
  5.1.5 Effect of magnetic field .............................................. 120
  5.1.6 Effect of particle size ................................................. 123
  5.1.7 Effect of magnetic fluid concentration ............................. 124
  5.1.8 Effect of concentration of polymer beads ......................... 125
  5.1.9 Effect of small changes in the magnet separation distance .... 127

5.2 Continuous separation ....................................................... 129
  5.2.1 Results and discussion ................................................ 131

5.3 Summary and conclusions .................................................... 132

6 Magnetophoresis Modelling .................................................... 137

6.1 Conservation equations ...................................................... 137

6.2 The chemical potential ...................................................... 141
  6.2.1 The electrostatic repulsion ........................................... 141

6.3 Model nondimensionalization .............................................. 144

6.4 Model parameters ........................................................... 145

6.5 Results and discussion ..................................................... 147
  6.5.1 Results of modelling of the precision magnet translation system 149
  6.5.2 Comparison with experiment .......................................... 152
  6.5.3 Parametric study ....................................................... 154
  6.5.4 Model utilization ....................................................... 156
  6.5.5 Evolution of the flux terms .......................................... 157
  6.5.6 Short time behavior ................................................... 161
  6.5.7 Long time simulation results ........................................ 162
  6.5.8 Steady state solution ................................................ 165
6.5.9  Peak relaxation ........................................ 168
6.6  Summary and conclusions ................................. 172
6.7  Appendix: Effect of migration of particles on the pressure gradient . 174

7  Summary, Conclusions and Future Directions ................. 179
7.1  Summary ................................................. 179
7.2  Conclusions and future directions ......................... 181
List of Figures

1-1 The two cycles, separation and regeneration, of high gradient magnetic separation taken from [3] .......................... 25

2-1 Schematic representation of a magnetic fluid on three length scales. 40
2-2 Chemical structure of the polymer used to stabilize the magnetic particles 43
2-3 Results of dynamic light scattering on a free polymer 46
2-4 Results of dynamic light scattering on a dilute magnetic fluid 47
2-5 A representative photograph taken by transmission electron microscopy. This image was provided by Geoffrey Moeser. 47
2-6 Magnetization curves for the magnetic fluids prepared at different temperatures measured by SQUID 48

3-1 Dimensions of the particles and the force field model 59
3-2 Potential energy profiles showing magnetic and van der Waals attraction and entropic repulsion 64
3-3 The well depth for both magnetite and cobalt as a function of the shell thickness. Particle size was 10 nm. 65
3-4 Correlation length and aggregation number of a cluster 66
3-5 Some of the clusters formed during simulation 68
3-6 Decay of position autocorrelation function 69
3-7 Incorporation of a small percentage of cluster moves results in a significant decrease in the number of MC steps needed for decay of the position autocorrelation function 70
3-8 Comparison between the two algorithms showing the stability of our algorithm to the different percent cluster moves. 71
3-9 Size distribution within a 1% magnetic fluid 72
3-10 End-to-end distance within a 1% magnetic fluid 73
3-11 An example of the calculations of the fractal dimension from the slope of log N versus normalized D 73
3-12 Effect of magnetic field on the net magnetic moment of magnetite clusters 74
3-13 Fractal dimension as a function of particle size for random clusters 75
3-14 Effect of magnetic field on the net magnetic moment of cobalt clusters 76
3-15 Effect of Hamaker constant on aggregation number and fractal dimension. 77
3-16 Configuration of magnetite and cobalt in the presence of a magnetic field 78
3-17 The effect of the magnetic field on the radial distribution function 79
3-18 Effect of surfactant thickness on aggregation number and fractal dimension of cobalt 79
3-19 Comparison of the structure factors determined by fitting the SANS data and simulation 81
3-20 A square is constructed around the cutoff circle and distances are only calculated for the particles inside the square 84
3-21 Difference in computational time between using the conventional method for calculating the pair potential energy and the rejection method 85
4-1 Schematic drawing of the cluster representation in the simple model 93
4-2 Estimates of particle-cluster interaction energies as a function of separation distance, with $R_p = 5 \times 10^{-9}$ m, $\kappa = 7.36 \times 10^8$ m$^{-1}$ (n = 0.05 M), $C_i = 2.27 \times 10^{18}$ m$^{-2}$, $A_p = 1 \times 10^{-19}$ J 95
4-3 Relative growth rate as a function of relative cluster size 95
4-4 Cluster configurations used in this study 97
4-5 Example of a 3-dimensional mesh created for configuration C. The approaching particle is at the top and the chain is at the center of the figure. 99
4-6 Comparison between energy profile for configuration C calculated using the pairwise additivity assumption □ and the numerical solution of Poisson-Boltzmann equation '◊' ........................................ 101

4-7 Total energy profiles for configurations A '☐', B '□' and C '◊' .... 101

4-8 Total energy profiles for configurations D '□' and E '◊' .......... 102

5-1 Illustration showing the concept of magnetophoresis ............... 108

5-2 Schematic diagram of the experimental setup ......................... 111

5-3 A digital photograph of the magnetic fluid cell (labelled as the precision controlled system), the camera and the emission filter wheel. ........ 112

5-4 Schematic diagram of the magnetic fluid cell ...................... 112

5-5 Photographic image of the precisely-controlled setup ............. 113

5-6 Magnetic field along the center line of the magnetic fluid cell for configurations 1 and 2 ......................................................... 114

5-7 The gradient of the square of the magnetic field strength along the center line of the magnetic fluid cell for the simple and the precision-controlled configuration ............................................. 115

5-8 Series of picture showing the buildup of the 840 nm particles at the focusing point 8 mm away from the center of the magnet. X and Y axis are in mm. ......................................................... 117

5-9 Evolution of the concentration profile of the polymer beads ....... 119

5-10 Evolution of the concentration profile of the magnetic particles 120

5-11 The evolution of the concentration profile for a 0.4% polymer beads in a mixture with 1% magnetic fluid when placed between the magnets as per the precisely-controlled configuration .................... 121

5-12 An enlarged magnetic force plot in the vicinity of the point of zero force showing three distinct regions ............................... 122

5-13 The dynamic evolution of the concentration profile for 240, 510 and 840 nm particles at three different times .......................... 123
5-14 Concentration profile for the 510 nm particle after 1780 s for 0.5%, 1%
and 1.5% magnetic fluid concentration ........................................ 125
5-15 Plot showing the effect of the volume fraction of the magnetic particles
on the ratio shown in Equation 5.9 and the experimental values for the
normalized concentration at three different volume fractions ............ 126
5-16 Concentration profile for the 510 nm particles after 2000 s at 0.2%,
0.4% and 0.6% .................................................................................. 126
5-17 Concentration profile for 510 nm particles in 1.5% magnetic fluid after
100 minutes when the magnets were moved in small steps ............... 128
5-18 Schematic diagram of a simple separation device ............................ 129
5-19 A photographic image of the simple separation device ..................... 130
5-20 Separation factors in the rich and lean stream for four different size
particles .................................................................................................. 131

6-1 Schematic diagram for the calculations of the excess potential energy
due to the electrostatic repulsion ............................................................. 143
6-2 The strength of the magnetic field and the magnetic force along the
center line of the magnetic fluid cell ....................................................... 146
6-3 The numerical results of the dynamic evolution of the magnetic parti-
cles concentration profile ..................................................................... 147
6-4 The numerical results of the dynamic evolution of the polymer beads
concentration profile ............................................................................ 148
6-5 The gradient of the square of the magnetic field strength along the
center line of the magnetic fluid cell for the simple and the precision-
controlled configuration ....................................................................... 150
6-6 Model prediction for the evolution of the polymer beads under the
high-magnetic field case ........................................................................ 151
6-7 The numerical results of the dynamic evolution of the polymer beads
concentration profile ............................................................................ 153
6-8 Effect of particle size on the maximum concentration at the focusing point and the maximum flux ................. 154
6-9 Effect of magnetic fluid concentration on the maximum concentration at the focusing point and the maximum flux .......... 155
6-10 Effect of particle size on the maximum concentration at the focusing point for different magnetic fluid concentration .......... 156
6-11 Evolution of concentration profile after introducing an equal concentration of 510 and 840 nm particles at the magnet. Time values are in minutes .......... 157
6-12 The dimensionless flux terms for the 840 nm particles at different times 158
6-13 The dimensionless flux terms for the magnetic particles at different times 160
6-14 Three dimensional representation of the model predictions for the dynamic evolution of the concentration profile .......... 162
6-15 Dimensionless concentration profile at different times for the long time simulation .......... 163
6-16 Maximum concentration versus log time .......... 164
6-17 Three dimensional representation of the dimensionless flux versus distance and time .......... 164
6-18 Dimensionless flux profile at different times .......... 165
6-19 The dimensionless variable $\Psi_m$ versus distance .......... 167
6-20 Steady state solution for $\Theta_3$ versus distance .......... 167
6-21 Concentration-distance curves for the diffusion of the particles starting from a square peak. Numbers on curves are time in seconds .......... 169
6-22 Adjustment for the initial peak .......... 171
6-23 Maximum concentration decay with time for the full model 'o' and the relaxation model 'x' .......... 171
List of Tables

1.1 References for different applications of magnetic separation .......... 27

2.1 Diameter measured by TEM for magnetic particles prepared at different temperatures ................................................. 48

4.1 Parameters used in calculations for the model system ................. 98

5.1 Size, color and excitation and emission wavelengths for the fluorescent particles used in this study ........................................ 110

6.1 Values of the different parameters used in the magnetophoresis model for the 840 nm particles ........................................ 146
Chapter 1

Introduction and Overview of Magnetic Separations

The overall goal of this thesis was to investigate the magnetophoretic focusing of non-magnetic particles suspended in a magnetic fluid. One potential application for this phenomenon is in the separation of submicron-sized biological particles such as viruses, cell fragments, DNA and inclusion bodies. This goal was accomplished through the use of novel magnetic fluids, synthesized and characterized specially for this purpose. This chapter outlines the principles, process applications, merits and limitations of magnetic separation.

1.1 Magnetic separation

Magnetic separation has historically served the mineral, water treatment and other industries. Other conventional applications include the removal of tramp metal to protect machinery and the extraction of ferrous contamination from industrial raw materials. It has been introduced to the bioseparation domain in the late seventies to separate bioproducts through magnetic carrier or magnetic tagging technology, both involving the attachment of magnetic particles or beads to the desired product to be purified. Currently, with the advances and improvements in superconducting magnetic technology and the design of more efficient electromagnets, the range of
applications of magnetic separation is expected to expand to include different additional techniques. Within the last decade, magnetic separation has undergone major technological advances: an increase in magnetic strength and the use of finite-element analysis (FEA) in designing magnetic separators.

1.1.1 Magnetic and nonmagnetic particles

When subjected to a magnetic field, particles can be classified as ferromagnetic, if they have a very high magnetic susceptibility, paramagnetic, if they have a low magnetic susceptibility and diamagnetic, if they have a negative magnetic susceptibility and can be considered nonmagnetic for all practical reasons. Ferromagnetic and paramagnetic materials will become magnetized when placed in a magnetic field according to the following equation

$$M = m \chi H$$  \hspace{1cm} (1.1)

where $M$ is the induced magnetization of the particle, $m$ is its mass, $\chi$ is its magnetic susceptibility, and $H$ is the magnetic field intensity.

A high magnetic field alone, although necessary for separating paramagnetic particles, is not sufficient; there must also be a high field gradient. When a uniform magnetic field is applied to a magnetized particle, the forces acting on the two poles of the particle will be equal and opposite. The forces therefore cancel each other, and the resulting net force is zero. Only if the applied field differs in intensity at the two sides of the particles will a net magnetic force act on the particle. In other words, the applied field must have a gradient, a spatial variation that is appreciable in terms of the dimensions of the magnetized particle.

1.1.2 Forces acting on a particle

For a particle flowing in an inhomogeneous magnetic field, several forces can be important in the analysis of the particle motion. The relative importance of these forces depends primarily on the type of magnetic separation and the size of the particle. The magnetic force $F_m$ on a paramagnetic particle of volume $V_p$ in a magnetic field
is given by

\[ F_m = \frac{\Delta \chi V_p}{\mu_o} (\mathbf{B} \cdot \nabla) \mathbf{B} \quad (1.2) \]

where \( \Delta \chi \) is the difference between the magnetic susceptibility of the particle and the surrounding medium, \( V_p \) is the volume of the particle, \( \mu_o \) is the permeability of free space, and \( \mathbf{B} \) is the magnetic flux density.

Other forces that act on the particle are the viscous drag force of the surrounding fluid medium, the gravity force, the inertial forces on the particle, the thermal diffusion and interparticle interactions forces.

For a stationary medium, the viscous drag force, \( \mathbf{F}_d \), can be approximated by Stokes equation, which assumes that the particles are spheres.

\[ \mathbf{F}_d = -3\pi \eta d \mathbf{v}, \quad (1.3) \]

where \( \eta \) is the fluid viscosity, \( d \) is the particle diameter, and \( \mathbf{v} \) is the terminal velocity of the particles.

The gravity force, \( \mathbf{F}_g \), which also includes the buoyancy force and is directed vertically downwards, is given by the following equation

\[ \mathbf{F}_g = (m - \rho_f V_p) \mathbf{g} \quad (1.4) \]

where \( m \) is the mass of the particle, \( \rho_f \) is the density of the fluid, and \( \mathbf{g} \) is the acceleration due to gravity. The inertial forces are in the direction of motion and are given by the simple relationship

\[ \mathbf{F}_i = m \mathbf{a} \quad (1.5) \]

where \( \mathbf{a} \) is the particle acceleration.

Interparticle forces (See Chapter 3) include the magnetic dipole-dipole interactions [1] given by,

\[ u_{ij} = k T \lambda \frac{d^3}{r_{ij}^3} [n_i \cdot n_j - 3 (n_i \cdot \hat{r}_{ij}) (n_j \cdot \hat{r}_{ij})] \quad (1.6) \]
where $k$ is the Boltzmann constant, $T$ is the temperature, $r_{ij}$ is the particle-to-particle distance, $\hat{r}_{ij}$ is the corresponding unit vector, and $\mathbf{n}_i$ is the unit vector of the magnetic dipole of particle $i$. In addition, $\lambda$ is a dimensionless parameter representing the strength of magnetic dipole-dipole interactions relative to the thermal energy, as given by Equation 3.7 on page 60.

The van der Waal's interaction for particles of equal size is given by,

$$u_{vdw} = -\frac{A_{eff}}{12} H \left( \frac{s}{d} \right) \quad (1.7)$$

$$H(x) = \frac{1}{x^2 + 2x} + \frac{1}{x^2 + 2x + 1} + 2 \ln \frac{x^2 + 2x}{x^2 + 2x + 1} \quad (1.8)$$

where $A_{eff}$, the effective Hamaker constant, is a quantity related to an optical dispersion frequency, the numerical magnitude of which is usually known only approximately, $H(x)$ is a mathematical function with one variable $x$, which is $s/d$ in the case of Equation 1.7, and $s$ is the surface-to-surface distance.

Fortunately, not all of these forces and processes are significant in any one instance. Gravity and buoyancy forces are often neglected for particle sizes less than 100 $\mu$m. For particle sizes greater than 100 $\mu$m, thermal diffusion is small compared to the other types of forces. In this range, the dominating forces are the magnetic force, the drag force and, to a small extent, the magnetic dipole-dipole interactions.

1.1.3 Types of magnetic separation

Based on Moffat et al.'s [2] classification of the different types of magnetic separation, we can divide the technology into the following categories.

**Magnetocollection** A magnetic force attracts a magnetically susceptible particle towards a collection element. This is further divided into two types; low gradient magnetic separation that separates particles with high magnetic susceptibility and high gradient magnetic separation (HGMS) that separates particles with low magnetic susceptibility.

**Magnetoflocculation** The particles are aggregated by the action of the magnetic
field. This results in easier separation through settling or filtration. Non-magnetic materials can also be separated through entrainment in the magnetic aggregates.

**Magnetosedimentation** Magnets are placed at the bottom of the vessel to accelerate the sedimentation of the magnetic particles.

**Magnetoflotation** The ability to vary the densities of magnetic fluids by the application of the magnetic field is used to separate particles with different densities by flotation in the magnetic fluids.

**Magnetotransport** The magnetic field used to transport a bed of magnetically susceptible particles.

**Magnetic Carrier Technology** Magnetic carrier particles are attached to the desired particles through specific interactions and the conventional magnetocollection methods are used for separation.

**Magnetic Tagging Technology (Magnetophoresis)** Magnetic tags are generally used for the separation of colloidal and biological species larger than those associated with magnetic carrier technology but smaller than those associated with conventional separation operations. Tags can take the form of ions or fine magnetic particles that coat or cluster around non-magnetic species to allow them to be manipulated using an external magnetic field.

### 1.2 Examples of magnetic separation devices

In this section, we introduce three different types of magnetic separation devices that are relevant to this work.

#### 1.2.1 High gradient magnetic separation

High gradient magnetic separation (HGMS) is widely used separation method in many areas. For example, it is used on a large scale to remove impurities from kaolin clay
in the ceramic industries and to remove magnetic particulates from stack gases in the iron and steel industries. It is also used commercially for wastewater treatment. Gerber and Birss [3] describe the basic HGMS system as follows.

The system consists of a non-magnetic (stainless steel) canister, filled with a matrix formed of compressed mats of thin magnetic fibers. The canister, through which either the suspension of mixed magnetic and non-magnetic particles or the flushing solution is passed, is placed in an iron-bound solenoid capable of generating high flux densities. The thin fibers of the matrix dehomogenize the background magnetic field to give a high value of magnetic force density in their immediate surroundings. When the magnetic field is on, the suspension of particles to be separated flows through the matrix, the magnetic particles are attracted to and captured on the fibers and the purified suspension leaves the system. At intervals, as the retention capacity of the matrix is reached, the feed is halted, the magnetic field is switched off and the magnetic particles are flushed out of the separator. Then the cycle is repeated as shown in Figure 1-1.

One of the drawbacks of such a system is the high power consumption of the electromagnets. Research is ongoing to overcome this problem by using superconducting solenoids [4, 5] or a switchable system of permanent magnets [6]. The advances in superconducting technology are expected to render HGMS an economic alternative for many current separation techniques. The first large superconducting separator has been operating successfully in the USA since May. There also appears to be an opportunity for retrofitting superconducting coils into conventional high-gradient separators [7].

1.2.2 Separation in magnetic fluids

It is possible to use magnetic fluids as a separation medium due to the ability to create antigravity magnetic levitation forces within them. Hence, materials can be
Figure 1-1: The two cycles, separation and regeneration, of high gradient magnetic separation taken from [3]

differentially separated according to their density [8]. One can distinguish three fields of application of such a separation:

1. The fractional analysis of materials in studying composition of fractions,

2. The quality control of particles by density

3. The separating of scrap into products into distinguishable metals

1.2.3 Nanoparticles magnetic separation

Although industrial application of nanoparticles magnetic separation is not established yet, some research has been done in this area. The basic difference between the conventional HGMS and HGMS for separtion nanoparticles (nano-HGMS) is that the thermal diffusion effects are comparable in magnitude to the other forces in the latter (see Section 1.1.2.) Fletcher [14], in a comprehensive review, classified the theoretical studies into different categories. His division is based on the following parameters:

- Flowing or stationary carrier medium
- One or two dimensional analysis
- The effect of interparticle interactions

Progress is still needed to complete the theoretical work on the HGMS of nano-sized particles. More importantly, there is a dearth of experimental data relating to fine particle HGMS. Such a deficiency renders the theory speculative in its details. Among the few reported experimental works are Takayasu et al. [15], van Kleef [16], Kramer et al. [17] and Kelland [18].

Ebner et al. [19] modelled nanolevel HGMS to study its feasibility and limitation. They propose a new separation concept in which large (0.1-1 μm) immobile spheres are used as adsorbent. The adsorbate is colloidal sized (20-80 nm) paramagnetic particles. Their results show the importance of the external field strength, the sizes of the adsorbent and the adsorbate particles, and their magnetic properties.

1.3 Examples of applications

Magnetic separation has found promising applications in many areas. Table 1.1 lists some examples of the applications of magnetic separation. There is no review that covers the whole field of magnetic separation. Different studies have been published that review the applications in specific areas as mentioned below.
Table 1.1: References for different applications of magnetic separation

<table>
<thead>
<tr>
<th>Separation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reviews</td>
<td>[7, 14, 20–24]</td>
</tr>
<tr>
<td>Water Treatment</td>
<td>[25–36]</td>
</tr>
<tr>
<td>Environmental Applications</td>
<td>[2, 33]</td>
</tr>
<tr>
<td>Biological Applications</td>
<td>See [24]</td>
</tr>
<tr>
<td>Minerals</td>
<td>[6, 7, 37–67]</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>[68–72]</td>
</tr>
</tbody>
</table>

### 1.3.1 Biological applications

Within the last twenty years, magnetic separation has taken an increasingly important role in the separation of the biological particles. Magnetic sorbents, carriers and modifiers have been used in many biotechnological processes. They have been used to immobilize enzymes and other biologically active compounds so that these compounds can be easily removed from the system or that they can be targeted to the desired place by using an external magnetic field. The same effect can be established through chemical modification of enzymes by conjugating a magnetite-polyethylene glycol complex to it.

Magnetic particles have also been used for the isolation of biological compounds by attaching an affinity ligand to the magnetic particles before mixing them with the desired solute. Also, they have been used to detect biological molecules by covalently immobilizing specific antibodies or antigens on the magnetic particles and using them in magnetic immunoassays. A recent review of the applications of magnetic separations in biotechnology is given by Safarik and Safarikova [24].

### 1.3.2 Water treatment

The massive volume of water that must be handled rapidly poses a continuous need for improvements to current water treatment methods. Magnetic separation of contaminants from aqueous solution has provided a viable alternative to filtration and sedimentation technology. Most pollutants in natural water systems are nonmagnetic, but it is possible to cause some contaminants to associate with a magnetic seeding
material. The water would pass through a high-gradient magnetic filter to remove the contaminants adhering to the magnetic seeding material. The seeding material that has been most often used is magnetite because of its large magnetic moment. A strong coupling between the seed and the contaminant is important so that the coagulant can withstand the shearing forces present in the flow stream. It is not necessary to develop large flocs, since small magnetic particles with adhering impurities will be held in the magnet matrix. Flocculation times on the order of 3 to 5 minutes are typical compared with 10 to 20 minutes for conventional physical-chemical treatment [25]. This method was first developed at MIT [26, 27] in 1973 and it has been used commercially since.

Magnetic separation has also been used successfully to remove phosphate from water [28, 29, 73], and iron fines that accumulate in the cold rolling coolant of steel sheets [74].

1.3.3 Mineral separations

Magnetic particles are often present in the slurries of mineral upgrading applications, which yields magnetic separation an important beneficiation step. Mineral beneficiation is perhaps the largest area in which magnetic separation is applied. A full comprehensive review is beyond the scope of this thesis. Some good review articles [7, 38] are available in the literature. In Table 1.1, we list the major publications in this field.

1.3.4 Coal treatment

The useful constituents of coal are diamagnetic while a good proportion of the undesirable sulfur is in paramagnetic iron compounds. These paramagnetic components can be held in the HGMS and thus separated. Other components in the coal, normally ending up as ash, are also paramagnetic and are removed together with the Fe-S. Analysis of coal beds throughout the U.S. indicates that a large proportion of the coals contain 1 to 4% total sulfur of which about 75% is paramagnetic compounds.
and is therefore removable by magnetic separation [20]. The organically bound sulfur can not be removed by magnetic separation.

1.3.5 Heavy metals removal

One of the new promising magnetic separation techniques used for heavy metals is the Magnetically Assisted Chemical Separation (MACS) introduced by researchers at Argonne National Laboratory [75–77]. Magnetic carrier microparticles are used to separate radionuclides and metals from waste at nuclear and industrial sites. These particles are composed of rare earths or ferromagnetic materials embedded in a polymer material. The surface of the particles is coated with selective chemical extractants that have an affinity for the target elements. The microparticles are poured, as a slurry or aqueous stream, into a treatment tank containing a contaminated solution, where they grab the contaminants. These particles can be separated later using magnetic separation techniques. Particles have to be coated by specific chemicals to meet individual separation needs.

1.4 Summary and conclusions

In this chapter, we outlined the principles, process applications, merits and limitations of magnetic separation. It is noted that the magnetic separation techniques are used in various applications. We considered a possibly new approach to biological and colloidal separation using magnetophoretic in magnetic fluids. Hence, the goals of this thesis are to synthesize a new class of polymer-based magnetic fluids, to characterize and understand their structure and to analyze, both experimentally and theoretically, the novel concepts of magnetophoresis in magnetic fluids.

The aim of Chapter 2 is to introduce magnetic fluids and their applications and also to present the experimental methods used to synthesize and characterize the magnetic fluids used in this study along with their results. In Chapters 3 and 4, theoretical characterization of the aggregation behavior occurring in these magnetic fluids is presented. Chapter 5 presents the experimental part of the magnetophoresis
in magnetic fluids as a potential separation technique, while Chapter 6 contains its theoretical foundations. The conclusions of this thesis are presented in Chapter 7 along with a summary of the important findings.
Bibliography


Chapter 2

Synthesis and Characterization of a Polymer-Based Magnetic Fluid

Magnetic fluids are suspensions of finely divided magnetic particles in a continuous medium. They are usually composed of small (3-15 nm), solid single-domain magnetic particles coated with a molecular layer of a dispersant and suspended in a liquid carrier. The dispersant is usually a long-chain molecular species whose main functions are to prevent the agglomeration of the particles to each other and form a stable suspension in the liquid phase. Thermal agitation also keeps the particles suspended because of Brownian motion. On the other hand, particles are attracted to each other by van der Waals and magnetic interactions arising from the magnetic dipoles that can lead to particle agglomeration and settling. An optimal particle size is sought that would ensure a balance between the different forces and keep the particles suspended in the liquid. A schematic drawing of a magnetic fluid, seen on three length scales, is shown in Figure 2-1. On the macroscopic level, it is a black liquid that reacts to the magnetic field as shown in the figure in which the magnetic fluid is attracted to the magnet on the top of the vial. On the colloidal level, the magnetic fluid is a suspension of nanoparticles stabilized by surfactant layers. On the nanoscopic level, the particles are slightly ellipsoidal in shape with the surfactant molecules attached to their surfaces via adsorption. The purpose of this chapter is to explain the procedure used for the synthesis of the polymer based magnetic fluid used in this thesis.
2.1 Overview of magnetic fluids

2.1.1 Synthesis

Magnetic fluids can be prepared via a range of different techniques. The most recent review on the preparation of magnetic fluids given by Blums et al. [1] is summarized here.

Physical methods for the preparation of magnetic fluids include the grinding of metals to small particles. In this process, a powder of magnetic material is mixed with the carrier liquid and the surfactant, and, to produce the required particle size, the grinding mills run at about 45 rpm for 1000 hours [2]. Other physical methods include evaporation of metals in vacuum [3] and spark erosion [4].

Coprecipitation of iron (II) and iron (III) oxides is the most common chemical method for the preparation of magnetite-based magnetic fluids. Several modifications of this method are found in the literature [5–7]. The coprecipitation method is also used to prepare aqueous magnetic fluids based on manganese and cobalt ferrites [8,9]
and copper and zinc ferrites [10]. Nakatani et al. [11,12] used both a plasma Chemical Vapor Deposition (CVD) technique and vapor-liquid reaction to prepare iron-nitride magnetic fluids.

Metal or mixed-metal magnetic fluids give higher saturation magnetization than those based on magnetite. Kilner et al. [13] prepared cobalt magnetic fluids through the condensation of cobalt vapor into a solution of a surfactant in toluene. Nickel magnetic fluids were prepared by Hoon et al. [14]. Mixed-metal magnetic fluids prepared include nickel-iron [15] and iron-cobalt [16, 17]. Other kinds of magnetic fluids include mercury-based magnetic fluids [18,19], ionic magnetic fluids [20] and transparent magnetic fluids [21].

2.1.2 Applications

Magnetic fluids are widely used in rotary shaft seals to prevent the leakage of gas under pressure through the gap surrounding the shaft. Bearings position the shaft out of contact with the surrounding structure, and a permanent magnet circuit concentrates the magnetic field into the gap where the magnetic fluid is held as discrete rings. This type of pressure seal has become a standard machine element used in semiconductor crystal growing, integrated circuit manufacturing, compressors, blowers and nearly all computer hard disk drives [22]. Magnetic fluids have also been applied to the separation of mixtures with different mass densities immersed in a magnetic fluid under the application of an external field. Magnetic fluids can also be used as inks and in microwave systems [23]. Raj et al. [24] give a review on other current and new applications of magnetic fluids.

2.2 Experimental

2.2.1 Desired characteristics of a magnetic fluid

Magnetic particles can be suspended stably in water by the use of a double layer of fatty acid surfactants [25]. While we have experience in the synthesis of this
type of magnetic fluid [26], it has some drawbacks for the targeted application. The secondary layer of surfactants in a fatty acid based magnetic fluid is kept in place by means of physical attraction which requires an equilibrium amount of free surfactants in the carrier fluid to keep the particles stable. Hence, upon dilution, the second layer desorbs and the particles aggregate. Additionally, the particles of the double-layer magnetic fluid are electrostatically stabilized which prevent their use in a high ionic strength environment. Similarly, fatty acids are protonated at low pH which renders the magnetic fluid unstable at these conditions. This will also hinder the usage of these particles with charge-sensitive molecules which might be damaged by the high charge density on the surface of the particles (e.g. proteins can be unfolded). To overcome these problems we synthesized a magnetic fluid that is stable against changes in pH, dilution and ionic strength and that has minimal effect on sensitive molecules.

2.2.2 Synthesis of PAA-PEO graft copolymer

Polymer Design

we overcame the limitations of the double layer fatty acid based magnetic fluids through the design of polymer stabilizer. To prevent the disassociation of the second layer on dilution, we designed the polymer to chemically attach to the particles. Moreover, problems associated with an electrostatically stabilized suspension such as sensitivity to pH and ionic strength changes were overcome by synthesizing a polymer that would provide steric stabilization to the particles as well as be hydrophilic to solubilize the particles in water. It is important that there be multiple points of attachments of the polymer to the particle surface to offer greater stability. The comb-like polymer that we selected, shown schematically in Figure 2-2, has carboxylic acid groups on its back bone and polyethylene oxide (PEO) branches. This structure imparts the sought characteristics because the carboxylic acid groups provide the chemical link to the surface of the particles while the PEO side chains provide the hydrophilic environment for the required steric stabilization for the magnetic
nanoparticles.

Figure 2-2: Chemical structure of the polymer used to stabilize the magnetic particles

The hydrophilicity of the polymer layer can be finely tuned by substituting polypropylene oxide (PPO) side chains for PEO to change the ratio of polyethylene oxide to polypropylene oxide in the polymer brushes. This ability provides a design tool for manipulation according to the separation need at hand [27]. The ability to chemically modify the surface of the particles and tailor their interfacial properties allows the general strategy to be made specific for a particular separation system.

Materials

Polyacrylic acid (PAA) of 5000 molecular weight was obtained from Aldrich and used as received. Amine-terminated polyethers (JEFFAMINE®,) provided by Huntsman Corporation (Salt Lake City, UT), contain primary amino groups attached to the terminus of a polyether backbone. They are thus polyether amines. The polyether side chain contained a PEO/PPO chain with 6.5 EO groups per PO group and a molecular weight of 3000. The JEFFAMINE® Mono-series products are prepared by reaction of a mono-alcohol initiator with ethylene and/or propylene oxide, followed
by conversion of the resulting terminal hydroxyl group to an amine. These polymers were used as received.

**Experimental procedure**

A 50% aqueous solution of the polyacrylic acid (5000 molecular weight) was combined with a stoichiometric equivalent of an amine-terminated polyether (3000 molecular weight). The mixture was heated and maintained at 180°C under flowing nitrogen for 2 hours. The water comprising the solution and formed by reaction was removed in the nitrogen gas stream. The resulting product was an amber viscous liquid. [27, 28]

### 2.2.3 Synthesis of a polymer-based magnetic fluid

The magnetic fluid was prepared by coprecipitation according to the following reaction, as detailed in [27]

\[
2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 8\text{NH}_4\text{Cl}
\]

In a typical reaction, 2.35 g FeCl₃·6H₂O, 0.86 g FeCl₂·4H₂O, and 1.25 g polymer were added to 40 mL of water. The temperature of the reaction was kept at 80°C and nitrogen gas was purged through the mixture to remove any dissolved oxygen that might oxidize iron (II) ions. On adding 5 mL NH₄OH, the magnetic particles form instantaneously. The reaction product was then sonicated to remove any aggregates. After sonication, ultrafiltration (100K Mwt cutoff) is used to remove free (unattached) polymers and any unreacted species.

### 2.2.4 Characterization of the magnetic fluid

The size of the magnetic particles was measured using transmission electron microscopy and dynamic light scattering. The magnetic properties were assessed using superconducting quantum interference device (SQUID).
Dynamic Light scattering

The magnetic fluid was diluted and filtered through 0.2 \( \mu m \) syringe filters. Dynamic light scattering (DLS) was used to measure the diffusion coefficient of the particles in the liquid. Assuming a spherical shape for the particle, its hydrodynamic diameter was calculated from the Stokes-Einstein equation:

\[
D = \frac{kT}{3\pi \eta d}
\]

where \( D \) is the measured diffusion coefficient, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature in K, \( \eta \) is the fluid viscosity, and \( d \) is the hydrodynamic diameter.

The hydrodynamic diameter calculated through Equation 2.1 is the apparent diameter of the whole colloid, including the magnetic core and the attached polymer layer.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used to determine the size of the magnetic particle. Only the core of the particle can be visualized using TEM. Using the core diameter measured through this method and with information from DLS, the effective polymer layer thickness was estimated.

Superconducting Quantum Interference Device

In the absence of an applied magnetic field, magnetic particles are randomly oriented. As the magnetic field magnitude is increased, the particles become more aligned with the field direction. At higher field strengths, the particles become completely aligned and the magnetization reaches its saturation value. Superconducting quantum interference device (SQUID), which is available in MIT Materials Science Department, was used to obtain magnetization values at different magnetic field strengths, to yield a magnetization curve. This curve was used to obtain the size of the magnetic dipole using the following relations [27,29].
\[ D_p = \left[ \frac{18kT}{\pi M_d} \left( \frac{\chi_i}{3\phi M_d H_s} \right) \frac{1}{3} \right]^{\frac{1}{3}} \]  

(2.2)

\[ \sigma = \frac{1}{3} \left[ \ln \left( \frac{3\chi_i H_s}{\phi M_d} \right) \right]^{\frac{1}{3}} \]  

(2.3)

where \( \chi_i \) is the initial magnetic susceptibility on a volume basis (i.e., the slope of the magnetization curve at \( H = 0 \)), \( \phi \) is the volume fraction of particles, \( M_d \) is the saturation magnetization of the particles on a volume basis, and \( H_s \) is determined from the intercept of a graph of \( M \) versus \( 1/H \) at high applied fields.

2.3 Results

Figure 2-3 shows the results of a dynamic light scattering measurement on a dilute solution of the polymer. The mean diameter of the free polymer was 9.5 nm.

![Histogram of Hydrodynamic Diameter](image)

**Figure 2-3: Results of dynamic light scattering on a free polymer**

Dynamic light scattering was also performed on a dilute solution of the magnetic fluid as shown in Figure 2-4.
Figure 2-4: Results of dynamic light scattering on a dilute magnetic fluid

A representative photograph taken by TEM is shown Figure 2-5. The TEM results for the particle diameters of magnetic fluids as a function of the synthesis temperature are summarized in Table 2.1. Magnetic fluids prepared at 80°C were synthesized by Geoffrey Moeser [27].

Figure 2-5: A representative photograph taken by transmission electron microscopy. This image was provided by Geoffrey Moeser.

The SQUID results are shown in Figure 2-6. They were used to calculate the median diameter of the magnetic core and it was found to be 7.4 nm, very similar to
Table 2.1: Diameter measured by TEM for magnetic particles prepared at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mean Diameter (nm)</th>
<th>St. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.1</td>
<td>2.8</td>
</tr>
<tr>
<td>50</td>
<td>7.0</td>
<td>2.9</td>
</tr>
<tr>
<td>80</td>
<td>7.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

TEM results except for the magnetic fluid prepared at 80°C.

Figure 2-6: Magnetization curves for the magnetic fluids prepared at different temperatures measured by SQUID

2.4 Summary

This chapter reports the synthesis a new class of water-based magnetic fluids, which consists of an aqueous suspension of \(~7.5\) nm diameter magnetic \(\text{Fe}_3\text{O}_4\) nanoparticles produced through the chemical coprecipitation of iron salts in aqueous solution in the presence of a PAA/PEO-g-PPO graft copolymer. The particles were coated with a \(9.4\) nm bifunctional polymer layer comprised of an outer hydrophilic PEO region that stabilizes the particles against agglomeration and a backbone of polyacrylic acid
that attaches to the surface of the particles.
Bibliography


Chapter 3

Monte Carlo Simulation of Sterically-Stabilized Magnetic Fluids

Magnetic fluids are colloidal suspensions of single-domain magnetic nanoparticles stabilized against flocculation and settling by surfactants attached to their surfaces. Owing to their unique physical and chemical properties, magnetic fluids have attracted much interest since their inception in the mid 1960s, and produced many suggested and realized commercial applications of these magnetic fluids. The performance and stability of the fluids are controlled by the nature of the particle-particle interactions as dictated by the surfactant layer coating the particles. It is the goal of this work to elucidate the aggregation behavior of sterically-stabilized magnetic nanoparticle suspensions using Monte Carlo simulations to provide a better understanding of the important parameters affecting their aggregation. In addition, this work provides an explanation of experimental observations for magnetite nanoparticles suspended in organic solvents [1]. Early simulation studies have suggested that magnetic particles do aggregate with and without the presence of the magnetic field [2,3]. This observation is also affirmed by experimental results [1,4]. This chapter introduces our work in the area of Monte Carlo simulation of magnetic fluids.

The conventional Metropolis algorithm has been used in two-dimensional Monte
Carlo simulations to analyze cluster configuration in magnetic fluids [2, 3] and to compare the results with theoretical predictions [5]. Two-dimensional Monte Carlo simulations have also been used to study the effect of size distribution on the magnetic fluid configuration [6]. For particles with strong interactions, the original Metropolis algorithm is not very efficient. As the particles aggregate through attractive particle–particle interactions, most single-particle moves are rejected since such moves are not favored energetically. Hence, the particles tend to reside in their clusters and the whole simulation freezes. A way to overcome this difficulty is to move whole clusters (also called secondary particles) when they are formed. The cluster-moving method has proved to be more efficient both in the 2-D [7–9] and in the 3-D cases [7]. However, it contained a violation of the detailed balance equation as will be discussed later.

### 3.1 Procedure

In this work, we used the conventional Markov chain Monte Carlo simulation. Two types of moves were used in our simulations: single-particle moves and cluster moves. In a single-particle move, a particle was selected at random and allowed to either translate or rotate. The energy of the new configuration was calculated and the move was accepted based on the Metropolis criterion

\[
\text{acc} (o \rightarrow n) = \min [1, \exp (-\beta \Delta U)]
\]

(3.1)

where \(\text{acc} (o \rightarrow n)\) denotes the probability of accepting a trial move from an old position \(o\) to a new position \(n\), \(\beta\) is the reciprocal temperature \((1/kT)\), and \(\Delta U\) is the change in the energy of the system from the old to the new configuration, \(\Delta U = U(n) - U(o)\). If the trial move resulted in a negative change in energy, the move was accepted, as the exponential term in Equation 3.1 is greater than 1. Otherwise, the move was accepted with a probability that is related to the change in energy. This criterion ensures that the detailed balance equation

\[
p(o) \pi (o \rightarrow n) = p(n) \pi (n \rightarrow o)
\]

(3.2)
is satisfied in which $p(i)$ is the \textit{a priori} probability of state $i$, and $\pi(1 \rightarrow 2)$ is the transition probability from state 1 to state 2. This expression means that the average number of accepted moves from $o$ to any other state $n$ at equilibrium is exactly cancelled by the number of reverse moves. Such a condition is important to ensure convergence to stationary equilibrium.

In a cluster move, clusters are identified according to the conventional method [10]. A particle is defined as being part of a cluster if it is within a prescribed distance (10% of particle diameter) of another particle in that cluster. Once identified, a cluster is selected at random and either translated or rotated. In the case of rotation, one particle in this particular cluster is selected at random and the whole cluster rotated around it about one of the three coordinate axes (randomly selected). This method of rotation is as rigorous as rotating around the center of mass and about one of the primary axes, yet it is more computationally efficient because it eliminates the need for the calculation of the center of mass. In the case of translation, each particle in the selected cluster is equally translated along a random direction, keeping the orientation of the cluster intact.

The move is accepted or rejected according to the following criterion, which was originally developed for Monte Carlo simulation of surfactant assemblies [11].

$$\text{acc} (o \rightarrow n) = \min \left[ 1, \exp (-\beta \Delta U) \prod_{i=1}^{N_1} \prod_{j=1}^{N-N_1} \frac{1 - p^{\text{new}} (r_{ij})}{1 - p^{\text{old}} (r_{ij})} \right]$$  \hspace{1cm} (3.3)

with

$$p(r_{ij}) = \begin{cases} 1 & r_{ij} < r_c \\ 0 & r_{ij} > r_c \end{cases}$$  \hspace{1cm} (3.4)

where $r_c$ is the critical distance for cluster recognition and $r_{ij}$ is the distance between particle $i$ of the cluster being moved and any other particle $j$ in the ensemble. If two particles that did not belong to the same cluster in the old configuration come within a distance less than $r_c$, the attempted move is rejected. This criterion en-
sures that the growth of clusters occurs only via single-particle moves, and that all the accepted moves are microscopically reversible. Hence, this criterion satisfies the detailed balance equation.

This criterion was recently applied to 2-D MC simulations of magnetic fluids [12]. However, in a previous cluster-moving algorithm published in [8], a move was accepted or rejected according to the criterion used for a one-particle move, which allowed the fusing of two clusters into one, but not the dissociation of one cluster into two (in a one cluster move), thereby violating the detailed balance equation. In that work, the authors attempted to alleviate this problem by reducing the frequency of cluster movements. It was claimed that an equilibrium by using Satoh's cluster-moving MC algorithm is almost equivalent to that by the algorithms without the cluster movements.

To ensure that no overlapping particles existed at the beginning of the simulations, we started all simulations with a face-centered cubic lattice array of particles. Simulations that were run to investigate the efficiency of the MC techniques were preformed on 256 particles, whereas those run to study the structural properties of a magnetic fluid with a particular set of parameters were performed on 864 particles. The volume fraction was 1% and the cutoff distance was 5 times the diameter of one particle. Each simulation was performed for up to 150,000 MC steps per particle and the mean values were evaluated after equilibrium was reached. The cluster moves were attempted at a rate of 2% of the total moves. Equilibrium was determined by the steady values of energy and number of clusters as well as the complete decay of the autocorrelation functions. Since the most time-consuming part of a Monte Carlo simulation is the calculation of the pair potential energy, which depends primarily on the magnitude of the pair separation $r_{ij}$, we developed a method to reduce the computational time that is explained in the appendix.
3.2 Force field description

We model here a system of hard magnetic particles within a magnetic field, with each particle coated with a soft layer of chemisorbed surfactant on its surface. For reasons to be described later, it is important to define a minimum thickness, $\alpha$, corresponding to the excluded volume of the soft surfactant layer. The interaction between particles is assumed to be pairwise additive, and consists of a magnetic dipole-dipole interaction, due to the magnetic cores, a van der Waals interaction, and an entropic elastic interaction associated with deformation of the surfactant layers when two particles are in close proximity as shown in Figure 3-1. In addition, the

![Diagram of particle interaction](image)

**Figure 3-1**: Dimensions of the particles and the force field model

magnetic core can couple to an external magnetic field. The magnetic contributions
to the force field are

\[ u_{ij} = kT \lambda \frac{d^3}{r_{ij}^3} \left[ n_i \cdot n_j - 3 (n_i \cdot \hat{r}_{ij}) (n_j \cdot \hat{r}_{ij}) \right] \]  \hspace{1cm} (3.5)

and

\[ u_i = -kT \xi n_i \cdot H \]  \hspace{1cm} (3.6)

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( r_{ij} \) is the particle-to-particle distance, \( \hat{r}_{ij} \) is the corresponding unit vector, \( n_i \) is the unit vector of the magnetic dipole of particle \( i \), and \( H \) is the magnetic field vector. In addition, \( \lambda \) and \( \xi \) are dimensionless parameters representing the strength of magnetic dipole-dipole and dipole-field interactions relative to the thermal energy, given by

\[ \lambda = \frac{m^2}{4\pi \mu_0 d^3 kT} \]  \hspace{1cm} (3.7)

\[ \xi = \frac{mH}{kT} \]  \hspace{1cm} (3.8)

where \( m \) is the magnitude of the magnetic moment of a particle given by \( m = \mu_o MV_p \), \( M \) is the magnetization of the particle material, and \( V_p \) is its volume. Equation 3.5 is used within the cut-off sphere beyond which a reaction field approach is used to describe the long-range magnetic dipole-dipole interactions. These long-range interactions have not been included in previous Monte Carlo simulations of magnetic colloids, although their truncation inevitably leads to underestimation of the interaction forces and errors in the structural properties. Dipole-dipole interactions drop off as \( 1/r^3 \), and thus are of significant range. To account for this, we used the Onsager reaction field approach that was originally developed to account for the long-range interactions of electrostatic dipoles. The net magnetic moment within the sphere of cut-off induces a moment in the surrounding fluid, through re-orientation of the particles. The surrounding fluid is modelled as a continuum, with magnetic permeability \( \kappa_m \), which exerts a reaction field on the particles within the cut-off sphere. The magnitude of the reaction field acting on a particle \( i \) is proportional to the moment of the
cavity surrounding \(i\),

\[
E_i = \frac{2(\kappa_m - 1)}{2\kappa_m + 1} \sum_{r_{ij} < r_c} \frac{1}{r_c^3} \ j
\]  

(3.9)

where the summation extends over the particles in the cavity, and \(r_c\) is the radius of the cavity. The contribution to the energy from the reaction field is \(-\frac{1}{2} \mu_i \cdot E_i\). We applied the same treatment to a magnetic dipole in a cavity, using magnetic permeability, \(\kappa_m\), calculated according to

\[
\kappa_m = 1 + 4\pi\chi
\]

(3.10)

where \(\chi\) is the initial magnetic susceptibility of the magnetic fluid as determined by

\[
\chi = 8\phi\lambda
\]

(3.11)

and \(\phi\) is the volume fraction of the magnetic solids and \(\lambda\) was defined in Equation 3.7. Based on the above, the long-range portion of the magnetic dipole interactions acting on a particle is calculated from the following equation.

\[
u_{rf,i} = -\frac{(\kappa_m - 1)}{2\kappa_m + 1} \frac{d^3 \lambda kT}{r_c^3} \left[ \vec{n}_i \cdot \sum_{r_{ij} < r_c} \vec{n}_j \right]
\]

(3.12)

Other forms of interactions are also present between the particles. The most important ones are van der Waals interactions and the entropic steric repulsion. The relative importance of these interactions depends upon the magnetic moment of the particles, their size and the nature and thickness of the surfactant coating layer. van der Waals interactions between a pair of particles of equal size are given by

\[
u_{vdw} = -\frac{A_{eff}}{12} H \left( \frac{s}{d} \right)
\]

(3.13)

where

\[
H(x) = \frac{1}{x^2 + 2x} + \frac{1}{x^2 + 2x + 1} + 2\ln \frac{x^2 + 2x}{x^2 + 2x + 1}
\]

(3.14)

where \(A_{eff}\), the effective Hamaker constant, is a quantity related to an optical dis-
persion frequency, the numerical magnitude of which is usually known only approxi-
mately, \( H(x) \) is a mathematical function with one variable \( x \), which is \( s/d \) in the case of Equation 1.7, and \( s \) is the surface-to-surface distance. The presence of a liquid dispersion medium, rather than vacuum, between the particles notably lowers the van der Waals interaction energy, requiring the use of an effective Hamaker constant defined as

\[
A_{\text{eff}} = \left( A_p^{1/2} - A_m^{1/2} \right)^2
\]

where the quantities \( A_p \) and \( A_m \) represent particle-particle interactions and particle-medium interactions, respectively. For the present case, we model the aggregation of magnetic particles coated with a fatty acid layer in a hydrocarbon medium. We assumed that the surfactant layer does not contribute to the van der Waals interactions and calculated the surface-to-surface distance based on the hard magnetic particles. This assumption is justified because the surfactant chains are of the same nature as those of the medium molecules, and hence have similar Hamaker constants.

There are many forms for the entropic steric repulsion caused by a surfactant or a polymer layer. We used a simple one that is based on a statistical mechanical treatment in which adsorbed species are regarded as rigid rods, each with a ball- joint attachment to the surface [13]. The repulsion is due to the decrease in the number of possible configurations of the adsorbed hydrocarbon chains when two particles approach one another.

\[
u_{\text{er}} = \frac{\pi}{2} d^2 NkT \left[ 2 - \frac{x + 1}{b} \ln \left( \frac{1 + 2b}{1 + x} \right) - \frac{x}{b} \right]
\]

where \( N \) is the number of adsorbed molecules per unit area, \( b = \delta/d \), and \( \delta \) is the surfactant layer thickness.

To apply the entropic repulsion, we calculated the point beyond which an approaching particle can not penetrate. Our calculation was based on the excluded volume of the surfactant layer. The volume of the surfactant molecules, for a close-packed surface, is given by
\[ V_s = \pi d^2 \delta \]  

(3.17)

Since the surfactant cannot shrink beyond a certain distance \( \alpha \) (see Figure 3-1), the total volume of the particle and the surfactant molecules is conserved,

\[ \frac{\pi}{6} (d + 2\alpha)^3 = \frac{\pi}{6} d^3 + \pi d^2 \delta \]  

(3.18)

The real root of the Equation 3.18 gives the value of \( \alpha \) as a function of \( \delta/d \).

\[ \frac{2\alpha}{d} = \left( \frac{6\delta}{d} + 1 \right)^{1/3} - 1 \]  

(3.19)

Thus, the entropic repulsion term is given by

\[
    u_r = \begin{cases} 
    \infty & r < d + 2\alpha \\
    u_{er} & d + 2\alpha < r < d + 2\delta \\
    0 & r > d + 2\delta 
    \end{cases}
\]  

(3.20)

The use of a volume-excluded minimum thickness, \( \alpha \), is essential to prevent the problem of having a primary minimum at close distances to the surface of the magnetic particle. This situation causes the random moves associated with MC simulations to simply overcome the energy barrier and stick at the point of contact of the magnetic particle. Truncating the potential energy at a distance \( \alpha \) prevents this artificial scenario.

The potential energy profile shown in Figure 3-2, gives a good representation of the interactions in an oil-based magnetic fluid with one layer of closely packed surfactant. The total pairwise potential energy exhibits a minimum of about -2 kT for the case of 10-nm magnetite particles with a 1-nm surfactant layer. In Figure 3-2, the average magnetic interaction energy was calculated using the Boltzmann statistical weighing factor that favors those orientations with more attractive potential energies via
Figure 3-2: Potential energy profiles showing magnetic and van der Waals attraction and entropic repulsion

\[
\langle u_{ij} \rangle = \frac{\int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} u_{ij} \exp\left(-u_{ij}/kT\right) \sin \alpha_1 \sin \alpha_2 d\alpha_1 d\alpha_2 d(\gamma_1 - \gamma_2)}{\int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \exp\left(-u_{ij}/kT\right) \sin \alpha_1 \sin \alpha_2 d\alpha_1 d\alpha_2 d(\gamma_1 - \gamma_2)}, \tag{3.21}
\]

where \(\alpha_1, \alpha_2, \gamma_1\) and \(\gamma_2\) are the four orientation angles of the magnetic moments of the two particles.

The aqueous magnetic fluids that we produced contain particles coated with either a polymer or a double layer of surfactant. For the polymer case, the thickness of the layer is not well defined and a different model for the entropic repulsion should be used. In the case of the double layer, the electrostatic repulsion prevents the particles from aggregation. These type of interactions comes from the ionic nature of the surfactant head groups. These aqueous magnetic fluids are kinetically stable and can not be modelled using this type of MC simulation analysis. Hence, we limited our simulation in this study to oil-based magnetic fluids.

The above calculations were repeated for both magnetite and cobalt at different surfactant thickness and the results are shown in Figure 3-3. Since cobalt has a
higher magnetic moment, its pairwise potential well is deeper than for magnetite.

![Graph showing well depth vs. shell thickness for Magnetite and Cobalt]

Figure 3-3: The well depth for both magnetite and cobalt as a function of the shell thickness. Particle size was 10 nm.

which should exhibit larger, more oriented aggregates as will be discussed later.

### 3.3 Simulation parameters

The model parameters were varied to investigate their effect on the efficiency of the algorithm and on the sensitivity of suspension structural properties. Finally, a set of values for these parameters was selected for the detailed analysis of the structural properties of a magnetic fluid in the absence of a magnetic field. The particle size was taken to be 10 nm. The effective Hamaker constant was chosen to be $1.5 \times 10^{-19}$ J, which is appropriate for magnetite in a hydrocarbon medium [14]. The surfactant layer thickness was chosen to be 1 nm, which is less than the extended length of a decanoic acid molecule. $\lambda$ was chosen to be that of magnetite and cobalt at room temperature at values of 1.4 and 13, respectively.
3.4 Structural properties

The configurational structure of the magnetic fluid is represented by the end-to-end distance, the aggregation behavior, the fractal dimension, the pair distribution function and the structure factor. The end-to-end distance, $d_{\text{max}}$, is calculated from the maximum diameters of the clusters as depicted in Figure 3-4. The aggregation number of a cluster is the number of particles associated with that cluster. The fractal dimension, $d_f$, is calculated by fitting the equation

$$ N \propto d_f^{d_{\text{max}}} $$

(3.22)

for all clusters of aggregation number greater than two.

The radial distribution function $g(r)$ is the number of particles at a distance $r$ from a given particle relative to the number at the same distance in an ideal gas at the same density. It is defined by

$$ g(r) = \frac{V}{N^2} \left( \sum_i \sum_{j \neq i} \delta (r - r_{ij}) \right) $$

(3.23)

where $\langle \rangle$ denotes the ensemble average. To describe the orientational ordering, the radial distribution function can be extended to include the orientation of the dipoles. This description, however, creates the need for a very large multidimensional table in the calculations, which requires a prohibitively high calculational overhead. For
simplicity, we limited our analysis of the radial distribution function to the dependence on $r$ only. We studied the orientational ordering by looking at the net magnetic moment of the cluster by vectorially adding the magnetic moments of the individual particles associated with that cluster.

To compare the simulation results with recent results from small angle neutron scattering experiments [15], we calculated the structure factor, $S(q)$, which is directly related to $g(r)$ by Fourier transformation, according to

$$S(q) = 1 + 4\pi \rho \int_0^\infty dr \frac{r^2 \sin(qr)}{qr} [g(r) - 1]$$  \hspace{1cm} (3.24)

where $q$ is the wave vector. Only particles within a cluster are included and the cluster-cluster interactions were ignored, as was done in the development of the S(q) model used in the SANS study [16].

### 3.5 Equilibration

It is important to know how long a simulation must be run to sample the equilibrium configuration space of the system representatively. For systems in which aggregation occurs, it has been shown that the simple criterion that equilibrium has been reached when the energy of the system has become constant, can be misleading [17]. In addition to energy, we used two different criteria to determine this time: the position autocorrelation function, $C_R(t - t_0)$, and the aggregation number autocorrelation function, $C_N(t - t_0)$. The autocorrelation function is generally defined as

$$C_{AB} = \frac{\langle [A(t + \tau) - \langle A(t + \tau) \rangle] \ [A(t) - \langle A(t) \rangle] \rangle}{\sigma(A(t + \tau)) \sigma(A(t))}$$  \hspace{1cm} (3.25)

where $A(t)$ is the value at $t = t_0$ of the relevant quantity, either the position of the particle (represented as distance from the origin) or the aggregation number of a cluster in which a particle resides, $A(t + \tau)$ is its value $\tau$ steps later. $\sigma(A)$ is the root
mean squared deviation defined as

$$
\sigma^2(A) = \langle A^2 \rangle - \langle A \rangle^2.
$$

(3.26)

The position autocorrelation function can be used to estimate the number of MC steps needed to remove any statistical correlation of particle positions. The aggregation number autocorrelation function similarly gives the number of MC steps needed to remove any statistical correlation between the aggregation numbers of the different clusters in the system.

### 3.6 Results and discussion

On running the simulation, it was clear that at certain conditions the particles form clusters of various sizes and configurations. Some of these clusters are shown on Figure 3-5. The four clusters shown in the figure have different aggregation numbers

![Clusters](image)

Figure 3-5: Some of the clusters formed during simulation

and end-to-end distances. In the figure, the small red cylinder protruding from one of the particles represents the direction of the magnetic moment for that particle. Under no external magnetic field, magnetite particles do not align in the direction of their magnetic moments. This behavior is because the magnetic interaction energy is not strong enough to dictate a certain orientation and the particles orient randomly by the effect of their thermal rotation energy.
3.6.1 Importance of autocorrelation function

The autocorrelation functions are important indicators of the progress of the simulation. Figure 3-6 shows that energy stationarity is a poor indicator of positional decorrelation. Although the simulation started from an equilibrium position, the position autocorrelation shows that more than 100,000 Monte Carlo steps are needed to remove statistical correlation of the positions of the particles. Hence, configurations are not independent within 100,000 Monte Carlo steps. Taking averages after equilibration based on the energy is misleading in this case. Equilibration is determined after the autocorrelation function decays completely.

The use of the cluster-moving algorithm results in an acceleration in the equilibration of the simulation. Figure 3-7 shows the position autocorrelation function for two simulations with and without the use of cluster moves. The incorporation of 2\% cluster moves reduced the number of MC steps needed to decay the autocorrelation function from 68,000 to 7,500 steps. Although this decrease in the number of steps resulted in a significant saving in the computational time, the corresponding reduction in time is not linearly proportional to the decrease in MC steps because one cluster step takes significantly more computational time than one individual particle.
Figure 3-7: Incorporation of a small percentage of cluster moves results in a significant decrease in the number of MC steps needed for decay of the position autocorrelation function.

step. Hence, a trial and error procedure is needed to identify an optimal percentage of cluster moving steps that would lead to a maximum time saving. For our case, a 2% cluster move provided significant computational time saving and was used throughout our work.

3.6.2 Validity of algorithm

Although the use of the cluster-moving algorithm proposed by Satoh [8] resulted in an acceleration in the equilibration of the simulation as shown in Figure 3-7, the algorithm does contain a violation of the detailed balance equation as discussed earlier. Consequently, one would expect that the equilibration value of the aggregation number depended on the percentage of cluster moves used in the simulation. Since the equilibrium value should be independent of the technique used, it is not recommended to use this cluster-moving algorithm as such. When the algorithm was modified to remove the violation, the equilibrium value of the aggregation number remained constant within statistical error as shown in Figure 3-8. The reason behind
Figure 3-8: Comparison between the two algorithms showing the stability of our algorithm to the different percent cluster moves.

This observation is that in the former cluster-moving algorithm, the equilibrium state was not preserved. Hence, there is a tendency to create more clusters than are broken, as the cluster move contains the joining of two clusters into one large cluster but not the breaking of a large cluster into two. Therefore, when the percentage of the cluster moves increases, the clusters become larger as the simulation proceeds. This problem is overcome in the modified cluster-moving algorithm because the equilibrium, once reached, is preserved. Hence, Figure 3-8 shows no effect of the percentage cluster moves on the final result, as it should be.

3.6.3 Cluster size distribution

It is important to note that for large clusters, the configuration contains fewer individual units and hence the statistics become less informative since the number of units decreases. The simulation of larger clusters requires starting with a larger number of particles. Nonetheless, the cluster size distribution calculated from the simulation gave accurate representation of the actual configuration for cluster sizes up to 15 particles. The number of individual units in this case was about 60. Figure 3-9 shows
the aggregation number distribution for a typical 1% magnetite magnetic fluid plotted on a log-log scale. The average aggregation number in this case is 7.5 while the average end-to-end distance is 25 nm. Figure 3-10 also shows the end-to-end distance distribution. These values agree well with the experimentally determined aggregation numbers between 8 and 12 and end-to-end distances of 32.4 ± 3.6 nm. [1]

3.6.4 Fractal dimension

The fractal dimensions are calculated through the fitting of Equation 3.22 as shown in Figure 3-11. It is notable that the fractal dimensions of the magnetite based magnetic fluids are small (~1.6). Two possible reasons can be attributed to this observation. First, clusters with small aggregation numbers inherently have small fractal dimensions. Another possible reason is that the formed clusters exhibit a linearly-oriented configuration due to the directional character of the magnetic dipole-dipole interactions. To investigate the cause of the small fractal dimension, we calculated the average cluster moment for magnetite as a function of the aggregation number through addition of the magnetic moment of each particle within a cluster. The
Figure 3-10: End-to-end distance within a 1% magnetic fluid

Figure 3-11: An example of the calculations of the fractal dimension from the slope of log N versus normalized D
process is repeated using random orientations of the magnetic moments within the clusters instead of orientations based on the simulation.

Figure 3-12 shows that the cluster magnetic moments based on the simulation results are similar to those based on random distribution of moments in the absence of a magnetic field. This result suggests that the magnetite particles orient randomly in the absence of the magnetic field. The magnetic moment of randomly-oriented magnetite particles would not have any effect on the configuration of the cluster which means that the particle magnetic moments have no effect on the small fractal dimension calculated. In the presence of the magnetic field, however, the net cluster moment is close to that of completely oriented magnetic particles as shown in Figure 3-12. In that case the magnetic moment of the oriented particles would be expected to have an effect on the fractal dimension on the cluster.

To investigate the plausibility of the first reason, namely that small fractal dimension is simply due to small aggregation numbers, we calculated the fractal dimension of randomly generated clusters as a function of their aggregation number. The results in Figure 3-13 show that literal interpretation of the fractal model for such low aggre-
Figure 3-13: Fractal dimension as a function of particle size for random clusters

gation numbers must be viewed with caution. The application of the equation relating the fractal dimension, aggregation number, and aggregate size (Equation 3.22) to reasonably compact small aggregates of aggregation numbers less than about 10-20 can still yield low numbers for the fractal dimension even in the absence of preferred directional interactions. For instance, tightly packed structures having two, three, and four particles have fractal dimensions of 1, 1.59, and 2, respectively, and these fractal dimensions fall quickly when the packing constraints are relaxed. This situation would certainly be the case when the attractive interparticle interactions are small as in this example. In such cases, the small forces ensure not only small aggregation numbers but also a random movement of particles about the cluster, leading to looser aggregates than would be obtained in the presence of strong particle-particle interactions, and hence lower apparent fractal dimensions. A cluster of eight particles, for instance, with a maximum correlation length of four particle radii will give a fractal dimension of 1.5, whereas if the correlation length corresponds to five particle radii, a fractal dimension of 1.29 is obtained. Results indicate that such structures are readily obtained even in the absence of directional forces between the particles. Thus, it is
likely that the low fractal dimensions obtained are a direct consequence of the small aggregates formed because of weak interparticle interactions and the constraints on the packing of particles in these small clusters.

However, if the magnetic dipole interaction is high as for cobalt, the individual particles show a non-random orientation within the clusters as shown in Figure 3-14. In large clusters, such an orientation would lead to a decrease in the fractal dimension.

![Graph showing normalized magnetic moment vs aggregation number](image)

Figure 3-14: Effect of magnetic field on the net magnetic moment of cobalt clusters

As for small clusters, both the particle orientation and the small aggregate numbers affect the fractal dimensions of the clusters.

In many cases, the structures of fractal aggregates can be interpreted in terms of the relative balance between diffusional or reactive limitations. For diffusion-limited systems, a particle sticks to the first particle it encounters in a cluster and the cluster growth normally results in loose extended aggregates of fractal dimension $\sim 1.8$. In contrast, reaction-limited systems tend to yield more compact structures (with larger fractal dimensions) as the particle can sample a significant portion of the open regions surrounding the cluster before adhering to it. Hence, the fractal dimension, along with the cluster size distribution, can give an indication of the mechanism of aggregation.
Although our system can be classified to be of the diffusion-limited type since there is no energy barrier for a reaction, the low fractal dimensions obtained cannot be correlated to the mechanism of aggregation as the small fractal dimension is a direct consequence of the low aggregation number.

### 3.6.5 Importance of van der Waals interactions

Figure 3-15 shows the effect of the value of the Hamaker constant on the average aggregation number and the fractal dimension of the clusters. It is clear that van der Waals interactions can play a significant role in the clustering process. Increasing the Hamaker constant resulted in an increase in both the aggregation number and the fractal dimension. In the case of magnetite where the magnetic dipole moment does not dominate the interactions, changing the value of the Hamaker constant has a significant effect on the structure of the clusters. This effect can be implemented practically by changing the quality of the solvent, for example. The fractal dimension increased because van der Waals interactions act in all directions; thus there is no orientational preference for the growth of the cluster, and its structure is more
compact. This fact was not appreciated in previous work in which van der Waals interactions were neglected relative to the magnetic dipole-dipole interactions. It is clear, however, that for magnetite, van der Waals attractions dominate over the magnetic dipole-dipole interactions in the absence of a magnetic field.

### 3.6.6 Effect of magnetic field

The magnetic field orients the particles in its direction. When the magnetic dipole moment is large compared to van der Waals interactions, the particles form chain-like structures, as shown in Figure 3-16 for magnetite ($\lambda=1.4$) and cobalt ($\lambda=13$) in the presence of a strong magnetic field ($\zeta=10$). The increase in the magnetic field also increases the height of the second peak in the radial distribution function as shown in Figure 3-17, which means that particles are closer together on average.

The effect of the magnetic field is to align the dipole moments of the particles in the direction of the field. This effect would slightly increase the average interactions between the particles. Yet, in the case of magnetite, this increase is not significant compared to the magnitude of van der Waals interactions; hence, no significant change in the aggregation number is expected. For cobalt, this effect can be significant as shown in Figure 3-18 which depicts the effect of the magnetic field on the aggregation number and the fractal dimensions of cobalt at different surfactant thickness. On
Figure 3-17: The effect of the magnetic field on the radial distribution function

Figure 3-18: Effect of surfactant thickness on aggregation number and fractal dimension of cobalt
the application of magnetic field for the case with 1.7 nm layer of surfactant, the average aggregation number of the clusters increased from 4.4 to 6.2 accompanied by a decrease in the fractal dimension from 1.33 to 1.27. The increase in the cluster size is due to the increase of the total interaction energy between the particles as they are oriented in one direction and their magnetic attraction is at its maximum. The decrease in the fractal dimension is because the aligned particles tend to form chain-like clusters.

3.6.7 Cluster net magnetic moment

One would expect that the net moment of the clusters to be proportional to the number of particles within that cluster, according to

\[
\frac{M_{\text{cluster}}}{M_{\text{particle}}} = f N_{\text{agg}}
\]

(3.27)

If the particles are completely oriented in one direction, \( f = 1 \). However, \( f \) is a function of the aggregation number. Figure 3-14 shows the dimensionless cluster magnetic moment versus the aggregation number for magnetite in the presence of magnetic field and for a completely random orientation. It is clear that in the absence of magnetic field, the orientation of magnetite particles is similar to the orientation of randomly oriented particles. The effect of the magnetic dipole moment on the orientation of the magnetic particles within a cluster is negligible. Since van der Waals interactions are dominant at close range and the magnetic dipole-dipole interaction is on the order of \( kT \), there is no preferred orientation for the particles within a cluster. On applying the magnetic field, however, all the particles orient towards the magnetic field. This orientation increases the cluster net magnetic moment considerably, which leads to larger clusters. This can have important relevance in application as in some cases, the increase in the magnetic field can yield the magnetic fluid unstable.
3.6.8 Structure factor and comparison with experiments

One way to compare our Monte Carlo simulation results with scattering experiments is to extract the structure factor from the configurations. Figure 3-19 compares the structure factor extracted from the simulation configurations, and that calculated from a fractal dimension model frequently used to describe experimental SANS results [16]. This extraction from the simulation configurations was done through an inverse Fourier Transform of the radial distribution function calculated based on particles within clusters only.

\[
S(q) - 1 = \frac{1}{(q r)^{d_f}} \frac{d_f \Gamma(d_f - 1)}{[1 + (q E)^{-2}] [(D - 1)/2]} \times \sin \left[ \frac{(D - 1) \tan^{-1}(q E)}{2} \right]
\]  

(3.28)

where \( r \) is the radius of the particle, \( d_f \) is the fractal dimension, and \( E \) is the radius of the clusters. The model assumes that aggregates are monodisperse, which is not the case for our clusters. This assumption could be the reason for the discrepancies in the structure factor calculated by the model and extracted from the simulation.

Figure 3-19: Comparison of the structure factors determined by fitting the SANS data and simulation
3.7 Conclusions

We investigated the structural features for sterically-stabilized magnetic fluids using Monte Carlo simulation techniques in which both particle and cluster moves were allowed. The cluster-moving algorithm was formulated to satisfy the detailed balance equation, as earlier simulation reports poorly represented equilibrium state of the aggregation phenomena because of violating the detailed balance principle. In addition to energy, it was found that autocorrelation functions should be used to determine the equilibration time representatively.

We showed that comparison between Monte Carlo simulation of magnetic fluids and experimental results can be achieved through the aggregation number, fractal dimension, end-to-end distance, and the structure factor. These variables permit the comparison of the results from both arenas and permit the validation of the simulation techniques.

Cobalt is a particularly interesting material for magnetic fluids since its magnetic moment is an order of magnitude higher than magnetite. The cobalt particles, however, are not stable with a 1-nm layer of surfactant and require a longer chain surfactant for stabilization of the suspension.

The results of Monte Carlo simulation are in reasonable agreement with experimental results for an oil-based magnetic fluid. Our new method gives good estimates of aggregation numbers, correlation lengths, and radial distribution functions which agree well with cluster characteristics determined by small-angle neutron and light scattering experiments.
3.8 Appendix: The rejection method

The most time-consuming part of a Monte Carlo or molecular dynamics simulation is the calculation of the pair potential energy, which depends primarily on the magnitude of the pair separation $r_{ij}$. The truncation of the potential beyond a specific cutoff diameter is used widely to reduce the simulation time. However, the use of a cutoff diameter may not dramatically reduce the time to compute the number of interactions because the distance between every pair of atoms in the system would still have to be calculated. This calculation is needed simply to decide whether they are close enough to calculate their interaction energy. Calculating $N(N-1)$ distances takes almost as much time as calculating the energy itself. Different methods that are used to decrease the simulation time are available in the literature [18]. They are based on creating a list of the atoms in the neighborhood of each atom and using this list for potential energy calculations.

We proposed the use of a simpler method, the rejection method, to enhance the computation efficiency. In our method, the distance between every pair of particles is not calculated unless it lies in a box with the cutoff diameter as the length of its side. Figure 3-20 shows a two-dimensional representation of the basic principle behind the rejection method. Every particle is tested whether it falls in the square surrounding the cutoff circle as shown. This decision is less expensive than calculating of the distance between the atoms as it merely involves a logical if statement. Its drawback is that it prohibits the parallelization of the code for the energy calculation loop.

To test if the distance between any particle $j$ and the center particle $i$ (with coordinates $x_i$ and $y_i$) is to be calculated or not, we check to see if this atom lies in the square with side $2r_{cut}$. The x-coordinate is checked first and if it lies within $x_i + r_{cut}$ and $x_i - r_{cut}$ of the center particle, the y-coordinate is checked. If an atom passed the test, its distance from the center atom is formally calculated. By using this method, the distance between any pairs of atoms is calculated only if there is a high probability ($\pi/4$ for $2 - d$ and $\pi/6$ for $3 - d$) that this atom is within the cutoff diameter.
Figure 3-20: A square is constructed around the cutoff circle and distances are only calculated for the particles inside the square.

Obviously, care should be taken to include the minimal image convention in the calculation, which is done by moving the x-coordinate of the center particle to the different side of the periodic box and performing the test on the surrounding atoms.

The above method was used to calculate the energy of a single particle in an ensemble of N particles. The results for a three-dimensional case show a substantial decrease in the computation time by the new method. Unlike the conventional method, the computational time of the rejection method depends on the value of the cutoff diameter as would be expected. As shown in Figure 3-21, there is about 6.3 times increase in computational efficiency for $r_{cut}=0.1$ on HP735/125MHz.
Figure 3-21: Difference in computational time between using the conventional method for calculating the pair potential energy and the rejection method.
Bibliography


Chapter 4

On the Finite Cluster Sizes of Aqueous-Based Magnetic Fluids

The stabilization of colloidal dispersions against aggregation is important in a large number of industrial applications, including the manufacture of plastics and paints, the emulsification of agricultural products, and the production of foods. Particle-particle clustering can be controlled by many different approaches, most commonly by steric interactions between polymer layers adsorbed on the particle surfaces, or by electrostatic interactions between charged groups on the particle surfaces. In these cases, the repulsive interaction energy overpowers the attractive van der Waals interactions up to some finite interparticle distance such that the close approach of the particles leading to sticking and clustering is inhibited. In some instances, the approaching particles have sufficient kinetic energy that they can overcome this barrier and be trapped in an attractive well. The fraction of particle-particle collisions that result in association, known as the sticking probability, \( \zeta \), can be shown through the DLVO theory to depend critically on the barrier height, \( U_{\text{max}} \), through the equation

\[
\zeta = \frac{1}{W} = \frac{4R\rho}{\pi^2} \exp \left( -\frac{U_{\text{max}}}{kT} \right)
\]  

(4.1)

where \( p = \sqrt{-\left(\frac{\partial^2 V}{\partial r^2}\right)_{\text{max}}/2kT} \), \( W \) is the stability ratio defined as the rate of aggregation in the presence of the barrier to the rate of diffusion controlled association,
in which each collision results in association, and \( R \) is the particle size. It is usually accepted that for barrier heights greater than about 15 kT, no association can occur, and the colloidal dispersion remains stable indefinitely [1]. For lower barrier heights, particles that have sufficient kinetic energy to overcome these barrier heights will stick on collision leading to indefinite aggregation.

In a recent paper [2], cryo-TEM and dynamic light and small angle neutron scattering experiments suggested that a fatty acid-stabilized aqueous colloidal system of magnetite particles formed finite cluster sizes with aggregation numbers of about 20-50. We postulated that the barrier height was insufficient to prevent the association of two particles, but that it increased as the clusters grew, such that a colloid that is initially unstable because of a low barrier height could eventually grow, given the right conditions, to form a stable colloid with larger clusters. This mechanism is consistent with our experimental results.

The purpose of this chapter is to explain the factors affecting the aggregation behavior of electrostatically-stabilized magnetic fluids. These colloidal suspensions have a different pair potential energy profile than that of the sterically-stabilized magnetic fluids studied in the previous chapter, and hence exhibit a different aggregation mechanism. It is important to note that the analysis presented in this chapter can be applied generally to any similar non-magnetic colloidal system since the magnetic interaction energies were not included in the analysis due to their relatively low value compared to van der Waals attraction and electrostatic repulsion. We explored the ideas inherent in this concept of growth-dependent sticking probabilities by performing more rigorous finite element calculations of the interaction energies as particles approach small clusters of particles of different sizes and orientations. Implicit in this analysis is the question of the reliability of the pair-wise interaction hypothesis used widely in describing intermolecular and colloidal interactions. We investigated the inherent errors in this assumption.
4.1 Equivalent-sphere cluster model

As a first approximation, we treated the cluster as a large particle of radius $R_{cl}$ and given surface potential interacting with a primary particle of radius $R_{p}$ as it approaches the cluster, as indicated schematically in Figure 4-1. The change in the barrier height, $E_b$, and hence also in the rate of attachment of individual particles to the clusters [$\sim\exp(-\frac{E_b}{kT})$] was estimated by considering a simple model of the electrostatic and van der Waals interactions between two spheres of different sizes. We assumed that the surface potentials, $\psi^{\infty}$, of all particles and clusters were constant and equal, justified on the basis that the charge density varies as particles approach one another in this self-regulating system owing to the local changes in proton concentrations near the surfaces within the diffuse part of the electrical double layer, and hence in the protonation-deprotonation equilibrium of the fatty acids. The behavior closely approximates that of a system of constant surface potential.

The variation of the electrostatic interaction energy with interparticle distance, $s$, was approximated by the analytical solution of the Poisson-Boltzmann equation
\[ u_e = 4\pi \varepsilon_0 \left( \frac{R_p R_{cl}}{R_p + R_{cl}} \right) (\psi^\infty)^2 \ln (1 + \exp(-\kappa s)) \] (4.2)

Similarly, we approximated the van der Waals interactions by treating the particles and clusters as uniform spheres of constant effective Hamaker constant, \( A_{eff} \), according to

\[ -12u_{vdw} = A_{eff} H \left( \frac{s}{2R_p}, \frac{R_{cl}}{R_p} \right) \] (4.3)

where

\[ H(x, y) = \frac{y}{x^2 + 2xy + x} + \frac{y}{x^2 + 2xy + x + y} + 2 \ln \frac{x^2 + 2xy + x}{x^2 + 2xy + x + y} \] (4.4)

The effective Hamaker constant for the interaction of the particle with the cluster depends on the particle density within the cluster and particularly on the particle density near the cluster surface, as the void spaces are filled with solvent and do not contribute to the particle/cluster interactions. We approximated these interactions through an averaged Hamaker constant for the particle cluster by the expression

\[ A_{eff} = (A_p A_{cl})^{1/2} = \sqrt{f} A_p \] (4.5)

where \( f \), the volume fraction of particles in the cluster, is estimated in terms of the fractal dimension, \( d_f \), through the equation

\[ f = (R_p / R_{cl})^{3-d_f} \] (4.6)

Figure 4-2 shows the variation of the barrier height with the size of the cluster.\(^1\)

The results show that the effective barrier height for particle/cluster interactions increases as the cluster size increases, shown in Figure 4-3, and hence that there should be a finite cluster size at which further growth of the clusters is prohibitively slow, thereby providing kinetic stability to the suspension. Similar postulates have

\(^1\)Note that there is a typographical error in the caption of the figure in the original paper [2] and that the correct value of \( \kappa \) is \( 7.36 \times 10^8 \, m^{-1} \).
Figure 4-2: Estimates of particle-cluster interaction energies as a function of separation distance, with $R_p = 5 \times 10^{-9}$ m, $\kappa = 7.36 \times 10^8$ m$^{-1}$ ($n = 0.05$ M), $C_t = 2.27 \times 10^{18}$ m$^{-2}$, $A_p = 1 \times 10^{-19}$ J

Figure 4-3: Relative growth rate as a function of relative cluster size
been made in a few previous studies [3, 4] but without physical justification.

While this analysis offers some insight into possible reasons for the growth of finite clusters in charge-stabilized colloidal suspensions, it suffers from the shortcomings of an implicit introduction of the pair-wise additivity assumption and the approximations inherent in the use of a volume averaged Hamaker constant. We address both of these concerns in the sections that follow by developing more detailed computations of the interactions between an approaching particle and clusters of various configurations and orientations.

4.2 Full particle-cluster interaction model

We investigate here the interactions between single particles and small clusters of different geometries by solving rigorously the linearized Poisson Boltzmann equation using finite element methods. By allowing specifically for the contributions of the individual particles in the clusters, and lifting the assumption of pair-wise additivity, we were able to capture the effects of both the topography of the interacting clusters and of the direction taken by the particle as it approaches the non-symmetric particle clusters. The cluster configurations investigated are shown in Figure 4-4.

The potential energy profile for the interaction of a particle with a given cluster was calculated by solving the Poisson-Boltzmann equation

\[
\nabla^2 \psi = \kappa^2 \sinh (\psi) \tag{4.7}
\]

for any given configuration of particles, where \( \psi \) is the electrical potential and \( \kappa \) is the reciprocal Debye length, given by

\[
\kappa = \left( \frac{e^2 \sum n_i^0 z_i^2}{\varepsilon k T} \right)^{1/2} \tag{4.8}
\]

Here, \( e \) is the electron charge, \( i \) is index of ions in solution, \( n_i \) is the number concentration of ions of type \( i \), \( z_i \) is their ionic charge, \( \varepsilon \) is the medium dielectric constant, \( k \) is the Boltzmann constant, and \( T \) is the temperature. For constant small surface
potentials, the linearized Poisson-Boltzmann equation

$$\nabla^2 \psi = \kappa^2 \psi$$  \hspace{1cm} (4.9)

can be used with little error, as shown in the calculations reported in this chapter.

The electrostatic contribution to the interaction potential energy is given by

$$V = \psi_o (Q_\infty - Q_l)$$  \hspace{1cm} (4.10)

where $\psi_o$ is the potential on the surface of the particle, $Q_\infty$ is the particle charge in isolation and $Q_l$ is its charge at distance $l$ from the other particle(s). The particle charge is calculated from

$$Q = -\varepsilon \varepsilon_o \int_S \nabla \psi \, dS$$  \hspace{1cm} (4.11)

where $S$ is the surface area of the particle, and $\varepsilon_o$ is the permittivity of free space.

The van der Waals attractive forces between the approaching particle and any
Table 4.1: Parameters used in calculations for the model system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter</td>
<td>D</td>
<td>10 nm</td>
</tr>
<tr>
<td>Surface potential</td>
<td>( \Psi_0 )</td>
<td>-0.07747 V</td>
</tr>
<tr>
<td>Debye parameter</td>
<td>( \kappa )</td>
<td>0.1645 nm(^{-1})</td>
</tr>
<tr>
<td>Hamaker constant</td>
<td>A</td>
<td>2 (*\ 10^{-19}) J</td>
</tr>
</tbody>
</table>

given sphere in the cluster is given by

\[
-12u_{vdw} = AH \left( \frac{s}{2R_p}, 1 \right)
\]  \( (4.12) \)

where \( A \) is the Hamaker constant. The total energy of interaction is thus given by

\[
E = V + \sum_{i}^{N} u_{vdw}
\]  \( (4.13) \)

where \( i \) is the index of the particles in a cluster containing \( N \) particles.

To evaluate \( V \), the Poisson-Boltzmann equation was solved using a Galerkin finite element method (FIDAP\textsuperscript{®}, Fluid Dynamics, Evanston, IL) on an HP 700 computer. The two- or three-dimensional domain was divided into triangular or tetrahedral elements respectively (using the GAMBIT\textsuperscript{®} mesh generator), and quadratic basis functions were used to approximate the potential field. Table 4.1 lists the typical values for the parameters used in all interaction energy calculations.

### 4.3 Cluster configurations

The five cluster configurations illustrated in Figure 4-4 were selected to demonstrate the effects of both cluster geometry (linear versus compact clusters) and the direction of approach of the particle to the cluster. In configuration A, in which two spherical particles interact, we solved both the non-linear and the linearized Poisson Boltzmann equations in a two-dimensional domain, making use of both axial and plane symmetry. In configuration B, a single particle approaches a chain of three particles horizontally. The axial symmetry of this configuration allowed the solution to be developed in
a two-dimensional domain. In configuration C, an individual particle approaches a chain of three particles vertically, and the three-dimensional mesh created to solve for one point on the energy profile for this configuration, exploiting the symmetry planes to reduce the size of the computational domain, is shown in Figure 4-5. The two perpendicular planes of symmetry cut the center particle and the approaching in an orthogonal way. Only one half of one other particle in the chain needs to be considered. The symmetry planes were made use of in all configurations to reduce the computational domain. In configuration D, a particle approaches an equilateral

Figure 4-5: Example of a 3-dimensional mesh created for configuration C. The approaching particle is at the top and the chain is at the center of the figure.

triangular cluster from above. In this case, the three-dimensional domain was divided into three parts using two planes of symmetry at 60° angles. I added another group of particles in configuration E to examine their effect on the height of the energy
4.4 Results and discussion

We performed finite element calculations initially to assess the viability of using the linearized approximation to the Poisson Boltzmann equations, using configurations A as the test case; the results were almost indistinguishable. Consequently, since the computational time required to solve the full PB equation for a two-dimensional problem was 15 times greater than that needed to solve the linearized equation, we used the linearized PB equation for the remainder this study.

The assumption of pairwise-additivity has long been known to be flawed and it has been the goal of a number of studies [5] to represent the electrostatic interactions correctly in a many-body environment. The DLVO framework asserts that the electrostatic repulsion between two particles is caused by the overlap of their respective double layers formed by the distribution of ions in solution. In a multi-particle system, the distribution of ions around any particular particle will depend on its proximity to the other particles in the system, thereby possibly rendering the pairwise additivity assumption invalid. The extent to which this assumption affects the values of the interaction profiles is examined in Figure 4-6, where the pairwise additive barrier height is 6.2 kT, in contrast to the value of 8.7 kT calculated using the full solution to the PB equation, i.e., the pairwise additivity assumption underestimates the electrostatic repulsions. Note that both barrier heights in Figure 4-6 are larger than the barrier height for the interaction of two isolated particles (5.8 kT), corroborating our earlier assertion that the barrier height increases with the size of the cluster and hence should be taken into account in any cluster growth calculations. Figure 4-7 shows the total energy profiles for the first three configurations. The barrier height for configuration C is higher than that of configuration B which in turn is higher than that of A. The increase in the cluster size results in increase in the barrier height and hence exponential decrease in the growth rate. The results also show that the rate of the cluster growth depends on the direction of approach of a particle to the cluster.
Figure 4-6: Comparison between energy profile for configuration C calculated using the pairwise additivity assumption '□' and the numerical solution of Poisson-Boltzmann equation '◇'.

Figure 4-7: Total energy profiles for configurations A '●', B '□' and C '◇'.
The barrier height of the third configuration is higher than for the first one. Since the growth in the linear directions is preferred due to a relatively lower barrier height, the formed clusters will have a fractal nature and not be highly compact.

Figure 4-8 shows the energy profile for configuration D and E, both with a separation distance of 2.5 nm. The barrier heights are 18.5 and 19.5 kT, respectively. It is clear that the effect of remote particles within the cluster can be ignored and only particles in the vicinity of contact must be taken into account.

The calculations of the energy profile and the barrier height using the full solution of the linearized Poisson-Boltzmann equation confirm our previous results from the simple equivalent-sphere cluster model. The barrier height is a function of the cluster size and configuration such that the rate of cluster growth decreases considerably as the clusters grow. The clusters grow to a finite size beyond which the barrier height is sufficiently high to limit any further growth, which makes the colloidal suspension kinetically stable at a certain finite size.
4.5 Conclusion

Experiments show that particles aggregate to form clusters of finite size in aqueous charged-stabilized colloids. The finite cluster sizes are the result of a decrease in the growth rate with an increase in the cluster size. This hypothesis was validated through a rigorous finite element solution of the Poisson-Boltzmann equation for different cluster configurations. The barrier height for aggregation is shown to depend on the cluster size and the approach to the cluster. We also showed that the usage of the pairwise additivity assumption for calculating the electrostatic repulsion energy yields inaccurate results.
Bibliography


Chapter 5

Magnetophoresis in Magnetic Fluids

Magnetophoresis refers to the movement of particles under the influence of an applied magnetic field. As shown in Figure 5-1, when a fluid containing suspended particles is exposed to gradient fields, magnetic forces act on both the fluid and the particles. The difference in the magnetic forces causes the particles to move either towards or away from the high magnetic field zones. The direction of the movement depends on the sign of the difference between the magnetic susceptibility of the fluid and the particle. If the magnetic susceptibility of the particle is greater than that of the fluid, the particle will move towards the high magnetic field zone. On the other hand, if its magnetic susceptibility is less than that of the fluid, the particle migrates in the direction of decreasing magnetic field.

Consider the case of a non-magnetic particle immersed in a magnetic fluid. Upon application of an inhomogeneous magnetic field, a magnetic force acts on the non-magnetic particle due to the difference in magnetic susceptibility between the particle and the surrounding magnetic fluid. This magnetic force is analogous to the buoyancy force, which can be viewed as a surface force caused by the difference in pressure on the surface of the immersed object. It is proportional to the volume of the immersed object and the density of the surrounding medium. Upon the application of a gravitational field, the immersed object feels a buoyancy force that pushes it upwards away
from gravity.

In the case of the magnetophoretic force, the important parameters are the difference in the magnetic susceptibility, the magnetic field gradient and the size of the suspended particle. The difference in the magnetic pressure is the cause for this magnetophoretic force pushing the particles away along the magnetic field gradient. Hence, when particles of different sizes are suspended in a magnetic fluid, they exhibit different magnetic velocities upon the application of an inhomogeneous magnetic field, providing the basis for a unique separation technique. Their magnetophoretic mobility, \( \mu_m \), is defined by

\[
\mu_m = \frac{\Delta \chi D^2}{18 \eta},
\]

where \( \Delta \chi \) is the difference in magnetic susceptibility between the particle, and the surrounding medium, \( D \) is the diameter of the particle and \( \eta \) is the viscosity of the fluid.

Studies [1–7] have been made to attach paramagnetic magnetite particles to cells and other biological particles, whereby the magnetophoretic mobilities of these par-
ticles change. On the application of an inhomogeneous magnetic field, these particles move with a velocity, \( v_m \), that varies with the particle magnetophoretic mobility and the localized magnetic field gradient according to

\[
v_m = \mu_m \frac{\nabla B^2}{2 \mu_o},
\]

where \( B \) is the magnetic flux density and \( \mu_o \) is the permittivity of free space.

In this chapter, we investigate of the magnetophoresis of fluorescent polymer beads suspended in magnetic fluids. The chapter introduces the important parameters affecting the magnetophoretic mobility of the particles and discusses the relevant experimental findings. It establishes magnetophoresis as a promising concept that can be used in a novel separation technique.

## 5.1 Fluorescent measurements experiments

We studied the phenomenon of magnetophoresis by monitoring the evolution in the concentration profile of fluorescently-tagged polymer beads as they moved in a capillary tube upon the application of an inhomogeneous magnetic field. By measuring the intensity of the light emitted due to the excitation of polymer beads, we determined the concentration of the polymer beads at different points along the axis of the capillary tube. We studied the effect of parameters such as the diameter of the particles, the concentration of the magnetic fluid, and the concentration of the polymer beads on the magnetophoretic phenomenon.

### 5.1.1 Materials

The magnetic fluid was prepared as described in Chapter 2. The fluorescently-tagged polystyrene beads were purchased from Spherotech, (Libertyville, IL) and diluted from 1% suspensions in water to 0.4% suspension in magnetic fluids. They were prepared by either staining the polystyrene particles with a solution of appropriate fluorophore or by polymerizing a fluorophore in styrene in the presence of polystyrene
core particles. These fluorophores do not leach and fluorescence remains stable for long periods of time. We confirmed the particle size using dynamic light scattering and measured their zeta potentials in deionized water using a Brookhaven Instruments ZetaPALS device. The important parameters of the particles used in this study are summarized in Table 5.1.

Table 5.1: Size, color and excitation and emission wavelengths for the fluorescent particles used in this study

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Color</th>
<th>Excitation Wavelength (nm)</th>
<th>Emission Wavelength (nm)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>Nile Red</td>
<td>514.5</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>Yellow</td>
<td>470</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>Yellow</td>
<td>470</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>Purple</td>
<td>590</td>
<td>610</td>
<td></td>
</tr>
<tr>
<td>510</td>
<td>Pink</td>
<td>560</td>
<td>590</td>
<td>41.8</td>
</tr>
<tr>
<td>840</td>
<td>Nile Red</td>
<td>514.5</td>
<td>560</td>
<td>31.1</td>
</tr>
</tbody>
</table>

5.1.2 Experimental

The setup used to monitor the effect of the magnetic field on the concentration profile of the fluorescent particles is shown schematically in Figure 5-2. It consisted of a light source, an excitation filter, the magnetic fluid cell, an emission filter and a computer controlled camera. Figure 5-3 shows a digital image of a part of the setup.

The light source was a 200 W mercury lamp mounted in a special lamp housing. The lamp housing has a dichroic mirror to remove the UV wavelengths and a heat absorbing filter to remove the IR wavelength. The light source was purchased from Oriel Instruments (Stratford, CT).

The optical filters were 2" visible interference filters. The narrow bands of these filters have a 10 nm width. They were also purchased from Oriel Instruments (Stratford, CT). The center wavelengths for the filters are listed in Table 5.1.

The excitation filter allowed the transmission of light at wavelengths within the absorptive spectrum of the fluorescent particles, but rejected light at wavelengths within the emission spectrum of the particles, which could consequently be reflected
by the magnetic fluid cell and incorrectly detected as emission energy.

The emission filter similarly transmitted light at wavelengths within the emission spectrum of the fluorescent particles and rejected the light at wavelengths within the absorptive spectrum of the particles which could consequently be incorrectly detected as emission energy.

The center wavelengths of the excitation and the emission filters were selected to be as close to the absorptive and emissive peaks as possible to ensure the optimal yield from the fluorescent particles (see Table 5.1).

Figure 5-4 shows a schematic diagram of the magnetic fluid cell. The glass capillary tube used had a diameter of 0.34 mm. The magnets were 0.5" in diameter with a maximum field at the center of about 4000 G. The amount of fluid suspension needed to fill the tube was less than 10 $\mu$L.

Two different magnetic field configurations were used in our experiments. In the first configuration - which we will call the simple configuration - a cuvette was used as a holder for the two magnets. The magnets were then placed on both sides of the cuvette. They were allowed to move freely in the horizontal direction which ensured that they are perfectly aligned due to the effect of the strong magnetic attraction
Figure 5-3: A digital photograph of the magnetic fluid cell (labelled as the precision controlled system), the camera and the emission filter wheel.

Figure 5-4: Schematic diagram of the magnetic fluid cell
forces. The distance between the magnets was 7 mm. On one side of the cuvette, one half inch magnet disk was placed. Two of the same type of magnets were placed on the other side. The cell was mounted on a plate with a small window that allowed the light to pass through to the capillary tube and the emission light to pass through to the camera. This plate was machined from aluminum so as not to interfere with the magnetic field.

To be able to control the location of the magnets precisely on both sides independently, a special device was designed and machined. Figure 5-5 shows a photograph of the device with all the different components. It is made of anodized aluminum to

![Figure 5-5: Photographic image of the precisely-controlled setup](image)

eliminate any effect on the magnetic field. With this device, the capillary tube can be placed in a groove that standardized its location. Also, the location of the magnets could be changed precisely within an accuracy of 0.01 mm. The device had a 50 mm wide viewing slit which defined the extent of the camera image. Two magnets were placed on each side and the spacing between them was exactly half that of the simple configuration, i.e. 3.5 mm.

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1We acknowledge Edward S. Park for the design of this precisely controlled magnet translation system which was machined in the MIT Central Machine Workshop.
The magnetic field strength was measured along the centerline of the cell using a Gauss/Tesla Meter (F.W. Bell Model 4048 with sensor Model 1386). Figure 5-6 shows the magnetic field strength measured using the magnetometer along the centerline of the cell for the two configurations, while Figure 5-7 shows the gradient of the square of the magnetic field strength which is an important factor that determines magnetophoretic force acting on the suspended particles.

The slow-scan charge coupled device (CCD) digital camera was purchased from Princeton Instruments (Trenton, NJ). It utilizes a large format, high pixel density (close to 1.5 million pixels) CCD array designed for high resolution imaging.

### 5.1.3 Data gathering and reduction

The pictures taken were converted to ASCII files for subsequent analysis. The background was subtracted from all the images, and the pictures were normalized to remove any non-uniformity in the beam by dividing the images by a beam image. The centerlines of the images were taken to represent the bead concentrations at the center of the capillary tube. These centerlines were collected from all the images
Figure 5-7: The gradient of the square of the magnetic field strength along the center line of the magnetic fluid cell for the simple and the precision-controlled configuration and plotted versus time to represent the dynamic evolution of the polymer beads concentration.

The concentration of the magnetic particles is linearly proportional to the absorbance and not the measured intensity. A separate experiment was performed with the purpose of monitoring the evolution of the their concentration profile, in which light was allowed to pass through the capillary tube and captured by the camera. The absorbance of light due to the magnetic particles is defined as

\[ A = -\ln \frac{I}{I_i}, \]  

(5.3)

where \( I \) is the intensity measured and \( I_i \) is the initial intensity measured when there were no particles inside the tube. This absorbance is linearly proportional to the concentration of the magnetic particles through

\[ A = \epsilon B c, \]  

(5.4)
where $B$ is the path length, $\epsilon$ is the molar extinction coefficient and $c$ is the concentration of the magnetic particles.

To normalized concentration of the polymer beads is related to the intensity of the emitted light captured by the camera. After subtracting the background and adjusting for the beam non-uniformity, the magnetic particles concentration was calculated using Equations 5.3 and 5.4 above. The beam intensity was not always constant; it could decrease slightly with time, particularly during the long experiments. To correct for the change in the beam intensity with time, a point was selected at which no change in the concentration was expected. Then, the intensities measured were multiplied by the ratio between the intensity measured at this point at time 0 and that measured at the same point at time $t$.

The magnetic particles are not fluorescent and hence do not emit any light. They are, however, capable of absorbing both the excitation and the emitted light. Hence, correction should be made to the emitted light intensity captured as a function of the concentration of the magnetic particles. However, since the concentration of the magnetic particles remains uniform along most of the length of the tube, the amount of absorbance remains constant. Thus, with the assumption that the concentration of the magnetic particles does not change significantly along most of the tube length, it is acceptable to define the normalized concentration at any point in time as

$$\frac{C(t)}{C(0)} = \frac{I(t)}{I(0)},$$

where $C(0)$ and $C(t)$ are the concentration of the polymer beads at time 0 and $t$, respectively, and $I(0)$ and $I(t)$ are the captured intensity at times 0 and $t$, respectively.

### 5.1.4 Results and discussion

In this section, we present the results from using the simple magnetic fluid cell configuration. We have used a mixture of 0.4% polymer beads with 1% magnetic fluid. This mixture was used to fill the capillary tube which was placed in the simple configuration. On the application of the magnetic field, there were no changes in the measured
intensity of 50, 80 and 190 nm particles. However, there was a significant change in the distribution of the fluorescent particles for the 510 and 840 nm particles. The buildup of the 840 nm beads at the focusing point is clear in the series of pictures taken by the CCD camera, shown in Figure 5-8. The color scale shown represents the concentration of the polymer beads normalized relative to the initial concentration. Initially, the concentration is uniform along the tube which is represented by the horizontal band in the first image. As time goes on, the concentration of the polymer beads increases at the focusing point as the rest of the images depict. A significant focusing occurs within the first ten minutes. The focusing point is equivalent to the point of zero force in Figure 5-7. In the region between the centerline and the edges of the magnets, the particles feel a net force repelling them away. Thus, the particles migrate with a mobility proportional to the square of the magnetic field gradient,

Figure 5-8: Series of picture showing the buildup of the 840 nm particles at the focusing point 8 mm away from the center of the magnet. X and Y axis are in mm.
represented in Figure 5-7. Hence, their velocity varies with their location. As they approach the point of zero force, the particles decelerate until their velocity reaches zero at the focusing point. This deceleration results in an accumulation prior to the focusing point as shown in later images of Figure 5-8.

The dynamics of the change in the concentration profile is shown in Figure 5-9 for both the 510 and the 840 nm particles, respectively. The x-axis represents the distance from the centerline of the magnets. The particles build up gradually at the point of zero force. The curves represent snap shots of the concentration profile as the particles migrate towards the focusing point. The concentration of the particles decreases significantly within the vicinity of the magnets centerline and increases at the edge of the magnets where the magnetic field goes to zero. Comparing the evolution of the 510 nm and the 840 nm particles, we can see how the latter migrate faster towards the focusing point. They also concentrate significantly more once they reach the focusing point. In addition to the magnetic force, the maximum concentration at the focusing point is a function of the size and the surface charge of the particles. This is explained in more details in Chapter 6. It suffices to say that as the particles concentrate, they start to feel the presence of each other and hence an upper limit on the concentration is affected by the interparticle forces.

The evolution of the concentration profile of the magnetic particles is plotted in Figure 5-10 for the simple configuration. Although the concentration changes significantly at the centerline of the magnets, it hardly changes at all along the rest of the capillary tube within the time range of the experiment. The accumulation of the magnetic particles at the centerline of the magnets is due to the magnetophoretic force acting on them attracting them to the high magnetic field zone. As far as the magnetic particles are concerned, the surrounding medium has a much lower magnetic susceptibility and hence, the presence of the inhomogeneous magnetic field results in a magnetophoretic force attracting the magnetic particles towards the center of the magnets. This force is a function of the magnetic particle size (\(\sim 7\) nm) and the difference in magnetic susceptibility between the particles and water (\(\sim 1\)).
Figure 5-9: Evolution of the concentration profile of the polymer beads
5.1.5 Effect of magnetic field

It is expected that the evolution of the concentration profile for the same particles would be different under the two configurations described above. The evolution of the concentration profile for a 0.4% polymer beads in a mixture with 1% magnetic fluid when placed between the magnets as per the precisely-controlled configuration is shown in Figure 5-11 at different times. Figure 5-11 shows the concentration profiles for 240, 510 and 840 nm particles.

Figure 5-11 shows the dynamic evolution of the concentration profile of three different-size particles. The profile is characterized by a broad distribution before the point of zero force. The amount of the particles within this broad distribution increases with time. Beyond the point of zero force, the normalized concentration of the polymer beads drops to below unity and then increases to unity again. To understand the reason behind the concentration profile at the focusing point, consider Figure 5-12 which shows an enlarged magnetic force plot in the vicinity of the point of zero force.

Figure 5-12 is divided into three regions. At the two interfaces between the three
Figure 5-11: The evolution of the concentration profile for a 0.4% polymer beads in a mixture with 1% magnetic fluid when placed between the magnets as per the precisely-controlled configuration.
regions, the magnetophoretic force is equal to zero. In region A, the magnetic force is positive and hence the particles migrate away from the magnets. In region B, the magnetic force is negative, and thus forces the particles towards the magnets. Although the force in region C is positive, and hence pushes the particles away from the magnets, its magnitude is three order of magnitude smaller than the maximum force in region A. Hence, the particles initially present in region A, will exhibit a force pushing them to the interface A/B, but they will not be allowed to pass the interface since there will be a negative force pulling them back. This explains the accumulation of the particles before the interface A/B. The particles initially present in region B, will be pulled towards the interface A/B. Since these particles do not get replenished, a reduction in the concentration in region B is expected with time. The particles originally present in region C, will be pushed away from the magnet. However, the magnetic force is relatively small in this region and can not prevent particles from diffusing back towards the magnet. The quantitative equations explaining all the relevant forces are presented in Chapter 6.
Figure 5-13: The dynamic evolution of the concentration profile for 240, 510 and 840 nm particles at three different times

An explanation for the two spikes observed at the magnet center and at the point of zero force is presented in section 5.1.9.

5.1.6 Effect of particle size

As per Equation 5.1, the magnetophoretic mobility is proportional to the square of the particle size. We have run our experiment using three different particle sizes, 240, 510 and 840 nm beads. The concentration profiles for the polymer beads are shown in Figure 5-13 for the three different sizes. It is clear from the figure how the dynamics evolution of the concentration profile is quite different for the three different sizes. This effect can be exploited in a variety of applications, such as the usage of this
behavior to separate non-magnetic particles in the submicron range based on their size.

5.1.7 Effect of magnetic fluid concentration

The magnetophoretic mobility of the polymer beads is linearly proportion to the difference in the magnetic susceptibility between the polymer beads and the surrounding magnetic fluid. For the relatively dilute magnetic fluids considered here, this difference is a linear function of the concentration of the magnetic particles in the mixture, according to

\[
\Delta \chi = \phi \chi_0,
\]

where \( \phi \) is the volume fraction of the magnetic particles and \( \chi_0 \) is their magnetic susceptibility.

The mobility is also inversely proportional to the viscosity of the magnetic fluid, which is generally a linear function of concentration, usually written as

\[
\eta = \eta_0 \left( 1 + \frac{5}{2} \phi \right).
\]

Hence, increasing the concentration of the magnetic particles from \( \phi_1 \) to \( \phi_2 \) is expected to increase the mobility of the polymer beads according to the ratio

\[
\frac{\phi_2}{\phi_1} \left( 1 + \frac{5}{2} \phi_1 \right).
\]

Figure 5-14 shows the concentration profiles for the polymer beads after 1780 s from the start of the experiment using three different concentrations of the magnetic particles, which clearly confirm the expected trend. The concentrations used are 0.5%, 1% and 1.5% by weight. Increasing the concentration further is expected to influence the mobility of the non-magnetic particles according to Equation 5.8. This is confirmed by plotting the ratio

\[
\frac{\phi}{1 + \frac{5}{2} \phi}
\]
on the left y axis as well as a plot of the experimental normalized concentration taken from Figure 5-14 at 6 mm versus the volume fraction of the magnetic particles, as shown in Figure 5-15. The concentration of the magnetic particles can be increased to as high as the synthesis procedure allows. However, with higher concentrations of the magnetic particles, the absorption of both the excitation and the emitted light increases, rendering optical measurements more difficult.

5.1.8 Effect of concentration of polymer beads

The absolute value of the initial concentration of the polymer beads is not expected to affect the normalized concentration profile measured in the course of the experiments. This was verified by repeating the experiment for three different initial concentrations, 0.2%, 0.4% and 0.6%. The results, depicted in Figure 5-16, show that the polymer beads concentration does not have a significant effect on the concentration profile and on the magnetophoretic migration of the beads, at least within the range of low concentration used in this thesis.
Figure 5-15: Plot showing the effect of the volume fraction of the magnetic particles on the ratio shown in Equation 5.9 and the experimental values for the normalized concentration at three different volume fractions.

Figure 5-16: Concentration profile for the 510 nm particles after 2000 s at 0.2%, 0.4% and 0.6%.
5.1.9 Effect of small changes in the magnet separation distance

The magnetic fluid cell consists of two magnets on the two sides of a capillary tube. The location of these two magnets can be controlled independently and precisely. In order to elucidate the effect of the small changes of the magnets separation distance, we plot the measured concentration profile of 510 nm particles in 1.5% magnetic fluids after 100 minutes at different separation distances in the following figures.

In Figure 5-17, there are two spikes, one at 0 mm and the other at 8 mm. The width and height of the spikes at any given moment are a function of the separation between the two magnets. Changes as small as 30 μm resulted in significant changes to the spike as is clear in Figure 5-17(b).

In order to understand the reasons behind the spike formation, consider the following. If the magnets are not perfectly aligned, localized high magnetic field gradients are established, especially at the edges. These high gradient will force the particles to concentrate quickly at the edges of the magnets. Hence, any small misalignment of the magnets would result in the formation of the spike at the edge. Since the magnetometer probe has a characteristic dimension of 3-4 mm, it is not possible to use it for measuring the variation in the magnetic field that occurs in one order of magnitude smaller than length scale.

Although there is a point of zero force at the center of the magnet, particles do not accumulate there because it is an unstable point. Since the magnetic field gradient is relatively small at this point, the particles exhibit a smaller force exactly at the centerline of the magnets. If the particles are perturbed in any direction, the magnetophoretic forces push the particles away from the center. However, if the magnets are misaligned, there exists a small region in which the direction the force is changed which causes particles to be trapped in this region and, thus, forming a small spike as observed in Figure 5-17.
Figure 5-17: Concentration profile for 510 nm particles in 1.5% magnetic fluid after 100 minutes when the magnets were moved in small steps
5.2 Continuous separation

One of the potential applications of magnetophoresis in magnetic fluids is in the separation of submicron particles. In this section, we present a simple device that was designed and built to perform crude separation to show the feasibility of such process. The device has one inlet streams and two outlet streams. On pumping magnetic fluid containing a certain concentration of non-magnetic polymer beads through the device, the magnetophoretic forces would act on the beads and affect their distribution inside the tube. Thus, the outlet streams would have different concentrations which would provide one successful separation step.

The simple device was made of PVC tubing and a T connection inserted between two permanent magnets as shown in Figure 5-18. The locus of the maximum force was calculated assuming axisymmetry along the axis of the two magnets. The measured magnetic field was approximated by a polynomial which was substituted in the force equation. The maximum force is at the point where the magnitude of $\frac{dH^2}{dx}$ is maximum. The plot in Figure 5-7 shows that this maximum occurs at distance of about 2.5 mm from the center of the magnet.

To build the device a larger magnet (1") was used to allow for more space to pass the tubing. For the large magnet, the distance of maximum force is 10 mm, which was calculated using the same procedure.
Consider the schematic diagram shown in Figure 5-18. A Magnetic fluid containing non-magnetic particles flows through a tube that passes along a part of the locus of the maximum force. Then the flow is divided into two outlets. As they flow between the magnets, the non-magnetic particles would suffer magnetophoresis forces repelling them away from the magnets. If the flow is divided along the center of the tube into two outlet streams, one stream would be have a higher concentration of the non-magnetic particles than the other one.

The PVC tubing has a inside diameter of $\frac{1}{32}\"$. A T-shaped connector is used to achieve the flow separation. A syringe pump (Orion Sage Model M365) was used with a 1 mL syringe to pump the fluid. The outlet tubes were also connected to the same pump to have the fluid equally sucked to ensure equal pressure and balanced flow distribution. The linear velocity of the fluid in the tubing was 5 mm/min. This arrangement was not optimized to obtain the best operating conditions. Its purpose is merely to demonstrate the feasibility of building a continuous separation device based on the ideas of magnetophoresis in magnetic fluids developed in this study. An image of this simple devise is shown in Figure 5-19.

![Figure 5-19: A photographic image of the simple separation device](image)

The inlet composition was feed mixture was varied. In the first experiment, the inlet feed contained a mixture of 840 nm particles and magnetic particles. In the second experiment, the feed contained a mixture of 190 nm and 510 nm particles and the magnetic particles.

130
The concentration of the particles is proportional to the magnitude of the intensity at their emission wavelength when excited with the appropriate wavelength. Fluorescence measurements for each sample were repeated three times using a SPEX Industries fluorometer.

5.2.1 Results and discussion

Figure 5-20 shows the results for four different sizes. The y-axis is the separation factor defined as the concentration of the polymer beads in the outlet stream divided by the their concentration in the feed stream. With the current simple arrangement, the separation factors for particles 190 nm and smaller are close to one. However, separation factor for 510 and 840 nm particles change considerably.

It is clear that a significant change in the concentration was achieved using this simple device. This creates a potential for further study to develop a complete separation system. The magnetic field can be designed to create a high force on the non-magnetic particles. This will allow increasing the throughput of such separation by increasing the linear velocity of the flow or by increasing the tubing diameter.
A two-dimensional flow with multiple outings can be designed with the appropriate magnetic field profile to fractionate particles on the basis of their size. Concepts used in electrophoresis [8] and field flow fractionation [9] can be used to use the principles developed to establish a continuous analysis or separation method. In brief, this section establishes the feasibility of building continuous high-throughput separation devices or more effective analysis techniques using the concepts of magnetophoresis in magnetic fluids. Possibilities exist for novel techniques that can be optimized for the particular separation at hand.

5.3 Summary and conclusions

In this chapter, we presented an experimental investigation of magnetophoresis in magnetic fluids. We have built a fluorescence measurement setup to capture the migration of polymer beads in an inhomogeneous magnetic field. The polymer beads were fluorescently tagged and were mixed in custom-made magnetic fluids synthesized according to the procedure outlined in Chapter 2. We obtained the normalized concentration of the polymer beads as a function of time. We have performed a series of experiments to investigate the effect of the important parameters. It was found that the magnetic field has a significant effect on the dynamics of the polymer concentration profile. Increasing the magnetic field gradient, for example, causes the increase in the migration rate of the particles as well as the maximum concentration at the focusing point. Other important parameters are the particle size and the magnetic fluid concentration. Larger particles migrate faster and accumulate more at the focusing point. Increasing the magnetic fluid concentration resulted in an enhanced effect on the migration of the particles. A particularly interesting observation with regards to spike formation at the center and edge of the magnets was investigated experimentally. It was explained experimentally to be due to high localized gradients at the edges due to small misalignment of the magnets.

The most important finding of this chapter is the possibility to manipulate non-magnetic particles remotely through the use of magnetic fields. A mixture of different
particles can be made to migrate at different rates when placed in a magnetic fluid. This is a significant finding that can be further developed into a variety of applications. For example, this phenomenon can be developed further to be used in the separation of particles according to their particle size. Since there is very low shear forces with the migration of the particles, it can be used to separate shear-sensitive cells. It can also be made into a continuous process, thus, providing a viable alternative to current particle separation methods. To show the feasibility of such separation method, we have built a simple continuous separation device that illustrate the possibility of the separation of submicron particles.

One current application of magnetophoresis is to cause a density gradient for proteins, DNA, and diamagnetic cells over a small distance [10,11]. This is analogous to electrophoresis, a standard biochemical analytical method. Replacing water with magnetic fluid in such applications can greatly enhance the effectiveness of separations and reduce the magnetic field requirements.

Obviously more studies need to be done to tailor magnetophoresis in magnetic fluids to any particular application. Yet, this chapter provides essential fundamental understanding for pursuing such an endeavor.
Bibliography


Chapter 6

Magnetophoresis Modelling

In this chapter, we present a model for the diffusion of the magnetic particles and the polymer beads in the presence of an applied magnetic field. The mixture can be represented as three components (1) water, (2) magnetite particles and (3) colloidal non-magnetic particles. There is no total flow associated with this mixture which is placed under an inhomogeneous magnetic field. Following is a formal Stefan-Maxwell approach for the derivation of the conservation equations governing the motion of the particles.

6.1 Conservation equations

The driving force acting on a species $i$, $d_i$, is defined as [1]

$$cRTd_i = c_i \nabla_T p \mu_i + (c_i \bar{V}_i - \omega_i) \nabla p - \rho_i \left( g_i - \sum_{k=1}^{n} \omega_k g_k \right) ,$$  

(6.1)

where $c$ is the total molar concentration, $\mu_i$ is the chemical potential of species $i$ per mole, $c_i$ is the molar concentration of species $i$, $\bar{V}_i$ is its volume per mole, $\omega_i$ is its mass fraction, $p$ is the pressure, and $\rho_i$ is the mass concentration of species $i$. Although Equation 6.1 assumes the mixture to be dilute, it can be applied for thermodynamically non-ideal mixtures [2].

To represent a suspension of particles, Equation 6.1 was rewritten in terms of
number density rather than molar concentration as follows

\[ nkT \mathbf{d}_i = n_i \nabla T \mu_i + (c_i \tilde{V}_i - \omega_i) \nabla p - \rho_i \left( \mathbf{g}_i - \sum_{k=1}^{n} \omega_k \mathbf{G}_k \right), \quad (6.2) \]

where \( n \) is the total number density of the particles, \( n_i \) is the number density of species \( i \), and \( \mu_i \) and \( \tilde{V}_i \) are redefined to be per particle.

The first term in Equation 6.2 is the driving force due to the gradient in the chemical potential which includes diffusion and any non-ideal effects like electrostatic repulsion or excluded volume. The pressure term is negligibly small for liquids in the absence of very strong centrifugal fields and we will not consider it any longer. The third term is the driving force due to the different body forces. In the absence of electrical forces, we can write the total body force per unit mass acting on a particle as

\[ \mathbf{g}_i = \mathbf{g} + \mathbf{g}_m, \quad (6.3) \]

where \( \mathbf{g} \) is the gravitational force per unit mass.

An inhomogeneous magnetic field would cause a force on a non-magnetic particle in a magnetic medium. [3]

\[ \mathbf{F}_m = -\mu_0 V_p \mathbf{M} \cdot \nabla H, \quad (6.4) \]

where \( V_p \) is the volume of the particle, \( \mu_0 \) is the permeability of free space, and \( H \) is the magnetic field strength which is related to to the magnetic flux density via

\[ \mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}), \quad (6.5) \]

where \( \mathbf{M} \) is the magnetization of surrounding fluid. For water, \( M = 0 \), while for a magnetic fluid \( \mathbf{M} \) has the direction of the applied field and its magnitude is equal to \( \chi_f H \) where \( \chi_f \) is the magnetic susceptibility of the magnetic fluid. Hence, we can write the magnetic force acting on a non-magnetic particle in a magnetic fluid as

\[ \mathbf{F}_m = -\frac{\chi_f V_p}{\mu_0 (1 + \chi_f)} \left( \mathbf{B} \cdot \nabla \right) \left( \frac{\mathbf{B}}{1 + \chi_f} \right). \quad (6.6) \]
In the case of dilute magnetic fluid in which $\chi_f \ll 1$, we can approximate the force equation to

$$F_m = -\frac{\chi_f V_2}{\mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B}, \quad (6.7)$$

which has the same form as the magnetic force acting on a magnetic particle in a nonmagnetic medium but only differs in sign.

We may write the magnetic body force per unit mass acting on a particle

$$g_m = \frac{\Delta \chi}{\rho_p \mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B}, \quad (6.8)$$

where $\rho_p$ is the density of the particle.

Since magnetite particles have high magnetic susceptibility compared to the surrounding medium, we can write

$$g_2 = g + \frac{\chi_2}{\rho_{p,2} \mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B}, \quad (6.9)$$

where $\rho_{p,2}$ is the density of the magnetic particle.

The medium surrounding the non-magnetic particles is in effect magnetic fluid with magnetic susceptibility of $\chi_f$.

$$g_3 = g - \frac{\chi_f}{\rho_{p,3} \mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B}, \quad (6.10)$$

where $\rho_{p,3}$ is the density of the colloidal non-magnetic particles.

Substituting Equations 6.9 and 6.10 in Equation 6.2, we get

$$nkT d_2 = n_2 \nabla T \rho_2 - \frac{(\mathbf{B} \cdot \nabla) \mathbf{B}}{\mu_0} \rho_2 \left[ \frac{\chi_2}{\rho_{p,2}} (1 - \omega_2) - \frac{\omega_3}{\rho_{p,3}} \chi_f \right]$$

and

$$nkT d_3 = n_3 \nabla T \rho_3 + \frac{(\mathbf{B} \cdot \nabla) \mathbf{B}}{\mu_0} \rho_3 \left[ \frac{\chi_f}{\rho_{p,3}} (1 - \omega_3) + \frac{\omega_2}{\rho_{p,2}} \chi_2 \right]. \quad (6.11)$$

For dilute magnetic fluid, the fluid magnetic susceptibility is a linear function of
the volume fraction of magnetite, $\phi$,

$$x_f = \phi x_2 + (1 - \phi) x_1,$$

(6.12)

where $\phi$ is the volume fraction of the magnetic core and $x_1$ is the magnetic susceptibility of water which can be negligibly small. Hence the magnetic susceptibility of the magnetic fluid is simply

$$x_f = \phi x_2.$$  (6.13)

Since the solution is dilute, we will use the pseudobinary assumption. This assumption is also valid in the focusing points where the maximum volume fraction of the polymer beads is below 2%. In dilute mixture, the diffusional flux of solute $i$ is written generally as

$$J_i = -D_i n_i d_i.$$  (6.14)

Using Equations 6.11 and 6.11, we get

$$J_2 = -\frac{D_2}{kT} \left\{ n_2 \nabla_{T,p} \mu_2 - \frac{(B \cdot \nabla) B}{\mu_o} \rho_2 \left[ \frac{x_2}{\rho_{p,2}} (1 - \omega_2) - \frac{\omega_3}{\rho_{p,3}} x_f \right] \right\}$$  (6.15)

and

$$J_3 = -\frac{D_3}{kT} \left\{ n_3 \nabla_{T,p} \mu_3 + \frac{(B \cdot \nabla) B}{\mu_o} \rho_3 \left[ \frac{x_f}{\rho_{p,3}} (1 - \omega_3) + \frac{\omega_3}{\rho_{p,2}} x_2 \right] \right\}.$$  (6.16)

Since there is no fluid flow or chemical reaction, the conservation equation for species $i$ is simply

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot (J_i + n_i v).$$  (6.17)

We will neglect the convective flux term in comparison with the diffusion flux. This assumption will be validated later by comparing the magnitudes of the two terms.
Using the flux equations for species 2 and 3, we get

\[
\frac{\partial n_2}{\partial t} = \frac{D_2}{kT} \nabla \cdot \left\{ n_2 \nabla T, \rho \mu_2 - \frac{(B \cdot \nabla) B}{\mu_o} \frac{\psi}{\rho_2} \left[ \frac{X_2}{\rho_{p,2}} (1 - \omega_2) - \frac{\omega_3}{\rho_{p,3}} \chi_f \right] \right\}
\]  \hspace{1cm} (6.18)

and

\[
\frac{\partial n_3}{\partial t} = \frac{D_3}{kT} \nabla \cdot \left\{ n_3 \nabla T, \rho \mu_3 + \frac{(B \cdot \nabla) B}{\mu_o} \frac{\psi}{\rho_3} \left[ \frac{X_f}{\rho_{p,3}} (1 - \omega_3) + \frac{\omega_2}{\rho_{p,2}} \chi_2 \right] \right\}. \hspace{1cm} (6.19)
\]

6.2 The chemical potential

To correctly describe the chemical potential of the polymer beads, we must include the excluded volume effect and the electrostatic repulsion effect that would become important at the focusing point. In this case, the chemical potential should contain a term that represents the effect of the physical volumes of the particles and the interparticle interactions on the driving force.

In general, the chemical potential of species \(i\) is given by

\[
\mu_i = \mu_i^0 + kT \ln (x_i) + \mu^{ex},
\]  \hspace{1cm} (6.20)

where \(x_i\) is the mole fraction of species \(i\).

Here, we present a formula for describing the excess chemical potential due the electrostatic repulsion.

6.2.1 The electrostatic repulsion

Modelling the polymer beads as hard spheres does not account for all non-idealities at the focusing point. When the beads are in close proximity, they repel each other due to the electrostatic forces. The maximum concentration attainable at one point will be a function of the strength of the electrostatic repulsion. Hence, one must model the effect of the electrostatic repulsion on the chemical potential of the polymer beads in order to have a more accurate representation of the concentration profile. The
electrostatic repulsion was included in the model through derivation of the excess chemical potential due to electrostatic repulsion following the framework of [4].

The excess chemical potential of the polymer can be obtain from an expression for the excess Gibbs free energy as follows:

\[ \mu^{ex} = \left( \frac{\partial G^{ex}}{\partial N_p} \right)_{T,P,N_k \neq p}, \tag{6.21} \]

where \( N_p \) is the number of polymer particles, \( N_k \neq p \) is the number of non-polymer particles (magnetic particles or water molecules) in the mixture, and \( T \) and \( P \) are the absolute temperature and pressure.

In order to derive an expression for \( G^{ex} \), we first derive an expression for the electrostatic contribution to the excess internal energy of the mixture, from which the electrostatic contribution to the excess Helmholtz free energy \( A^{ex} \) can be evaluated as follows.

\[ A^{ex} = U^{ex} - TS^{ex}, \tag{6.22} \]

where \( S^{ex} \) is the electrostatic contribution to the excess entropy of the mixture. Once an expression for \( A^{ex} \) is available, \( G^{ex} \) can be evaluated as follows

\[ G^{ex} = A^{ex} + PV^{ex}. \tag{6.23} \]

As a first approximation, the electrostatic contribution to the excess entropy and volume will be assumed to be zero and, hence, the excess chemical potential of the polymer particles can be written as

\[ \mu^{ex} = \left( \frac{\partial U^{ex}}{\partial N_p} \right)_{T,P,N_1,N_2}, \tag{6.24} \]

where \( N_1 \) is the number of water molecules and \( N_2 \) is the number of magnetic particles.

The expression for \( U^{ex} \) can be written as follows [5]

\[ U^{ex} = \frac{1}{2} \int_{2a}^{\infty} N_3 u(r) C_3 4 \pi r^2 dr, \tag{6.25} \]
where $r$ is the radial distance from the center of the polymer particle, $u(r)$ is the interaction potential between the polymer particles, $C_3$ is the number density (number/m$^3$) of the polymer particles in the mixture, $N_3$ is the number of polymer particles in the mixture and $a$ is the radius of the polymer particle. Figure 6-1 shows a schematic diagram for this equation. Since the lower limit of integration in Equation 6.25 is the diameter of the particle, the effect of the excluded volume of the particles is included in this analysis.

For thick double layers, the electrostatic repulsion can be written as follows [6].

$$u(r) = \frac{4\pi a^2 \epsilon \Psi_0^2}{r} \exp\left(-\kappa (r - 2a)\right),$$  \hspace{1cm} (6.26)

where $\epsilon$ is the dielectric constant of the medium (water), $\Psi_0$ is the electrostatic potential at the surface of the polymer particle, $\kappa$ is the Debye-Hückel parameter and $r$ is the distance between the centers of two approaching particles.
Thus the excess internal energy can be written as
\[
U^{ex} = 8\pi^2 a^2 \epsilon_o \epsilon_r \Psi_o^2 \left( \frac{2a\kappa + 1}{\kappa^2} \right) N_3 C_3.
\] (6.27)

We can write the number density of the polymer beads, \( C_3 \), as
\[
C_3 = \frac{N_3}{N_1\omega_1 + N_2\omega_2 + N_3\omega_3},
\] (6.28)

where \( \omega_1, \omega_2 \) and \( \omega_3 \) are the effective volumes of one water molecule, one magnetic particle, and one polymer bead, respectively.

The combination of equations 6.24, 6.25 and 6.26 yields the following expression for \( \mu^{ex} \).
\[
\mu_3^{ex} = 8\pi^2 a^2 N_A \epsilon_o \epsilon_r \Psi_o^2 \left( \frac{2\kappa a + 1}{\kappa^2} \right) C_3 (2 - \phi_3),
\] (6.29)

where \( N_A \) is Avogadro's number.

### 6.3 Model nondimensionalization

The following non-dimensional parameters were used in our model:

\[
\Theta_i = \frac{c_i}{c_{i,o}},
\] (6.30)

\[
X = \frac{x}{L'},
\] (6.31)

\[
\tau = \frac{D_2}{L^2} t,
\] (6.32)

\[
\alpha_3 = \frac{D_3}{D_2},
\] (6.33)

\[
\Psi_i = \frac{X_2\mu_o}{2c_{o,i}RT} H^2,
\] (6.34)

and

\[
\Omega = \frac{16\pi^2 a^2 \epsilon_o \epsilon_r N_A^2}{RT} \left( \frac{2a\kappa + 1}{\kappa^2} \right) \Psi_o^2 c_3,o.
\] (6.35)
We then write the conservation equations in one dimension as

\[
\frac{\partial \Theta_2}{\partial \tau} = \frac{\partial}{\partial X} \left\{ \frac{\partial \Theta_2}{\partial X} - \rho_{2o} \frac{d}{dX} \Psi_2 \Theta_2 \left[ (1 - \omega_{2o} \Theta_2) + \frac{\omega_{3o}}{\rho_{p,3}} \rho_{2o} \Theta_3 \Theta_2 \right] \right\} \tag{6.36}
\]

and

\[
\frac{\partial \Theta_3}{\partial \tau} = \alpha_3 \frac{\partial}{\partial X} \left\{ \frac{\partial \Theta_3}{\partial X} + \Omega \Theta_3 (1 - \phi_{3,o} \Theta_3) \frac{\partial \Theta_3}{\partial X} \right. \\
&\quad + \left. \rho_{2o} \frac{d}{dX} \Psi_3 \Theta_3 \left[ \frac{\rho_{2o}}{\rho_{p,3}} \Theta_2 \left( 1 - \omega_{3o} \Theta_3 \right) + \omega_{2o} \Theta_2 \right] \right\} \tag{6.37}
\]

These two equations can be solved simultaneously to obtain the concentration profiles of the magnetic particles and the polymer beads as functions of time and distance. The initial conditions are constant uniform concentrations while the boundary conditions are symmetry at \( x = 0 \) and constant concentrations at infinity.

### 6.4 Model parameters

The particular system considered is that presented in the experimental section. The magnetic field profile used in the model is that of the simple configuration shown in Figure 6-2. The experimentally measured magnetic field was fitted to a polynomial which was subsequently used in the model. Since the probe of the magnetometer used to measure the magnetic field has finite dimensions, the magnetic field values at each point is in essence an average value over a distance of about 3 mm.

The values of the different parameters used are given in Table 6.1.

The diffusion coefficient of the magnetic particles was obtained from the dynamic light scattering experiments, while that of the polymer beads was calculated using the Stokes-Einstein equation

\[
D_3 = \frac{kT}{3\pi \eta d_3}, \tag{6.38}
\]

where \( \mu \) is the magnetic fluid viscosity, and \( d_3 \) is the particle diameter. The viscosity
Figure 6-2: The strength of the magnetic field and the magnetic force along the center line of the magnetic fluid cell

Table 6.1: Values of the different parameters used in the magnetophoresis model for the 840 nm particles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_2$</td>
<td>Magnetic susceptibility</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Permittivity of free space</td>
<td>$4\pi \times 10^{-7}$</td>
<td>Tm/A</td>
</tr>
<tr>
<td>L</td>
<td>Characteristic length</td>
<td>$10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>8.314</td>
<td>J/(mole K)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>298</td>
<td>K</td>
</tr>
<tr>
<td>$c_{2,o}$</td>
<td>Initial concentration</td>
<td>0.0145</td>
<td>moles of particles / m$^3$</td>
</tr>
<tr>
<td>$c_{3,o}$</td>
<td>Initial concentration</td>
<td>$9.11 \times 10^{-8}$</td>
<td>moles of particles / m$^3$</td>
</tr>
<tr>
<td>$\omega_{2,o}$</td>
<td>Initial mass fraction</td>
<td>0.0177</td>
<td>-</td>
</tr>
<tr>
<td>$D_2$</td>
<td>Diffusion coefficient</td>
<td>$1.7191 \times 10^{-11}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_3$</td>
<td>Diffusion</td>
<td>$6.03 \times 10^{-13}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$\phi_{2,o}$</td>
<td>Initial volume fraction</td>
<td>0.0749</td>
<td>-</td>
</tr>
<tr>
<td>$\rho_{p,3}$</td>
<td>Density</td>
<td>1050</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{2,o}$</td>
<td>Initial mass concentration</td>
<td>18</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{3,o}$</td>
<td>Initial mass concentration</td>
<td>4</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\psi_o$</td>
<td>Polymer surface charge</td>
<td>0.035</td>
<td>V</td>
</tr>
</tbody>
</table>
of the magnetic fluid is a function of its concentration and is given by [3]

$$\eta = \eta_0 \left(1 + \frac{5}{2} \phi_2\right),$$  \hspace{1cm} (6.39)

where \(\eta_0\) is the viscosity of the carrier liquid. This equation was incorporated into the model to account for the different magnetic fluid concentration used in the parametric study.

### 6.5 Results and discussion

The set of partial differential equations developed above was solved using the MATLAB® software package of MathWorks. Figure 6-3 shows plots of the evolution of the dimensionless concentration profile of the magnetic particles, while Figure 6-4 shows plots of the evolution of the dimensionless concentration profiles for the 510 and 840 nm polymer beads.

Figure 6-3 shows that the magnetic particles move slowly towards the center of the
Figure 6-4: The numerical results of the dynamic evolution of the polymer beads concentration profile
magnets and that the effect of the magnetophoretic forces on the magnetic particles is small in the time frame used in the model. As shown in Figures 6-4(a) and 6-4(b), the model captures the experimentally observed dynamic behavior of the polymer beads, which move rather quickly towards the point of zero magnetic force where the magnetic field and force are equal to zero, and they get depleted from the region between the magnet and the focusing point. Their flux decreases significantly as the particles approach the point of zero force and hence they accumulate in the region before it. In their journey towards the point of zero force, they have a strong initial acceleration, but as they proceed to the last stages of their journey, they lose stamina, and slow down drastically. Given sufficient time, the maximum concentration would gradually move to the point of zero force.

Afterwards, the concentration of the particles at the focusing point decreases slowly with time due to diffusion. This relaxation period is not considered here because the focusing effect has a more technical interest than the relaxation of the peak at long times. However, the long time behavior of the focusing point is examined in details in section 6.5.7.

### 6.5.1 Results of modelling of the precision magnet translation system

The difference in the magnetic force profile between the two configurations is clear from Figure 6-5. The maximum force of the precision-controlled configuration is more than twice as much as that of the simple configuration. The two force profiles also differ in one subtle, yet important, point. For the simple configuration, the slope of the increase of the magnetic force is greater than the slope of its decrease, whereas for the precision-controlled configuration, the rate of the increase of the magnetic force is less than the slope of the decrease after the maximum concentration.

The model was used to simulate the evolution of the concentration profile under the high magnetic field used in the precision controlled magnet translation system. The results for the 240 nm, 510 nm and 840 nm particles are shown in Figure 6-6.
Figure 6-5: The gradient of the square of the magnetic field strength along the center line of the magnetic fluid cell for the simple and the precision-controlled configuration.

For the 240 nm particles, Figure 6-6(a) shows how the model predicts the dynamic evolution of the concentration profile. The particles behavior in this case is similar to their behavior in the simple configuration. They migrate away from the magnet towards the point of zero force. The figure also shows a dip at the concentration before the focusing point. This dip was not present in the concentration profile predicted for the simple configuration. In the case of the precision-controlled configuration, the rate of the migration of the particles towards the point of maximum force is greater than the rate of their migration from the point of maximum force to the point of zero force. This resulted in a dip of the concentration, which was present in the case of the simple configuration.

Figure 6-6 also shows some humps in the concentration profiles at the small distances. Since the experimentally-measure magnetic field was approximated into a function using the cubic-spline interpolation method, the regions between the experimental points exhibit artificial variations that would lead to the humps seen in the figure.
Figure 6-6: Model prediction for the evolution of the polymer beads under the high-magnetic field case.
The 510 and 840 nm particles show similar behavior, as plotted in Figures 6-6(b) and 6-6(c), respectively. However, their mobility increases with their size. Such difference in the rate of migration among the different sized particles can be used as the basis for their separation.

### 6.5.2 Comparison with experiment

Although there are some subtle experimental peculiarities that are not captured by the model, the model does capture the major features and trends. A representative comparison is done by considering the simulation of the 840 nm particles as shown in Figure 6-7.

Figure 6-7 shows that the a priori predictions are in reasonable agreement with the experimental results, since all the general features are captured. The model predicts the experimental observation that the peak moves gradually towards the point of zero force. It also predicts the maximum concentration at the focusing point. The model differs, however, in a few details. It predicts a broader peak and a slower dynamics. The depth of the dip after the focusing point was not predicted favorably by the model.

The difference in the breadth of the peak is related to the representation of the electrostatic repulsion between the particles. The model predicts stronger repulsions. It is important to note that the electrostatic repulsion model developed in section 6.2.1 contained few assumptions such as using the mean field approximation and only including the pair-wise interactions. For better performance, some of these assumptions would need to be relaxed.

The magnetic field measured by the magnetometer was used as an input to the magnetophoresis model. The probe measures an average value over a distance of about 3 mm. This averaging effect would result in a smoothening of the magnetic field. Hence, it is unexpected that the model would predict highly localized effects that are due to changes in the field gradients smaller than that of the magnetometer resolution. This explanation provides a possible reason the model did not predict the dip that occurs after the focusing point.
Figure 6-7: The numerical results of the dynamic evolution of the polymer beads concentration profile
Also, since the developed is one-dimensional, it is expected that it will not capture all the effects of the three-dimensional experimental system.

6.5.3 Parametric study

The effect of the particle size on both the maximum concentration at the focusing point and the maximum flux is shown in Figure 6-8. The maximum concentration shown is normalized by the initial concentration. While the maximum flux is normalized according to the flux terms in Equation 6.37.

![Graph showing the effect of particle size on maximum concentration and flux](image)

Figure 6-8: Effect of particle size on the maximum concentration at the focusing point and the maximum flux

As expected the maximum concentration increases with the increase of the particle size in the range of interest, providing the basis for establishing size-based separation process. The maximum flux is a good way to represent the initial dynamics of the system. It is also shown that larger particles react more quickly to the magnetic field.

In all the experiments, the concentration of the magnetic fluid was limited to 1% because larger concentrations would make it difficult to visualize the fluorescent beads as the fluid as the fluid becomes less transparent preventing the transmission of light. However, the model can give us a good estimation for the effect of magnetic
fluid concentration on the magnetophoretic focusing. It is expected that higher magnetic fluid concentration would increase the difference in the magnetic susceptibility between the polymer beads and their surrounding medium, which in turn would increase the forces on the polymer beads. The magnetic fluid concentration was varied in the simulation the resulting maximum concentration and maximum flux are shown in Figure 6-9.

![Graph showing the effect of magnetic fluid concentration on the maximum concentration at the focusing point and the maximum flux.](image)

**Figure 6-9:** Effect of magnetic fluid concentration on the maximum concentration at the focusing point and the maximum flux.

Figure 6-10 shows the effect of the particle size at different magnetic fluid concentrations. Larger particles concentrate more at the focusing point. Also the increase in the magnetic fluid concentration increases the magnetophoresis effect. However, this increase is not linear as is clear by the curves of the 2 and 5% magnetic fluid. As described in section 5.1.7, increasing the magnetic fluid concentration has two opposing effects, it increases the differences in the magnetic susceptibility and it increases the viscosity. Since it is challenging to perform experiments on concentrated magnetic fluids because of optical difficulties, the model provides an alternative for predicting the evolution of the concentration profiles.

155
Figure 6-10: Effect of particle size on the maximum concentration at the focusing point for different magnetic fluid concentration

6.5.4 Model utilization

Since we can run the model using different variables such as the magnetic field profile or the initial concentration distribution, we can use the model to aid us in the design of new processes. We used the model to demonstrate the separation concepts by monitoring the evolution of an initial pulse of particles containing a mixtures of 510 and 840 nm particles. The initial conditions for the model was modified to simulate a square pulse of polymer beads concentrated at the magnet at the beginning of the run. When the magnetic field is turned on, the model captures the dynamic effect of the concentration profile as the polymer beads move towards the focusing point. The initial concentration of the polymer beads is 0.4% for x less than 1 mm and zero elsewhere.

Figure 6-11 shows the evolution of the concentration profiles for the 540 and the 840 nm particles. The dynamics of the change in the distribution is a function of the particle size. Although different size particles accumulate at the same focusing point, their path to this point varies significantly because they have different mobilities.
Figure 6-11: Evolution of concentration profile after introducing an equal concentration of 510 and 840 nm particles at the magnet. Time values are in minutes

This phenomenon can be exploited to separate particles by removing the magnetic field, and hence stopping their migration, at a midpoint during the experiment. In our example, the distributions of the particles are significantly different at 30 minutes and hence they can be separated with good efficiency.

Since the particles migrate at different rates, it is expected that their distribution would be a strong function of time. As shown in Figure 6-11, complete separations can be attained at some point in time. The maximum concentration for the different particles is a function of the particle size and hence change in the relative concentration of the particle is also attained during this process. This simple phenomenon can be exploited further to establish a separation technique for different submicron sized particles.

6.5.5 Evolution of the flux terms

The purpose of this section is to gain more insight from the model as to the behavior of our system in the short time and equilibrium limits. To be able to make meaningful
approximations, we use the full numerical solution to plot the different flux terms for the 840 nm particles and for the magnetic particles. Figure 6-12 shows the magnetic, non-ideal diffusion due to electrostatic interactions and ideal diffusion flux terms.

Figure 6-12: The dimensionless flux terms for the 840 nm particles at different times

These are the three dimensionless flux terms inside the curly braces of Equation 6.37. The first dimensionless term represents the flux due to the concentration gradient diffusion, the second term represents the dimensionless flux due to the electrostatic repulsion effects and the third term represents the dimensionless flux due to the magnetophoretic force.

Initially, the magnetic flux, shown in Figure 6-12(a) is higher at the region between the magnet center and the focusing point. As time goes on, most of the particles migrate towards the focusing point and hence the concentration decreases significantly.
at this region, thereby, decreasing the flux. The flux peak moves with the particles
towards the focusing point. The electrostatic flux term, shown in Figure 6-12(b) shows
an opposite effect. Initially, it is relatively small and can be neglected. However, as
the particles accumulate near the focusing point, and they come closer together, the
electrostatic repulsion forces become more important and hence the electrostatic flux
term is most important at the vicinity of the focusing point. As for the diffusion flux,
shown in Figure 6-12(c), it resembles the electrostatic repulsion term in shape but its
value is at least two orders of magnitude smaller and can be neglected.

Figure 6-13 shows the magnetic and the diffusion flux terms for the magnetic
particles. The magnetic flux term is two orders of magnitude less than its counterpart
for the polymer beads. This explains the significantly slow mobility of the magnetic
particles that was predicted by the model. The magnetic flux term, shown in Figure 6-
13(a) does not change during the course of the simulation, while the diffusion flux
term, shown in Figure 6-13(b) follows the gradient of the concentration. The latter
is 1-2 orders of magnitude less than the former and thus is not as important.

It is clear from the figures showing the different flux terms that the diffusion
term is negligible compared to the magnetic and the electrostatic repulsion terms for
the polymer beads. Initially, the magnetic term is the dominant one. However, this
term decreases while the electrostatic repulsion term increases until they balance each
other. The change in the concentration of the magnetic particles in the time frame
of our model is negligible and its effect on the concentration profile of the polymer
beads can be neglected. Based on the above discussion, we can simplify our model by
removing the ideal diffusion term and by removing the dependence on the magnetic
particles concentration from the polymer beads conservation equation (Equation 6.37)
as follows

$$
\frac{\partial \Theta_3}{\partial \tau} = \alpha_3 \frac{\partial \Theta_3}{\partial X} \left\{ \Omega \Theta_3 (1 - \phi_{3,o} \Theta_3) \frac{\partial \Theta_3}{\partial X} + \frac{\rho_{3o}}{\rho_{mag}} \frac{d \Psi_3}{dX} \Theta_3 \left[ \frac{\rho_{2o}}{\rho_{p,3}} (1 - \omega_{3o} \Theta_3) \right] \right\} \quad (6.40)
$$

where \( \Omega \) is a dimensionless constant representing the electrostatic repulsion effect,
Figure 6-13: The dimensionless flux terms for the magnetic particles at different times
defined as
\[ \Omega = \frac{16\pi^2 a^2 \epsilon_{\alpha\epsilon} N_A^2}{RT} \left( \frac{2\alpha \kappa + 1}{\kappa^2} \right) \Psi_{o,\alpha}^2. \] (6.41)

### 6.5.6 Short time behavior

At short times, the dominant term in the conservation equation for the polymer beads is the magnetic term. Also at short times, the concentration of the magnetic particles remains constant and can be set to 1. The other terms can be neglected. So the equation would be simplified to
\[ \frac{\partial \Theta_3}{\partial \tau} = \alpha_3 \frac{\partial}{\partial X} \left\{ \frac{\rho_{3o}}{\rho_{mag}} \frac{d\Psi_3}{dX} \Theta_3 \left[ \frac{\rho_{2o}}{\rho_{p,3}} (1 - \omega_{3o} \Theta_3) \right] \right\}. \] (6.42)

Looking closely at the above equation, we find that at relatively dilute concentration, we can neglect the last term so that we are left with
\[ \frac{\partial \Theta_3}{\partial \tau} = \alpha_3 \phi_{2o} \phi_{3o} \frac{\partial}{\partial X} \left( \frac{d\Psi_3}{dX} \Theta_3 \right), \] (6.43)

where \( \phi_{2o} \) and \( \phi_{3o} \) are the volume fraction of the polymer beads and the magnetic core respectively. \( d\Psi/dX \) is of the order of \( 10^7 \) while \( \Theta \) is of the order of 1.

To make all the terms of order one, we define two new dimensionless constants, \( \psi \) and \( \tau_s \) short times as follows
\[ \psi_3 = \frac{\Psi_3}{\Psi_{3,\text{max}}} \] (6.44)

and
\[ \tau_s = \tau \alpha_3 \phi_{2o} \phi_{3o} \Psi_{3,\text{max}}, \] (6.45)

which allows us to write the short time response for the dimensionless concentration of the polymer beads as
\[ \frac{\partial \Theta_3}{\partial \tau_s} = \frac{\partial}{\partial X} \left( \frac{d\psi_3}{dX} \Theta_3 \right). \] (6.46)
The above relatively simpler equation is valid as long as the electrostatic repulsion term can be neglected compared to the magnetic term. Since \( \omega_{3,o} \sim \phi_{3,o} \) because the density of the polymer beads is close that of water and the concentration is small, we can write the criterion for validity of the short time analysis as

\[
\Omega \frac{\partial \Theta_3}{\partial X} \ll \phi_{2,o} \phi_{3,o} \frac{d \Psi_3}{dX}.
\]  

(6.47)

### 6.5.7 Long time simulation results

We performed long time simulation for the 840 nm particles suspended in 1% magnetic fluids. The total time captured in the simulation is \( 6 \times 10^8 \) s which is about a week. The purpose of this run is understand the relaxation process and the time scales involved.

The concentration of the particles is shown in Figure 6-14.

![Three dimensional representation of the model predictions](image)

Figure 6-14: Three dimensional representation of the model predictions for the dynamic evolution of the concentration profile

As the particles move towards the point of zero force, their maximum concentration increases until it reaches a maximum and decreases slowly afterwards. Plotting the dimensionless concentration profile at different times, we get Figure 6-15. As
shown in the figure, after the particles migrate to the focusing point, they slowly move away and the peak is relaxation. The high concentration gradient at the right hand side of the focusing point results in a diffusional driving force. Given sufficient time, the concentration levels off to 1. This is also clear on the plot the maximum concentration versus log time, as shown in Figure 6-16. The maximum concentration increases rather quickly, but then it slowly decreases as the particles diffuse away.

To understand the dynamic evolution of the concentration, it is worthwhile to plot the evolution of the dimensionless flux, which is related to the net driving force acting on the particles. The net flux is shown in Figure 6-17.

The flux is initially at its maximum value and decreases with time. Plotting the dimensionless flux profile at different times, we get Figure 6-18. The magnetic component of the flux equation is initially dominant but as the particles deplete away, diffusion dominates the peak relaxation period. Although the flux decreases, it has not reached zero after 7 days.
Figure 6-16: Maximum concentration versus log time

Figure 6-17: Three dimensional representation of the dimensionless flux versus distance and time
6.5.8 Steady state solution

We can arrive at the steady state solution by solving the zero flux equation. With some scaling assumptions, we can write the steady state solution as

$$\frac{\partial \Theta_3}{\partial X} + \Omega \Theta_3 \frac{\partial \Theta_3}{\partial X} + K \frac{d \Psi_3}{dX} \Theta_3 = 0,$$  \hspace{1cm} (6.48)

where $\Omega$ is a dimensionless constant representing the electrostatic repulsion effect, and $K$ is given by

$$K = \frac{\rho_{30}}{\rho_{mag}} \left[ \frac{\rho_{20}}{\rho_{p,3}} + \omega_{20} \right].$$  \hspace{1cm} (6.49)

The first term in Equation 6.48 represents the ideal diffusion term, while the second term represents the non-ideal diffusion due to the electrostatic repulsion. The third term represents the magnetophoretic flux term. These terms are the important terms in the flux equation. Since the non-ideal diffusion is a function of concentration, it becomes unimportant as the concentration approaches zero. In that case, the ideal diffusion term can not be neglected.
Equation 6.48 can be written as

\[
\left(\frac{1}{\Theta_3} + \Omega\right) d\Theta_3 = -Kd\Psi. \tag{6.50}
\]

On integration, we get

\[
\ln \Theta_3 + \Omega \Theta_3 = -K\Psi + C. \tag{6.51}
\]

To find the constant C, we use the far field boundary condition

\[
X \to \infty, \Psi \to 0, \Theta_3 \to 1. \tag{6.52}
\]

Hence,

\[
C = \Omega. \tag{6.53}
\]

We define a more appropriate dimensionless parameter for the magnetic field

\[
\Psi_m = K\Psi. \tag{6.54}
\]

Equation 6.51 becomes

\[
\ln \Theta_3 + \Omega (\Theta_3 - 1) = -\Psi_m. \tag{6.55}
\]

For the case of 840 nm particles under the simple configuration,

\[
\Omega = 717 \tag{6.56}
\]

and \(\Psi_m\) is given in Figure 6-19 as a function of \(X\).

Equation 6.55 was solved numerically for \(\Theta_3\) and the solution is plotted in Figure 6-20 which represents the steady state solution. Note that if \(\Psi_m \ll \Omega\), we can approximate \(\Theta_3\) by

\[
\Theta_3 = \exp (-\Psi_m). \tag{6.57}
\]
Figure 6-19: The dimensionless variable $\Psi_m$ versus distance

Figure 6-20: Steady state solution for $\Theta_3$ versus distance
6.5.9 Peak relaxation

Close to the magnets, the magnetophoretic force is substantial and pushes the particles to a barrier where the force goes to zero. There is a substantial concentration gradient established in the peak area, and this will lead to an eventual diffusional relaxation over very long periods of time. In that case, the governing equation is

\[
\frac{\partial n_3}{\partial t} = - \frac{dJ_3}{dy}
\]  
(6.58)

where \( n_3 \) is the normalized number density. The flux, \( J_3 \), is given by

\[
J_3 = -\frac{D}{kT} n_3 \frac{\partial \mu}{\partial y},
\]  
(6.59)

where \( \mu \) is the chemical potential per particle and \( n_3 \) is the number density. \( y \) starts from the point of zero force.

To arrive at a simple analytical expression for the time scale of the peak relaxation, we first consider the ideal chemical potential, the equation is simplified to

\[
\frac{\partial n_3}{\partial t} = D \frac{\partial^2 n_3}{\partial y^2}
\]  
(6.60)

with the boundary condition of \( \frac{\partial n_3}{\partial y} = 0 \) at \( y=0 \) and \( n_3 \) tends to 1 as \( y \) approaches infinity.

To find a solution for this equation, we need to select a suitable initial condition. A good approximation to the accumulation at the point of zero force is to have a square peak with a thickness of \( h \) with is in to the order of 1 mm. The normalized number density is equal to 1 elsewhere. Mathematically, the initial condition is written as

\[
n_3 = \begin{cases} 
  n_{3,o} & 0 < y < h \\
  1 & y > h 
\end{cases}
\]  
(6.61)
The solution is given by [7]

\[ n_3 = 1 + \frac{n_{3,0} - 1}{2} \left\{ \text{erf} \left( \frac{h - y}{2 \sqrt{(Dt)}} \right) + \text{erf} \left( \frac{h + y}{2 \sqrt{(Dt)}} \right) \right\}. \]  

(6.62)

Now we plot the solution at different times for the case of 840 nm particles with the peak initially at 4.68, which is the maximum value attained in the long-time simulation. This is shown in Figure 6-21.

![Figure 6-21: Concentration-distance curves for the diffusion of the particles starting from a square peak. Numbers on curves are time in seconds.](image)

Next, we get the time required for the concentration to reach \( \Theta_f \) which is a final value close to 1 by solving Equation 6.62 for time when \( \Theta_3 = \Theta_f \). Rewriting Equation 6.62 for \( y=0 \), we get

\[ 2 \left[ \frac{\Theta_f - 1}{\Theta_{3,0} - 1} \right] = 2 \text{erf} \frac{h}{2 \sqrt{(Dt)}}. \]  

(6.63)

The error function is approximated as follows

\[ \text{erf}(x) \sim 1 - \frac{\exp(-x^2)}{\sqrt{\pi}} \left( 1 - \frac{1}{2x^2} + \frac{1.3}{(2x^2)^2} - \ldots \right). \]  

(6.64)
For our scaling purposes, we can use the first term in Equation 6.64.

\[
\text{erf}(x) \sim 1 - \frac{\exp(-x^2)}{\sqrt{\pi}}.
\] (6.65)

Hence, we can write Equation 6.63 as

\[
\left[ \frac{\Theta_f - 1}{\Theta_{3,0} - 1} \right] \sim \left[ 1 - \frac{4Dt}{\sqrt{\pi h^2}} \exp \left( \frac{-h^2}{4Dt} \right) \right].
\] (6.66)

When the time is large, as in our case, the exponential term goes to 1. Now, we can get a time scale for the relaxation

\[
t \sim \frac{\sqrt{\pi h^2}}{4D} \left[ \frac{\Theta_{3,0} - \Theta_f}{\Theta_{3,0} - 1} \right].
\] (6.67)

The square bracket is of order one and hence we can write the time scale as

\[
t \sim \frac{\sqrt{\pi h^2}}{4D}
\] (6.68)

To compare with the full model results, we start with a square peak of the same height as the maximum height as that of the full model. Then we calculate the time for this square peak to diffuse till it gets a similar shape as that predicted by the full model. The time was \(10^5\) and the results are shown in Figure 6-22. The circles represent the full model results after 3000 s while the line represents the solution of the relaxation model after \(10^5\) s.

Now we plot the decay of the maximum concentration for both the relaxation model and the full model in Figure 6-23.

The decay of the full model is faster than that of the relaxation model which only includes the ideal diffusion. It is expected that the relaxation model would predict a much slower decay since it only includes the ideal diffusion. Whereas the full model captures the decay process due to both the ideal and non-ideal diffusion parts.

Including the non-ideal diffusion component of the chemical potential, the conser-
Figure 6-22: Adjustment for the initial peak

Figure 6-23: Maximum concentration decay with time for the full model 'o' and the relaxation model '.'
vation equation can be written as

\[
\frac{\partial \Theta_3}{\partial \tau} = \alpha \frac{\partial}{\partial Y} \left[ \frac{\partial \Theta_3}{\partial Y} + \Omega \Theta_3 \frac{\partial \Theta_3}{\partial Y} \right].
\] (6.69)

For the concentration range of interest, the dominant flux term in Equation 6.69 is the non-ideal diffusion part. We can write the conservation equation as

\[
\frac{\partial \Theta_3}{\partial \tau} = \alpha \Omega \frac{\partial}{\partial Y} \left( \Theta_3 \frac{\partial \Theta_3}{\partial Y} \right),
\] (6.70)

which can be written as

\[
\frac{\partial \Theta_3}{\partial \tau} = \frac{\alpha \Omega \partial^2 \Theta_3}{2 \partial Y^2}.
\] (6.71)

Solving the non-linear diffusion equation given in Equation 6.71 will yield the relaxation profile for the concentration peak.

6.6 Summary and conclusions

In this chapter, we present a transport model of the magnetophoretic migration of the non-magnetic polymer bead suspension in magnetic fluids. The model takes into account the non-ideality of the polymer beads to include the electrostatic repulsion effects. The simultaneous partial differential equations were solved numerically in one dimension. For a given magnetic field, the model predicts the evolution of the concentration profiles of both the magnetic particles and the polymer beads.

Since it was found that the electrostatic repulsion is an important factor at the focusing point and can not be neglected, a thermodynamic model was developed to be used for excess chemical potential due to the electrostatic repulsion of the polymer beads.

Despite the fact that the model does not use any adjustable parameters, its predictions favorably agree with the experimental observations. The model was used to study the effect of the different parameters on the concentration profile and to investigate one possible separation technique. This model proved to be a valuable
tool to provide further insight into the concepts behind magnetophoresis in magnetic fluid and to be used for design of new experiments.
6.7 Appendix: Effect of migration of particles on the pressure gradient

In the developed model, the convective flux was assumed to be negligible compared to the diffusive flux. However, due to the migration of particles by the effect of the magnetic field, there will be a net mass-average velocity. Can one ignore the effect of this mass-average velocity on the diffusion of particles? Does the existence of this mass-average velocity result in an opposing pressure gradient? If so, how significant and should it be included in our analysis?

After the numerical solving of the multicomponent diffusion model, the velocity of the polymer beads is calculated based on a balance between the magnetic and the drag forces as follows

$$v_3 = \frac{2\pi a^2 \Delta \chi}{9\mu_0 \eta} (\mathbf{B} \cdot \nabla) \mathbf{B}. \quad (6.72)$$

Then the velocity of the water is calculated based on a volume balance equation as follows

$$\phi_3 v_3 + (1 - \phi_3) v_1 = 0, \quad (6.73)$$

where $\phi_3$ is the volume fraction of the polymer beads.

Then we make the assumptions that the flow inside the the tube would be governed by Poiseuille flow as follows

$$v_1 = \frac{R^2}{8\mu} \frac{dP}{dx}, \quad (6.74)$$

where $R$ is the radius of the tube and $\mu$ is the viscosity of the water. Then we can approximate the pressure force exerted on one polymer bead as

$$F_p = \frac{dP}{dx} r \pi r^2, \quad (6.75)$$

where $r$ is the radius of the polymer beads. The order of magnitude for the pressure force is $10^{-21}$.

To compare the pressure force with the magnetic force, we extract the magnetic
force from our numerical solution using

\[ F_m = \frac{4\Delta \chi \mu_0 \pi r^3}{6} \frac{dH^2}{dx} \]  

(6.76)

where \( \Delta \chi \) is the difference in magnetic susceptibility between the polymer beads and the surrounding magnetic fluid, \( \mu_0 \) is the permeability of free space and \( H \) is the magnetic field strength. The order of magnitude of the magnetic force is \( 10^{-14} \).

It is clear that the pressure force is, on average, 6 to 7 orders of magnitude less that the magnitude of the magnetic force and can be neglected.
Bibliography


Chapter 7

Summary, Conclusions and Future Directions

There still exist opportunities for innovative new techniques in separation technologies. Our goal was to develop one such technique based on colloidal magnetic nanoparticles. These nanoparticles (~10 nm) have several characteristics that make them attractive for use as separation agents. They can be tailored to the separation needs at hand, manipulated using external magnetic fields and completely removed through magnetic filtration. The scope of our work was limited to the use of physical forces in attaining the desired separations. The magnetic nanoparticles were designed and synthesized without any chemical affinity to the solute to be separated.

7.1 Summary

The overall goal was to investigate the magnetophoretic focusing of non-magnetic particles suspended in a magnetic fluid. One potential application for this phenomenon is in the separation of submicron biological particles such as viruses, cell fragments, DNA and inclusion bodies. Since the structure of the magnetic fluid is an important parameter in its application in any magnetophoretic separation, we studied the aggregation behavior of the magnetic fluids using different characterization techniques. Monte Carlo simulation was used to understand the clustering in steri-
cally stabilized magnetic fluids. Simulation results agree favorably with the scattering experiments with regards to the cluster sizes and fractal dimensions. The characterization of closely related system, charge stabilized magnetic fluids, was also carried out to analyze the reasons behind the finite cluster size observed experimentally.

Next we investigated the concepts of magnetophoretic focusing in a polymer-based magnetic fluids, which can be used as a separation technique for colloidal particles of size range 0.2 - 1 micron based on size. In this separation technique, a mixture of submicron colloidal particles can be classified using magnetic fluids and inhomogeneous magnetic fields. With the magnetic fluid as the solvent, the colloidal particles behave as if they were diamagnetic due to the difference in magnetic susceptibility between them and the surrounding magnetic continuum. When an inhomogeneous magnetic force is applied, a magnetic force acts on the colloidal particles. The magnitude of this magnetic force is linearly proportional to the volume of the particles, the difference in the magnetic susceptibilities of the particles and the surrounding magnetic fluid and the gradient of the square of the magnetic field.

This concept was validated experimentally by monitoring the dynamic evolution of the concentration profile of fluorescently-tagged polymer beads using digital imaging techniques. An experimental system was built to monitor the movement of fluorescently-tagged polymer beads of various sizes in a mixture with a magnetic fluid on the application of an inhomogeneous magnetic field. Results show that the polymer beads larger than 0.2 μm focus at the point of zero force. The effect of the magnetic field on the particles was correlated with their size. A transport model was developed that favorably predicts the experimental results. This model was based on the Stefan-Maxwell multicomponent diffusion approach. The diffusional flux model included the effect of the magnetophoretic forces and the electrostatic repulsion, both of which were proven to be the dominant terms for the size range of interest. The model provided an a priori predictions which are in good agreement with the experimental observations. The simulations were used to study the effect of the concentration of the polymer beads and the magnetic fluid on the concentration profile and the beads mobility. Results indicate that there is a potential for using the dynamic response of
different size particles to attain their separation.

The model was then used to design a simple separation device to show the feasibility of performing separation based on the ideas developed in this thesis. 0.2 μm particles were separated from 0.51 μm particles using this simple device.

7.2 Conclusions and future directions

We investigated a novel concept for separating submicron particles using magnetophoresis principles. A polymer-stabilized magnetic fluid was synthesized and characterized for application in this new technique. Fluorescent experiments, mathematical models and preliminary separation runs show the potential of developing this technique further for use in industrial applications such as separation of biological and colloidal particles.

The future directions proposed to continue this study lie mainly in the development of different separation and analytical processes. In these processes, it is imperative to be able to control the magnetic field for elaborate manipulation of the particles in their migration in the magnetic fluids. This can be done through an assembly of electromagnets. Among the important factors that needs to be studied is the scale and throughput that can be obtained with any developed system.

Another important avenue for study is the development of steady-state type magnetophoresis processes, which can be achieved by building a two-dimensional channel in which the particles experience a balance between magnetophoretic and drag forces. A balance between the forces of magnetic origin and the drag forces emerging from the flow field can be used to manipulate particles based on their size and provide the basis for continuous separation.

Magnetophoresis in magnetic fluids can prove to be a possible alternative for biological analysis methods like electrophoresis. Although magnetophoresis is now being investigated to analyze diamagnetic material, the replacement of water with magnetic fluids in such system would extend its application to different particles and macromolecules that exhibit difference in magnetic susceptibility or size. More study
is needed to investigate its technical possibility and economic feasibility.

Different materials can be manipulated using the concepts developed in this thesis. An important application would be to investigate magnetophoresis of random coil polymers. A continuous separation system that can separate polymers based on their molecular weight is one of the applications envisioned for magnetophoresis in magnetic fluids. There need to be more studies to provide better understanding of all the factors involved in such application.
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