# Composite Films with Magnetic Nanorods: Fundamentals, Processing and Applications 

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# COMPOSITE FILMS WITH MAGNETIC NANORODS: FUNDAMENTALS, PROCESSING, AND APPLICATIONS 

A Dissertation<br>Presented to<br>the Graduate School of Clemson University

In Partial Fulfillment<br>of the Requirements for the Degree<br>Doctor of Philosophy<br>Materials Science and Engineering

by<br>Yu Gu<br>December 2014

Accepted by:
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#### Abstract

This dissertation is centered on studying the composite films with magnetic nanorods. In recent years, one-dimensional magnetic nanostructures, such as magnetic nanorods, chains of magnetic nanoparticles, and nanotubes filled with magnetic nanoparticles have caught great attentions due to the breadth of applications. Their unique magnetic and geometrical features open new avenues of studies in medicine, sensors, optofluidics, magnetic swimming, and microrheology. In particular, they offered great opportunities for design of multifunctional devices and for manufacturing of anisotropic nano- and microstructures with unprecedented magnetic and mechanical properties. However, the strategy for nanorod alignment in both Newtonian and complex fluids has not been developed and this remains the main challenge in materials engineering and processing. On the other hand, the basic understanding of the properties of the fabricated composite material is also lacking. These challenges and problems are addressed in this dissertation.

In chapter I, some basic concepts and common terminologies of ferromagnetism such as magnetic anisotropy, domain structure, etc. are introduced. The magnetic hysteresis for a single domain ferromagnetic nanoparticle is also explained. In chapter II, the magnetostatic problems for both single domain magnetic nanosphere and nanorod are solved. The interactions between both spherical nanoparticles and nanorods are also studied based on the solutions of magnetostatics. In chapter III, the synthesis of nickel


and cobalt nanorods using electrochemical deposition method is described and various methods are applied to characterize the synthesized nanorods. In chapter IV, the strategies for the alignment of magnetic nanorods in Newtonian and complex fluids are developed. The nanorod alignment in complex fluids is found to be very tricky and deserves further study. In chapter V , the evaporation kinetics and viscosity change of a ceramic precursor (an example of complex fluid) is studied during the sol-gel processing. Together with chapter IV, they provide a basis for the fabrication of ceramic composites containing of magnetic nanorods. In chapter VI, the interactions between magnetic nanorods under magnetic field gradient are studied both theoretically and experimentally. This chapter provides a method of using field gradient to defeat repulsion between nanorods and achieve very high local concentration of nanorods. In chapter VII and VIII, the theory describing the property of composite film is proposed. The ferromagnetic resonance and heating properties of a single domain nanoparticle is studied in chapter VII. In chapter VIII, interactions of electromagnetic waves with magnetic nanocomposite films are discussed. We predict an unusual transmission, reflection, and absorption properties of these films and discuss the Faraday and Kerr effects as well.

## DEDICATION

This dissertation is dedicated to my family for their support and encouragement throughout my PhD study.

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## CHAPTER I

## MAGNETISM OF A SINGLE DOMAIN NANOPARTICLE

### 1.1 Background

Magnetite $\left(\mathrm{Fe}_{3} \mathrm{O}_{4}\right)$, an iron oxide rich in lodestone, is the first magnetic material discovered by human beings[1]. Ever since its discovery, magnetic materials have been widely used for many different applications. In 19th century, the invention of electromagnet and its applications in electric motors and generators was a landmark for the beginning of practical utilization of magnetic materials. Despite the great success in engineering, the research on the origin of ferromagnetism was far behind. In 1826, Andre-Marie Ampere discovered that electric current loop can generate magnetic field similar to that of a permanent magnet. Following Ampere's law, it was proposed that the ferromagnetic nature of materials is originated from a collective effect of infinitesimal "atomic current" loops forming magnetic dipoles. However, without an external magnetic field, a random orientation of infinitesimal current loops will be energetically favored and material shouldn't exhibit any magnetic feature at the macro scale. In 1907, Pierre-Ernest Weiss proposed a molecular field theory stating that there is a molecular magnetic field forcing all the magnetic dipoles existing in the material to orient in one direction: below a so-called Curie temperature, material will be magnetic even if external magnetic field is
absent. Despite its success in explaining ferromagnetism and phase transition at Curie temperature, the physical nature of this molecular field cannot be found within classical physics. Later on, the development of quantum mechanics allowed scientists to approach this problem from a more fundamental perspective. It was shown that the "atomic current" loop originates from both orbital and spin angular momentum of the electrons. The effective molecular field actually originates from the exchange interaction between spins which forces adjacent spins to align parallel (ferromagnetic) or antiparallel (antiferromagnetic).

In this chapter, we will introduce some of the basic concepts and common terminologies for ferromagnetism: magnetic anisotropy, domain structure, etc. and explain the magnetic hysteresis for a single domain ferromagnetic nanoparticle. All these fundamentals will be actively used throughout the dissertation.

### 1.2 Magnetic moments of electrons

There are two different kinds of magnetic moments for electrons: one originates from the orbital angular momentum and the other originates from the spin angular momentum. The orbital angular momentum can be understood within classical physics. Imagine that an electron with mass $m_{\mathrm{e}}$ and elementary charge $e$ is circulating around the nucleus in a circular orbit (radius $r$ ) with angular velocity $\omega$. The orbital angular momentum $p_{l}$ will be $m_{\mathrm{e}} r^{2} \omega$ and the effective current $I$ will be $e \omega / 2 \pi$. From the classical electromagnetism, the magnetic moment $m$ of a closed current loop with area $S$ and current $I$ is defined as $m=I S$ [2]. Following this definition, the magnetic moment $m_{l}$ associated with the orbital angular momentum of an electron will be $m_{l}=e \omega r^{2} / 2=$
$\left(e / 2 m_{\mathrm{e}}\right) p_{l}$. However, the orbital angular momentum is postulated to be quantized i.e. $p_{l}=l \hbar$, in which $l$ is an integer and named as orbital angular momentum quantum number, $\hbar$ is the Planck's constant $h$ divided by $2 \pi$ and has a unit of angular momentum ( $\mathrm{m}^{2} \mathrm{~kg} / \mathrm{s}$ ). Following this definition, the magnetic moment is obtained as $m_{l}=l\left(e \hbar / 2 m_{\mathrm{e}}\right)$. Thus the magnetic moment is measured in units of $e \hbar / 2 m_{\mathrm{e}}$. The term $e \hbar / 2 m_{\mathrm{e}}$ is named as Bohr magneton $\mu_{\mathrm{B}}=e \hbar / 2 m_{\mathrm{e}}$.

Spin is a pure quantum concept. It was introduced to model electrons spinning around their own axes. Spin is a vector and its angular momentum $p_{\mathrm{s}}$ is defined through the spin angular momentum quantum number $s= \pm 1 / 2: p_{\mathrm{s}}=s \hbar$. The magnetic moment $m_{\mathrm{s}}$ associated with spin will be $m_{\mathrm{s}}=2 s \mu_{\mathrm{B}}$.

For an atom with multiple electrons, the quantum numbers $L$ and $S$ of the atom are obtained as the summation of quantum numbers of each individual electron: $L=\sum l$, $S=\sum s$. The magnetic moment of an isolated atom includes both orbital and spin contributions. However, in most solids, the orbital angular momentum of an electron is almost quenched to the lattice by the electric field generated by the surrounding atoms and its contribution to the magnetic moment can be ignored. The saturation magnetization $M_{\mathrm{s}}$ of the material is therefore determined by the spin quantum number $S$ and is defined as:

$$
\begin{equation*}
M_{\mathrm{s}}=\frac{\sum 2 S \mu_{\mathrm{B}}}{V} . \tag{1.1}
\end{equation*}
$$

The summation is over all the atoms within the volume $V . \mu_{\mathrm{B}}=e \hbar / 2 m_{\mathrm{e}}$ is the Bohr magneton as defined above. For bulk materials, we usually introduce magnetization vector $\boldsymbol{M}$ to describe the density of the magnetic moment $\boldsymbol{m}$ and its orientation.

$$
\begin{equation*}
\boldsymbol{M}=\boldsymbol{m} / V \tag{1.2}
\end{equation*}
$$

In most cases, magnetization is less than the saturation value: $M<M_{\mathrm{s}}$. In some special cases, e.g. single domain particle or material under sufficiently strong external magnetic field, the magnetization can reach the value of saturation magnetization $M=M_{s}$.

### 1.3 Magnetic anisotropy

The exchange interaction between spins is the origin of the ferromagnetism. The energy of interaction is postulated to depend on the relative orientation between two adjacent spins. However, in the real ferromagnetic materials, there are always some preferential directions named easy axes for the magnetic moment to follow. It means that these directions are energetically favored. The energy variation depending on the orientation of magnetic dipoles is called the energy of magnetic anisotropy.

### 1.3.1 Magnetocrystalline anisotropy

Magnetocrystalline anisotropy is an intrinsic property of crystals and closely related to the crystal structure of the material. We take nickel and cobalt as examples. nickel is known to have a face centered cubic (fcc) lattice while cobalt has a hexagonal close-packed (hcp) structure (Figure Figure 1.1) [3].


Figure 1.1 Crystal structures of nickel and cobalt
Magnetocrystalline anisotropy arises mainly from spin-orbit coupling[4]. As mentioned above, the orbital angular momentum of an electron is almost quenched to the lattice by the electric field generated by surrounding atoms. On the other hand, the spin angular momentum is weakly coupled to the orbital momentum. Because of this coupling, spins interactions are not isotropic but acquire an anisotropy following the crystal symmetry. Phenomenologically, the magnetocrystalline energy $E_{\mathrm{a}}$ is interpreted by a series expansion of the direction cosines of magnetic spins with respect to the crystal axis.

In case of cobalt, the direction of spins is defined with respect to the $c$-axis and energy $E_{\mathrm{a}}$ per sample volume $V$ is expanded as[3]:

$$
\begin{equation*}
E_{\mathrm{a}} / V=K_{1} \sin ^{2} \theta+K_{2} \sin ^{4} \theta+\ldots \tag{1.3}
\end{equation*}
$$

This kind of anisotropy is called uniaxial magnetic anisotropy. Only terms of even orders appear in the expansion because energy doesn't change after flipping spins upside down i.e. $E_{\mathrm{a}}(\theta=0)=E_{\mathrm{a}}(\theta=\pi)$. This follows from the crystal symmetry. The higher order terms are small and can be ignored. In some cases, only the second order term is sufficient to describe the behavior of spins. The $c$ axis can be an easy or hard axis depending on signs of the two coefficients $K_{1}, K_{2}$ and the relation between them. For
cobalt, $K_{1}=4.5 \times 10^{5} \mathrm{~J} / \mathrm{m}^{3}, K_{2}=1.5 \times 10^{5} \mathrm{~J} / \mathrm{m}^{3}[3]$. Therefore, the energy minimums correspond to $\theta=0$ or $\theta=\pi$, hence the $c$-axis will be the easy axis. The basal plane ( $\theta=\pi / 2$ ) perpendicular to $c$-axis is an isotropic hard plane i.e. spins don't want to go to this plane because this movement would cost them the maximum energy.

In case of nickel, the direction cosines $\alpha, \beta, \gamma$ are defined relative to $a, b, c$ axes respectively. The magnetocrystalline energy is defined as[3]:

$$
\begin{equation*}
E_{\mathrm{a}} / V=K_{1}\left(\alpha^{2} \beta^{2}+\beta^{2} \gamma^{2}+\alpha^{2} \gamma^{2}\right)+K_{2} \alpha^{2} \beta^{2} \gamma^{2}+\ldots \tag{1.4}
\end{equation*}
$$

The cubic magnetocystalline anisotropy starts from the forth order terms. The second order term is excluded due to the relation $\alpha^{2}+\beta^{2}+\gamma^{2}=1$. Similar to the uniaxial anisotropy, the higher order terms are also ignored. For nickel, $K_{1}=-5 \times 10^{3} \mathrm{~J} / \mathrm{m}^{3}, K_{2}=-$ $2 \times 10^{3} \mathrm{~J} / \mathrm{m}^{3}[3]$. As follows from the analysis of energy landscape in $\operatorname{Ref}[3]$, the <111> direction will be the easy axis and the <100> direction will be the hard axis.

Nickel and cobalt are both ferromagnetic i.e. these materials remain magnetic in the absence of the external magnetic field. The anisotropy coefficients of cobalt are about two orders of magnitude greater than those of nickel indicating that spins in cobalt are much more strongly bonded to the easy axis than those in nickel. Cobalt requires more energy to rotate the spins away from the easy axis. This also leads to a much higher Curie temperature for cobalt since it takes much more thermal energy to kick off spins from the easy axis.

### 1.3.2 Shape anisotropy

Different from magnetocrystalline anisotropy, the shape anisotropy is not an intrinsic property of the material. It is convenient to introduce the demagnetization field $H_{\mathrm{d}}$ to elucidate this anisotropy. Demagnetization field $H_{\mathrm{d}}$ is a magnetic field generated inside the magnetic particle by magnetization $M$ itself and is proportional to the magnetization $M$,

$$
\begin{equation*}
H_{\mathrm{d}}=-N M \tag{1.5}
\end{equation*}
$$

$N$ is a dimensionless parameter called demagnetization factor. It is always positive. The negative sign in eq.(1.5) means that the demagnetization field is antiparallel to the magnetization $M$. An external magnetic field $H_{\mathrm{e}}$ tends to align the magnetization $M$ in the field direction. The negative sign shows that the demagnetization field $H_{\mathrm{d}}$ tends to shield the external field $H_{\mathrm{e}}$. This shielding reduces the total magnetic field inside magnetic particle. One can calculate the magnetostatic energy by an integral over infinitesimal volume $d V[4]$ :

$$
\begin{equation*}
E_{\mathrm{s}}=-\frac{1}{2} \int \mu_{0} M H_{\mathrm{d}} d V=\frac{1}{2} \mu_{0} N M^{2} V \tag{1.6}
\end{equation*}
$$

$\mu_{0}=4 \pi \times 10^{-7} \mathrm{~T} \cdot \mathrm{~m} / \mathrm{A}$ is the vacuum permeability. The demagnetization factor $N$ depends on the direction of magnetization $M$. Smaller $N$ will result in a lower $E_{\mathrm{s}}$ suggesting that the material is easier to be magnetized in this direction. The demagnetization factor $N$ can be found by solving a magnetostatic boundary value problem. This magnetostatic problem will be discussed in details in the next chapter. We can also interpret the demagnetization field by introducing effective magnetic charges. The idea is that, at the boundary between
magnetic particle and exterior environment, the effective magnetic charges are accumulated (similar to the surface charge of a polarized material in electrostatics). The charge density is expressed by the equation [5]:

$$
\begin{equation*}
\sigma_{m}=\boldsymbol{M} \cdot \boldsymbol{n} \tag{1.7}
\end{equation*}
$$

where $\boldsymbol{n}$ is the normal vector for the surface. The demagnetization field will be considered as the field generated by the surface charge. The demagnetization factor for different particles has been well studied[6]. We are mostly interested in spherical and cylindrical particles. The demagnetization factors for the sphere and cylinder can be found following some simple arguments. Before doing that, one has to note that Eqs (1.5) and (1.6) are only applicable along certain directions for a particle. For an ellipsoid shown in Figure Figure 1.2, these directions are the three principal axes $a, b, c$. The demagnetization factors along these axes are denoted as $N_{a}, N_{b}, N_{c}$ respectively. They satisfy the relation $N_{a}+N_{b}+N_{c}=1[6]$.


Figure 1.2 Demagnetization factor for a magnetic sphere and cylinder

In spherical particles where $a=b=c$, the demagnetization factors in the three directions are the same due to the isotropic nature of sphere: $N_{a}=N_{b}=N_{c}=1 / 3$. For a long cylindrical particle, $a=b \ll c$, the demagnetization factor along the $c$ axis is almost zero $\left(N_{c} \approx 0\right)$. This can be understood by considering an infinitely long cylinder $(c=\infty)$, field generated by the surface charge on basal faces can be neglected $\left(N_{\mathrm{c}}=0\right)$. On the other hand, the $a$ and $b$ axes are equivalent i.e. $N_{a}=N_{b}=1 / 2$. The relation $N_{c}<N_{a}=N_{b}$ indicates that a magnetic cylinder is more magnetizable along the long axis. The demagnetization factor of a general ellipsoid with uniform magnetization was analyzed by J.A. Osborn and can be found in $\operatorname{Ref[6].}$

### 1.3.3 Comparison of crystalline and shape anisotropy

To quantify the shape anisotropy for a long cylinder, we can introduce an angle $\theta$ with respect to the $c$ axis of the cylinder. For a magnetic cylinder with magnetization vector forming angle $\theta$ with respect to the $c$ axis, the magnetostatic energy reads:

$$
\begin{equation*}
E_{\mathrm{s}} / V=\frac{1}{2} \mu_{0} M^{2}\left(N_{a} \sin ^{2} \theta+N_{c} \cos ^{2} \theta\right)=\frac{1}{4} \mu_{0} M^{2} \sin ^{2} \theta \tag{1.8}
\end{equation*}
$$

It has the same form as the second order term of the uniaxial magnetocrystalline anisotropic energy. We can define the pre-factor $K_{\mathrm{s}}=\mu_{0} M^{2} / 4$ as the shape anisotropy coefficient for the cylinder and use the saturation magnetization for a rough estimation of $K_{\mathrm{s}}$. For the nickel nanorod, the saturation magnetization $M_{\mathrm{s}}=4.9 \times 10^{5} \mathrm{~A} / \mathrm{m}$ and $K_{\mathrm{s}}$ will be $7.5 \times 10^{4} \mathrm{~J} / \mathrm{m}^{3}$, It is about one order of magnitude greater than the crystalline anisotropy coefficient $K_{1}=-5 \times 10^{3} \mathrm{~J} / \mathrm{m}^{3}, K_{2}=-2 \times 10^{3} \mathrm{~J} / \mathrm{m}^{3}$. Therefore, for a long nickel cylinder, one can safely neglect the crystalline anisotropy. For the cobalt nanorod, $M_{\mathrm{s}}=1.44 \times 10^{6} \mathrm{~A} / \mathrm{m}$ and
$K_{\mathrm{s}}$ will be $6.5 \times 10^{5} \mathrm{~J} / \mathrm{m}^{3}$ which is of the same order of magnitude as the crystalline anisotropy $K_{1}=4.5 \times 10^{5} \mathrm{~J} / \mathrm{m}^{3}, K_{2}=1.5 \times 10^{5} \mathrm{~J} / \mathrm{m}^{3}$. Therefore, both crystalline and shape anisotropy are important for a cobalt cylinder.

In this section we introduced magnetocystalline anisotropy and shape anisotropy for the ferromagnetic materials. Magnetic anisotropy is the origin of the magnetic hysteresis which will be introduced later in this chapter. The crystalline anisotropy follows the crystal symmetry while the shape anisotropy makes the long axis of a cylinder the easy axis. Nickel and cobalt were taken as examples and their properties are summarized in Table 1.1.

Table 1.1 Summary of the magnetic anisotropic properties of nickel and cobalt nanorods

|  | Nickel | Cobalt |
| :---: | :---: | :---: |
| Crystal Structure | fcc | Hcp |
| Magnetocrystalline | $K_{1}\left(\alpha^{2} \beta^{2}+\beta^{2} \gamma^{2}+\alpha^{2} \gamma^{2}\right)+K_{2} \alpha^{2} \beta^{2} \gamma^{2}$ | $K_{1} \sin ^{2} \theta+K_{2} \sin ^{4} \theta$ |
| anisotropy | $K_{1}=-5 \times 10^{3} \mathrm{~J} / \mathrm{m}^{3}$, | $K_{1}=4.5 \times 10^{5} \mathrm{~J} / \mathrm{m}^{3}$, |
|  | $K_{2}=-2 \times 10^{3} \mathrm{~J} / \mathrm{m}^{3}$ | $K_{2}=1.5 \times 10^{5} \mathrm{~J} / \mathrm{m}^{3}$ |
| Easy axis | $<111>$ | $c$-axis |
| Hard axis/plane | $<110>$ | Basal plane |
| Shape anisotropy for a | $K_{\mathrm{s}} \sin ^{2} \theta$ | $K_{\mathrm{s}} \sin ^{2} \theta$ |
| cylinder | $K_{\mathrm{s}}=7.5 \times 10^{4} \mathrm{~J} / \mathrm{m}^{3}$ | $K_{\mathrm{s}}=6.5 \times 10^{6} \mathrm{~J} / \mathrm{m}^{3}$ |
| Easy axis | Long axis | Long axis |
| Hard axis/plane | Basal plane | Basal plane |

### 1.4 Division of magnetic materials into domains

### 1.4.1 Multi-domain structure of bulk magnets

Bulk ferromagnetic materials prefer to form domains to decrease the total magnetostatic energy. Consider a single cubic sample with saturation magnetization $M_{\mathrm{s}}$, Figure Figure 1.3(a), the magnetostatic energy can be estimated as:

$$
\begin{equation*}
E_{\mathrm{s}} \propto \mu_{0} M_{\mathrm{s}}^{2} a^{3} \tag{1.9}
\end{equation*}
$$

where $a$ is the size of the cube. If this cube is divided into several slab-like domains following the manner shown in Figure Figure 1.3(b), the total magnetostatic energy will be reduced to:

$$
\begin{equation*}
E_{\mathrm{s}} \propto \mu_{0} M_{\mathrm{s}}^{2} a^{2} d \tag{1.10}
\end{equation*}
$$

where $d$ is the thickness of a single slab-like domain. The detailed derivation of prefactors in eqs(1.9) and (1.10) can be found in Ref[3]. For us, it is important to see the dependence of the energy on sample and domain sizes.


Figure 1.3 Division of a cubic sample into multiple slab-like domains
Eq. (1.10) indicates that to decrease the magnetostatic energy, the number of domains has to be maximized. If the cubic sample is divided into infinite number of domains, $d=0$, the magnetostatic energy will be zero corresponding to the lowest energy
state. However, in the real case, each domain is not infinitely small and always has a finite size. Each interfacial layer separating the adjacent domains contribute energy $E_{\mathrm{f}}$ :

$$
\begin{equation*}
E_{\mathrm{f}}=\gamma \frac{a^{3}}{d} \tag{1.11}
\end{equation*}
$$

where $\gamma$ is the interfacial energy per unit area. The width of the domain can be determined by minimizing the total energy $E=E_{\mathrm{s}}+E_{\mathrm{f}}, \partial E / \partial d=0$ [3]:

$$
\begin{equation*}
d \propto \sqrt{\frac{\gamma a}{\mu_{0} M_{\mathrm{s}}^{2}}} \tag{1.12}
\end{equation*}
$$

Thus, the greater the saturation magnetization $M_{\mathrm{s}}$, the smaller the domain will be. The magnetic domains can have many different configurations and the sample's subdivision into domains is not necessarily following scenarios in Figure 1.3(b). However, Eq.(1.12) gives a good order of magnitude estimation of the domain size in the material [3].

### 1.4.2 Single domain nanoparticle

Equation (1.12) shows that the size of a domain will decrease as the particle size decreases. One would expect that if the domain size calculated from eq.(1.12) is smaller than the thickness of interfacial layer separating the domains, the formation of domains cannot be done. Therefore, the magnetic domain is expected to occupy the whole particle.

Consider a spherical particle and define the critical diameter $D_{\mathrm{c}}$ below which the particle will form a single domain. This critical diameter should satisfy the relation: $E_{\mathrm{s}}\left(D_{\mathrm{c}}\right)=E_{\mathrm{f}}\left(D_{\mathrm{c}}\right)+E_{\mathrm{d}}\left(D_{\mathrm{c}}\right)$, where $E_{\mathrm{s}}$ is the magnetostatic energy of a single domain nanoparticle, $E_{\mathrm{d}}$ is the magnetostatic energy of a multi-domain nanoparticle. We assume
that the spherical nanoparticle is divided into two hemispherical domains. The interfacial energy is written as $E_{\mathrm{f}}=\gamma \pi D^{2} / 4$. The magnetostatic energy for a single domain nanoparticle is $E_{\mathrm{s}}=(1 / 6) \mu_{0} M_{\mathrm{s}}^{2}(4 / 3) \pi(D / 2)^{3}=\mu_{0} M_{\mathrm{s}}^{2} \pi D^{3} / 36$. The magnetostatic energy $E_{\mathrm{d}}$ for a nanoparticle with two hemispherical domains is approximately half of $E_{\mathrm{s}}: E_{\mathrm{d}}=E_{\mathrm{s}} / 2=$ $\mu_{0} M_{\mathrm{s}}{ }^{2} \pi D^{3} / 72[3]$. The critical diameter $D_{\mathrm{c}}$ is determined from the equation $E_{\mathrm{s}}\left(D_{\mathrm{c}}\right)=E_{\mathrm{f}}\left(D_{\mathrm{c}}\right)+E_{\mathrm{d}}\left(D_{\mathrm{c}}\right)$ as:

$$
\begin{equation*}
D_{\mathrm{c}}=\frac{18 \gamma}{\mu_{0} M_{s}^{2}} \tag{1.13}
\end{equation*}
$$

Depending on the domain structure used in the model i.e. depending on the number of domains and their shape, the estimated critical diameter $D_{\mathrm{c}}$ will be different. However, eq. (1.13) provides a good order of magnitude estimation of the critical particle diameter. The critical size for a spherical nanoparticle to be single domain is usually smaller than $100 \mathrm{~nm}[7]$. This critical size also depends on the shape of the particle. Ref[7] shows that a rod with high aspect ratio ( $\sim 20$ ) can be several micron long and still remains single domain.

In this section, we discussed the physical origin of magnetic domains in ferromagnetic materials. The competition between the magnetostatic energy and the interfacial energy between domains results in the domain formation. When the particle size is sufficiently small, the domain size will be smaller than the domain wall thickness. The critical size can be estimated by comparing the energy of a single domain structure with a multi-domain structure. Eq. (1.13) provides a good order of magnitude estimation for this critical size.

### 1.5 Magnetism of single domain nanoparticles

### 1.5.1 Magnetic hysteresis in a single domain nanoparticle



Figure 1.4 The orientation of magnetization vector $\boldsymbol{M}_{\mathrm{s}}$ and external magnetic field $\boldsymbol{H}$ with respect to the easy axis. (a) magnetic nanorod (b) magnetic nanosphere.

Consider a single domain magnetic nanoparticle with a uniaxial magnetic anisotropy. It can be a magnetic nanorod with high aspect ratio or a spherical nanoparticle with uniaxial crystalline anisotropy (for example: cobalt). As shown in Figure 1.4, we can define the direction of the magnetization vector $\boldsymbol{M}_{\mathrm{s}}$ and external magnetic field $\boldsymbol{H}$ with respect to the easy axis by introducing angles $\theta$ and $\varphi$ respectively in both cases.

Keeping only the second order term, the energy density can be written as:

$$
\begin{equation*}
\frac{E}{V}=K \sin ^{2} \theta-\mu_{0} M_{\mathrm{s}} H \cos (\varphi-\theta) \tag{1.14}
\end{equation*}
$$

where $E$ is the total energy of the particle, $V$ is the volume of the particle, $K$ is the anisotropy coefficient and $\mu_{0}$ is the magnetic permeability of vacuum. First term on the right hand side corresponds to the uniaxial anisotropic energy and shows how strong the spins are bonded to the easy axis. The second term is the magnetostatic energy between the particle and external magnetic field.


Figure 1.5 (a) The total energy density as a function of orientation of magnetization $\theta$ for different external magnetic fields $H$. (b) Correspondence of the energy minimums to the points on the hysteresis loop.

Figure 1.5 (a) shows an example of the calculated energy as a function of magnetization orientation $\theta$ under five different external magnetic fields $H= \pm 1.2 K / \mu_{0} M_{\mathrm{s}}$, $\pm 0.6 K / \mu_{0} M_{\mathrm{s}}, 0$. In all cases, the magnetic fields are in the same direction: $\varphi=\pi / 3$. The energy minimums correspond to possible equilibrium orientations of the magnetization vector. In the real experiment, the direction of the magnetic field $\varphi$ is fixed and only the field magnitude $H$ is varied. The instrument can only measure the component of
magnetization along the field direction which is $M_{s} \cos \left(\varphi-\theta_{\min }\right) . \theta_{\min }$ corresponds to an energy minimum at a particular $H$. At $H= \pm 1.2 K / \mu_{0} M_{\mathrm{s}}$, there is only one energy minimum and magnetization vector will always follow that direction. At $H=0, \pm 0.6 K / \mu_{0} M_{s}$, there are two energy minimums, equilibrium direction of magnetization vector depends on the history of application of the external magnetic field. If $H$ is decreasing from $+\infty$ $(1.2 \rightarrow 0.6 \rightarrow 0 \rightarrow-0.6 \rightarrow-1.2), \theta_{\min }$ varies in the following order: $\theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}, \theta_{5}$ (Figure 1.5 (a)). These equilibrium positions sit on the upper branch of the hysteresis loop (Figure 1.5 (b)). If $H$ is increasing from $-\infty(-1.2 \rightarrow-0.6 \rightarrow 0 \rightarrow 0.6 \rightarrow 1.2), \theta_{\text {min }}$ doesn't follow the same path but varies in a different order: $\theta_{5}, \theta_{6}, \theta_{7}, \theta_{8}, \theta_{1}$ (Figure 1.5 (a)). These points sit on the lower branch of the hysteresis loop(Figure 1.5 (b)). The presence of the multiple equilibrium positions is the origin of hysteresis for a single domain ferromagnetic nanoparticle.

Scanning the magnitude of external magnetic field $H$ from $+\infty$ to $-\infty$ and picking the correct energy minimum for each $H$, one can construct the hysteresis loop for a particular angle $\varphi$. Figure 1.6(a) shows a series of hysteresis loops calculated using the developed algorithm for the external fields with different directions $\varphi$. When external magnetic field $H$ is parallel to the easy axis $(\varphi=0)$, the hysteresis loop takes on a rectangular shape. In the other limit, when $H$ is perpendicular to the easy axis $(\varphi=\pi / 2)$, no hysteresis can be observed. As a result, the magnetization $M(H, \varphi)$ is a function of both the magnitude of external magnetic field $H$ and its orientation $\varphi$.


Figure 1.6 (a) Hysteresis loop for a single domain nanoparticle with uniaxial anisotropy. Shape of the hysteresis loop varies as the direction ( $\varphi$ ) of external magnetic field $H$ changes. (b) The hysteresis loop for an assembly of single domain nanoparticles with randomly oriented easy axes. (c) The experimental hysteresis loop for a powder of nickel nanorods (see details in chapter III ).

Experimentally, we usually deal with an assembly of magnetic nanoparticles. We consider them as the single domain nanoparticles and assume their easy axes to be randomly oriented. To construct the theoretical hysteresis loop for this case, one should scan $\varphi$ from 0 to $\pi / 2$ and obtain a series of hysteresis loops $M(H, \varphi)$ for different $\varphi$ (Figure 1.6(a)). Then the average hysteresis loop for the assembly of nanoparticles is interpreted as:

$$
\begin{equation*}
\bar{M}(H)=\frac{\int_{0}^{\pi / 2} M_{\mathrm{s}} \cos \left[\theta_{\min }(H)-\varphi\right] \sin \varphi d \varphi}{\int_{0}^{\pi / 2} \sin \varphi d \varphi} \tag{1.15}
\end{equation*}
$$

The average magnetization is calculated in 3-D space with the orientation distribution function $f\left(\varphi, \varphi_{\mathrm{a}}\right)=1 / 4 \pi$ and the average over azimuth angle $\varphi_{\mathrm{a}}$ is not considered due to the uniaxial symmetry. The calculated averaged hysteresis loop is shown in Figure 1.6(b).

There are usually three parameters characterizing the hysteresis loop: Saturation magnetization $M_{\mathrm{s}}$, Remanence magnetization $M_{\mathrm{r}}$ and Coercive force $H_{\mathrm{c}}$. These parameters are defined from the hysteresis loop shown in Figure 1.6(b) and (c). Figure $1.6(\mathrm{c})$ is the experimental hysteresis loop for the powders composed of nickel nanorods.

Saturation magnetization $M_{\mathrm{s}}$, as defined in section 1.2, is the maximum magnetization achievable by the material. For a single domain nanoparticle, the magnitude of the magnetization vector is always $M_{\mathrm{s}}$ : magnetization vector only rotates under the external magnetic field.

Remanence magnetization $M_{\mathrm{r}}$ is also named as the spontaneous magnetization. It is the magnetization remained in the material when the external magnetic field is removed. It is only proportional to the saturation magnetization $M_{\mathrm{s}}$. At $H=0$, the magnetization vector will follow the direction of the easy axis $\left(\theta_{\min }=0, \pi\right)$. As a result, the remanence magnetization for a particular $\varphi$ is written as: $M_{\mathrm{r}}=M_{\mathrm{s}} \cos \varphi$. Substituting it into eq.(1.15), the remanence magnetization for an assembly of single domain nanoparticles with randomly oriented easy axes is interpreted as:

$$
\begin{equation*}
M_{\mathrm{r}}=\frac{\int_{0}^{\pi / 2} M_{\mathrm{s}} \cos \varphi \sin \varphi d \varphi}{\int_{0}^{\pi / 2} \sin \varphi d \varphi}=\frac{M_{\mathrm{s}}}{2} \tag{1.16}
\end{equation*}
$$

Thus, for an assembly of randomly orientated single domain nanoparticles, remanence magnetization $M_{\mathrm{r}}$ is always half the saturation magnetization $M_{\mathrm{s}}$.

Coercive force $H_{\mathrm{c}}$ is the magnetic field needed to demagnetize the ferromagnetic material. The external magnetic field in Figure 1.6 is normalized by the term $K / \mu_{0} M_{\mathrm{s}}$, meaning that the coercive force will be proportional to this term. According to the numerical results, for an assembly of single domain nanoparticles, the coercive force $H_{\mathrm{c}} \approx 0.96 K / \mu_{0} M_{\mathrm{s}}$.

The model of an assembly of randomly orientated nanoparticles is very attractive: it provides a simple method for the estimation of uniaxial coefficient $K$ by measuring the saturation magnetization $M_{\mathrm{s}}$ and coercive force $H_{\mathrm{c}}$ experimentally.

It should be noted that the calculation above assumed a coherent rotation of magnetization vector i.e. all the spins rotate in unison. In reality, different modes of magnetization reversal are possible.


Figure 1.7 Different modes of magnetization reversal (a) coherent rotation (b) curling (c) buckling (d) fanning (e) domino effects[8].

Figure 1.7 is taken from $\operatorname{Ref}[8]$ and shows different modes of magnetization reversal. The idea behind these modes is to decrease the magnetostatic energy of the single domain nanoparticles without creating new domains. For all the modes shown in Figure 1.7 (b-e), the calculated coercive force will be lower than that of the coherent rotation case Figure 1.7 (a) [8].

### 1.5.2 Superparamagnetic nanoparticle

Temperature is always an important factor in magnetism. For any ferromagnetic material, there's a Curie temperature $T_{\mathrm{c}}$, above which the material will become paramagnetic. For a single domain nanoparticle, if there are no thermal fluctuations, the spins will be frozen at the easy axis. For a spherical nanoparticle without shape anisotropy, the strength of the spin bonding the easy axis is characterized by magnetocrystalline energy $E_{\mathrm{a}}$. This energy $E_{\mathrm{a}}$ is proportional to the particle volume $V$. As the particle size decreases, at some critical size the thermal energy $k_{\mathrm{B}} T$ will be able to overcome the energy barrier $E_{\mathrm{a}} \sim k_{\mathrm{B}} T$ to flip the spins. If the observation time $\tau_{\mathrm{m}}$ is much greater than the characteristic flipping time $\tau$, the observed magnetization will be zero and material behaves as paramagnetic. However, in this case, the magnetic susceptibility $(\chi=M / H)$ is very high hence the material is called superparamagnetic. The superparamagnetic nanoparticles do not exhibit any hysteresis i.e. $M_{\mathrm{r}}=H_{\mathrm{c}}=0$.

To quantify the effects of thermal fluctuations, we consider a particle with a uniaxial symmetry. The anisotropy energy $E_{\mathrm{a}}$ is the first term on the right hand side of eq.(1.14), $E_{\mathrm{a}}=K V \sin ^{2} \theta$.


Figure 1.8 The uniaxial anisotropy energy as a function of the spin orientation $\theta$.
Figure 1.8 shows that, $K V$ is the energy barrier for the spins sitting along the easy axis $(\theta=0)$ to jump through the hard direction $(\theta=\pi / 2)$ to reach the opposite direction $(\theta=\pi)$ of the same easy axis. Following the Neel-Arrhenius equation, we can estimate the Neel relaxation time $\tau[9]$ :

$$
\begin{equation*}
\tau=\tau_{0} \exp \left(\frac{K V}{k_{\mathrm{B}} T}\right) \tag{1.17}
\end{equation*}
$$

$\tau_{0}$ is the characteristic time scale for a single jump over the energy barrier $K V$. It is a material parameter and has the typical value $10^{-9}$ to $10^{-10}$ second[10]. The Neel relaxation time $\tau$ characterizes the time needed for a successful jump over the energy barrier. If the measurement time $\tau_{\mathrm{m}}$ is much greater than $\tau$, the nanoparticle behaves as a superparamagentic nanoparticle because the spin will flip many times during the measurement and the measured average spontaneous magnetization will be zero. On the other hand, if $\tau_{\mathrm{m}} \ll \tau$, the spin wouldn't flip during the experiment and the material behaves as ferromagnetic. Assuming that $\tau_{\mathrm{m}}=\tau$, one can define the blocking temperature $T_{\mathrm{B}}$ from eq.(1.17):

$$
\begin{equation*}
T_{\mathrm{B}}=\frac{K V}{k_{\mathrm{B}} \ln \left(\frac{\tau_{\mathrm{m}}}{\tau_{0}}\right)} \tag{1.18}
\end{equation*}
$$

At the blocking temperature $T_{\mathrm{B}}$, the measurement time $\tau_{\mathrm{m}}$ equals to the characteristic jumping time $\tau$. Eq.(1.18) defines the transition of material's behavior from superparamgentic to ferromagnetic. Below this temperature $T_{\mathrm{B}}, \tau_{\mathrm{m}}<\tau$, the flip of spin is blocked and the material behaves as ferromagnetic. Above $T_{\mathrm{B}}, \tau_{\mathrm{m}}>\tau$, the flip of spin is allowed, hence the material behaves as superparamagnetic.

We can also calculate the critical size for a nanoparticle to be superparamagnetic. Assume that the nanoparticle has a spherical shape, $V=\pi D^{3} / 6$. Substituting this volume in eq. (1.18) and solving for $D$, one can define the critical size $D_{\mathrm{s}}$ of a nanoparticle, below which the particle is expected to behave as superparamagnetic at temperature $T_{0}$.

$$
\begin{equation*}
D_{\mathrm{s}}=\left[6 \ln \left(\frac{\tau_{\mathrm{m}}}{\tau_{0}}\right) \frac{k_{\mathrm{B}} T_{0}}{\pi K}\right]^{1 / 3} \tag{1.19}
\end{equation*}
$$

Equations (1.13) and (1.19) show that there are two critical sizes for magnetic nanoparticles. One particle size distinguishes a multi-domain structure from a single domain one. The other critical size sets the boundary between ferromagnetic and superparamagnetic behavior of nanoparticles. Figure 1.9 is taken from Ref[11] showing these critical particle sizes for different materials estimated from this theory.


Figure 1.9 Superparamagnetic, single domain and multidomain regions for spherical magnetic nanoparticles. The shaded region corresponds to superparamagentism. The black bar represents the ferromagnetic single domain nanoparticle. The multi-domain particles sit to the right of the black bar[11] .

### 1.6 Conclusions

In this chapter, we introduced some of the basic concepts and terminologies in magnetism. The magnetocystalline anisotropy and shape anisotropy for ferromagnetic materials were first introduced. We discussed the crystalline anisotropy for cubic and hexagonal crystals. The crystalline anisotropy follows the crystal symmetry. The shape anisotropy for long cylinder and sphere were discussed. Sphere is isotropic while the long axis of cylinder will be easy axis according to the shape anisotropy. Nickel and cobalt were taken as examples and their properties were summarized in Table 1.1.

Then, we introduced the concept of domain for the ferromagnetic material. We showed that it was the competition between magnetostatic energy and interfacial energy between domains that result in the formation of domains. When the particle size is
sufficiently small, the domain size will be smaller than the interfacial layer thickness and particle will form a single domain structure. The critical size to be a single domain particle was also estimated.

Furthermore, we demonstrated the magnetic hysteresis of a single domain nanoparticle based on uniaxial magnetic anisotropy. The shape of the hysteresis loop depends on the orientation of the external magnetic field relative to the easy axis of the nanoparticle. The hysteresis loop can be changed from a rectangle $(\varphi=0)$ to a straight line ( $\varphi=\pi / 2$ ). We also introduced hysteresis loop for an assembly of magnetic nanoparticles with a random distribution of easy axes. The saturation $M_{\mathrm{s}}$, remanence $M_{\mathrm{r}}$ and coercivity $H_{\mathrm{c}}$ were also introduced.

At last, we discussed the superparamagentism. If the particle is sufficiently small, it will behave as paramagnetic but with very large magnetic susceptibility. There's no hysteresis for the superparamagnetic nanoparticles $\left(M_{\mathrm{r}}=H_{\mathrm{c}}=0\right)$. The blocking temperature and critical particle size were defined for spherical nanoparticles with uniaxial anisotropy.

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## CHAPTER II

## SPHERICAL NANOPARTICLES VS NANORODS

### 2.1 Magnetostatics: Magnetic nanospheres and nanorods

### 2.1.1 Basis of Magnetostatics

If there's no free current in space, the two Maxwell equations connecting the magnetic field and magnetic induction can be written as:

$$
\begin{align*}
\nabla \times \boldsymbol{H} & =0  \tag{2.1}\\
\nabla \cdot \boldsymbol{B} & =0 \tag{2.2}
\end{align*}
$$

Eq.(2.1) can be automatically satisfied by introducing magnetic potential $\varphi: \boldsymbol{H}=-$ $\nabla \varphi$. Magnetic induction $\boldsymbol{B}$ is related to magnetic field $\boldsymbol{H}$ and magnetization $\boldsymbol{M}$ through the relation $\boldsymbol{B}=\mu_{0}(\boldsymbol{H}+\boldsymbol{M})$. For a single domain ellipsoidal particle, the magnetization is uniform inside and zero outside, equation $\nabla \cdot \boldsymbol{M}=0$ is satisfied everywhere except at the boundary. Therefore, eq.(2.2) can be transformed to $\nabla \cdot \boldsymbol{H}=0$. Substituting $\boldsymbol{H}=-\nabla \varphi$ into $\nabla \cdot \boldsymbol{H}=0$, Eqs. (2.1) and (2.2) will be transformed into the Laplace equation:

$$
\begin{equation*}
\nabla^{2} \varphi=0 \tag{2.3}
\end{equation*}
$$

The tangential component of magnetic field $\boldsymbol{H}$ and normal component of magnetic induction $\boldsymbol{B}$ have to be continuous at the interface separating the magnetic
material from the nonmagnetic one. Therefore, the following boundary conditions are imposed to solve the Laplace equation:

$$
\left\{\begin{array}{l}
\boldsymbol{n} \times\left(\boldsymbol{H}_{1}-\boldsymbol{H}_{2}\right)=0  \tag{2.4}\\
\boldsymbol{n} \cdot\left(\boldsymbol{B}_{1}-\boldsymbol{B}_{2}\right)=0
\end{array}\right.
$$

where $\boldsymbol{n}$ is the normal vector to the interface pointing from the magnetic materials towards the non-magnetic material and index 1 specifies the field outside the particle and index 2 corresponds to the field inside the particle. The tangential component of the magnetic field $\boldsymbol{H}$ is the derivative of potential along the interface. If $\boldsymbol{s}$ is the unit tangential vector along the interface, one can write $\boldsymbol{n} \times \boldsymbol{H}_{1}=-\partial \varphi_{1} / \partial s, \boldsymbol{n} \times \boldsymbol{H}_{2}=-\partial \varphi_{2} / \partial s$. Integrating these equations over the interface, the boundary condition for magnetic field $\boldsymbol{H}$ is replaced by the continuity condition for potential at the interface $\left(\varphi_{1}=\varphi_{2}\right)$.

### 2.1.2 Spherical nanoparticle



Figure 2.1 Spherical coordinate system for a spherical nanoparticle with radius $a$ and uniform magnetization $M$ pointing up.

Figure 2.1 is a schematic showing a uniformly magnetized nanoparticle with radius $a$ and magnetization $M$. The origin of the spherical coordinate system is placed at the center of the particle. The position of observation point in space is defined by its
distance from the origin $r$ and polar angle $\theta$. The azimuth angle is excluded due to the axial symmetry of the spherical nanoparticle. Eq.(2.3) is applicable everywhere and can be written in spherical coordinates as:

$$
\begin{equation*}
\frac{1}{r} \frac{\partial^{2}}{\partial r^{2}}(r \varphi)+\frac{1}{r^{2} \sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \varphi}{\partial \theta}\right)=0 \tag{2.5}
\end{equation*}
$$

We seek the solution in the form:

$$
\begin{equation*}
\varphi_{i}=\alpha_{i}(\boldsymbol{M} \cdot \boldsymbol{r})+\beta_{i} \frac{(\boldsymbol{M} \cdot \boldsymbol{r})}{r^{3}} \tag{2.6}
\end{equation*}
$$

The boundary condition at the interface $r=a$ can be written as:

$$
\left\{\begin{array}{l}
\varphi_{1}(a)=\varphi_{2}(a)  \tag{2.7}\\
\boldsymbol{B}_{1}(a) \cdot \frac{\boldsymbol{a}}{a}=\boldsymbol{B}_{2}(a) \cdot \frac{\boldsymbol{a}}{a}
\end{array}\right.
$$

where $a / a$ is the radial unit vector of the particle. Subscript 1 stands for the medium surrounding the particle and 2 stands for the magnetic nanoparticle. We take the surrounding medium as air and the magnetic permeability is the vacuum permeability $\mu_{0}$.

There are four coefficients: $\alpha_{1} \beta_{1} \alpha_{2} \beta_{2}$ to be determined. To ensure the finiteness of potential at $r=0$, we must set $\beta_{2}$ to zero. To make the magnetic field at infinity zero, $\alpha_{1}$ must be equal to 0 . The remaining two coefficients $\beta_{1}$ and $\alpha_{2}$ are determined by solving eq.(2.7). Substituting eq.(2.6) into eq.(2.7) yields:

$$
\left\{\begin{array}{l}
\beta_{1} \frac{(\boldsymbol{M} \cdot \boldsymbol{a})}{a^{3}}=\alpha_{2}(\boldsymbol{M} \cdot \boldsymbol{a})  \tag{2.8}\\
\mu_{0} \beta_{1}\left[-\frac{(\boldsymbol{M} \cdot \boldsymbol{a})}{a^{4}}+\frac{3(\boldsymbol{M} \cdot \boldsymbol{a})}{a^{4}}\right]=\mu_{0} \frac{\left(-\alpha_{2} \boldsymbol{M} \cdot \boldsymbol{a}+\boldsymbol{M} \cdot \boldsymbol{a}\right)}{a}
\end{array}\right.
$$

$\beta_{1}$ and $\alpha_{2}$ are solved as:

$$
\begin{equation*}
\alpha_{2}=\frac{1}{3} \quad, \quad \beta_{1}=\frac{a^{3}}{3} \tag{2.9}
\end{equation*}
$$

The magnetic field $\boldsymbol{H}(r)=-\nabla \varphi$ and magnetic induction $\boldsymbol{B}(r)=\mu_{0}[\boldsymbol{H}(r)+\boldsymbol{M}(r)]$ are interpreted as:

$$
\left\{\begin{array}{l}
\boldsymbol{H}=-\frac{\boldsymbol{M}}{3} ; \boldsymbol{B}=\frac{2 \mu_{0} \boldsymbol{M}}{3}(r \leq a)  \tag{2.10}\\
\boldsymbol{H}=\frac{a^{3}}{3}\left(\frac{3(\boldsymbol{M} \cdot \boldsymbol{r}) \boldsymbol{r}}{r^{5}}-\frac{\boldsymbol{M}}{r^{3}}\right) ; \boldsymbol{B}=\frac{\mu_{0} a^{3}}{3}\left(\frac{3(\boldsymbol{M} \cdot \boldsymbol{r}) \boldsymbol{r}}{r^{5}}-\frac{\boldsymbol{M}}{r^{3}}\right)(r>a)
\end{array}\right.
$$

Magnetic field $\boldsymbol{H}$ inside the spherical nanoparticle is uniform and antiparallel to the magnetization vector $\boldsymbol{M}$. The magnitude of this internal field is three times smaller than the magnetization $M . N=1 / 3$ is the demagnetization factor for a magnetic sphere introduced in chapter 1 and it shows the effect of the field shielding. The magnetic field outside the nanoparticle is equivalent to the field generated by a magnetic dipole with dipole moment $4 \pi a^{3} M / 3$ sitting at the center of the nanoparticle. Thus, a spherical nanoparticle can be treated as a point dipole.


Figure 2.2 (a) Distribution of magnetic field generated by a uniformly magnetized sphere. The distribution is simulated (Finite Element Method) using COMSOL 4.2. (b) Distribution of magnetic field generated by a magnetic dipole sitting at the center of the sphere with the same magnetic moment of the sphere in (a). The magnitude of the magnetic field is normalized by the magnetization $M$.

Figure 2.2(a) shows the distribution of magnetic field generated by a spherical nanoparticle with magnetization $M$ and radius $a$. Color represents the magnitude of the magnetic field $H$ and the value is normalized by $M$. The field outside is equivalent to that generated by a magnetic dipole sitting at the center of the particle with dipole moment $4 \pi a^{3} M / 3$ (Figure 2.2(b)).

### 2.1.3 Magnetic nanorod

(a)


$$
M_{\|}=M
$$

(b)

$M_{\perp}=M$
(c)


$$
M_{\|}=M \cos \theta
$$

$$
M_{\perp}=M \sin \theta
$$

Figure 2.3 Direction of the magnetization with respect to the long axis of magnetic nanorod (a) parallel to the long axis (b) perpendicular to the long axis (c) arbitrary angle $\theta$

The magnetostatic problem of a magnetic nanorod is different from that of a spherical nanoparticle. Due to the shape anisotropy, the field distribution of a magnetic nanorod will be different depending on the direction of the magnetization vector $\boldsymbol{M}$. We consider two limiting cases: I) magnetization vector is along the long axis of the magnetic nanord (Figure 2.3(a)); II) magnetization vector is perpendicular to the long axis (Figure 2.3(b)). For the general case, when the magnetization vector forms an arbitrary angle $\theta$ relative to the long axis, one can always find the parallel and perpendicular components of the magnetization (Figure 2.3(c)). Due to the linearity of Laplace eq.(2.3),
magnetostatic problem for any magnetization orientation can be considered as the superposition of the magnetostatic problems for the two orientations I: parallel, II: perpendicular.
(a)

(b)


Figure 2.4 Cylindrical coordinate system for an infinitely long magnetized cylinder. (a) Magnetization is along the long axis. Only one parameter $r$ (distance from the $z$ axis) is needed. (b) Magnetization is perpendicular to the long axis. Both $r$ and azimuth angle $\theta$ are needed.

To simply the problem, we consider an infinitely long cylinder so that the edge effects of the two poles can be ignored. In reality, this is a good approximation for the magnetic nanorods with high aspect ratio.

When the magnetization vector is codirected with the long axis of the cylinder, the problem becomes one dimensional (Figure 2.4(a)). Introducing cylindrical coordinates as shown in Figure 2.4(a), the Laplace equation (2.3) for magnetic potential $\varphi$ is written as:

$$
\begin{equation*}
\frac{1}{r} \frac{d}{d r}\left(r \frac{d \varphi}{d r}\right)=0 \tag{2.11}
\end{equation*}
$$

where $r$ is the distance from the central axis of the cylinder to a certain point in space. The solution of eq.(2.11) is:

$$
\begin{equation*}
\varphi_{i}=\alpha_{i} \ln r+\beta_{i} \tag{2.12}
\end{equation*}
$$

We follow the same rule for superscripts as that for spherical nanoparticle. To avoid the singularity at the center, we must set $\alpha_{2}=0$. As a result, $\varphi_{2}=\beta_{2}$ meaning that the potential is constant inside the cylinder and the magnetic field is zero inside. Since the magnetization inside the cylinder is parallel to the surface, the magnetic induction $\boldsymbol{B}=\mu_{0}(\boldsymbol{H}+\boldsymbol{M})$ is also parallel to the surface. However, the magnetic field outside the cylinder is perpendicular to the surface because eq.(2.12) is only a function of $r$. Since the magnetization outside is zero, the only way to match the perpendicular component of the magnetic induction is to make the magnetic field outside also zero. As a result, $\alpha_{1}=0$. The continuity of potential will force $\beta_{1}=\beta_{2}$. As a result, potential is constant everywhere in space. The magnetic field and magnetic induction distribution are as follows:

$$
\left\{\begin{array}{l}
\boldsymbol{H}=0 ; \boldsymbol{B}=\mu_{0} \boldsymbol{M}(r \leq a)  \tag{2.13}\\
\boldsymbol{H}=0 ; \boldsymbol{B}=0 \quad(r>a)
\end{array}\right.
$$

If one applies an external magnetic field $H_{\mathrm{e}}$ along the long axis of the cylinder, the magnetic cylinder wouldn't disturb this field $H_{\mathrm{e}}$. In other words, the demagnetization factor along the long axis of an infinitely long cylinder is zero.

In case II, the magnetization is perpendicular to the long axis. The problem becomes two dimensional (Figure 2.4(b)). If we introduce cylindrical coordinates as shown in Figure 2.4(b), both $r$ and azimuth angle $\theta$ will appear in the Laplace equation(2.3):

$$
\begin{equation*}
\frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial \varphi}{\partial r}\right)+\frac{1}{r^{2}} \frac{\partial^{2} \varphi}{\partial \theta^{2}}=0 \tag{2.14}
\end{equation*}
$$

We seek the solution in the form:

$$
\begin{equation*}
\varphi_{i}=\alpha_{i}(\boldsymbol{M} \cdot \boldsymbol{r})+\beta_{i} \frac{(\boldsymbol{M} \cdot \boldsymbol{r})}{r^{2}} \tag{2.15}
\end{equation*}
$$

The same boundary conditions eq.(2.7) are imposed. To make potential finite at $r=0$ and $r=\infty$, we have to impose the conditions $\alpha_{1}=\beta_{2}=0$. The remaining coefficients $\alpha_{2}$ and $\beta_{1}$ are obtained by solving eq.(2.7):

$$
\left\{\begin{array}{l}
\beta_{1} \frac{(\boldsymbol{M} \cdot \boldsymbol{a})}{a^{2}}=\alpha_{2}(\boldsymbol{M} \cdot \boldsymbol{a})  \tag{2.16}\\
\mu_{0} \beta_{1}\left[-\frac{(\boldsymbol{M} \cdot \boldsymbol{a})}{a^{3}}+\frac{2(\boldsymbol{M} \cdot \boldsymbol{a})}{a^{3}}\right]=\mu_{0} \frac{\left(-\alpha_{2} \boldsymbol{M} \cdot \boldsymbol{a}+\boldsymbol{M} \cdot \boldsymbol{a}\right)}{a}
\end{array}\right.
$$

$\beta_{1}$ and $\alpha_{2}$ are obtained as:

$$
\begin{equation*}
\alpha_{2}=\frac{1}{2} \quad, \quad \beta_{1}=\frac{a^{2}}{2} \tag{2.17}
\end{equation*}
$$

The magnetic field $\boldsymbol{H}(r)=-\nabla \varphi$ and magnetic induction $\boldsymbol{B}(r)=\mu_{0}[\boldsymbol{H}(r)+\boldsymbol{M}(r)]$ are interpreted as:

$$
\left\{\begin{array}{l}
\boldsymbol{H}=-\frac{\boldsymbol{M}}{2} ; \boldsymbol{B}=\frac{\mu_{0} \boldsymbol{M}}{2}(r \leq a)  \tag{2.18}\\
\boldsymbol{H}=\frac{a^{2}}{2}\left(\frac{2(\boldsymbol{M} \cdot \boldsymbol{r}) \boldsymbol{r}}{r^{4}}-\frac{\boldsymbol{M}}{r^{2}}\right) ; \boldsymbol{B}=\frac{\mu_{0} a^{2}}{2}\left(\frac{2(\boldsymbol{M} \cdot \boldsymbol{r}) \boldsymbol{r}}{r^{4}}-\frac{\boldsymbol{M}}{r^{2}}(r>a)\right.
\end{array}\right.
$$

Magnetic field $\boldsymbol{H}$ inside the infinitely long cylinder is uniform and antiparallel to the magnetization vector which is perpendicular to the long axis. Magnitude of the magnetic field is half of the magnetization $M$. The demagnetization factor $N=1 / 2$ shows the effect of shielding of the external magnetic field i.e. the total magnetic field $H_{\mathrm{t}}$ inside the nanorod is smaller than the external magnetic field: $H_{\mathrm{t}}=H_{\mathrm{e}}-N M=H_{\mathrm{e}}-M / 2$.

### 2.1.4 Effective charge model for magnetic nanorod

As discussed in the previous section, magnetic nanorod is much easier to be magnetized along its long axis. For some ferromagnetic material, the shape anisotropy might overpower the crystalline anisotropy and magnetization will always follow the long axis when the external magnetic field is absent (comparison between shape and crystalline anisotropy in chapter I). We will discuss this particular case more carefully. In previous sections, we always assumed that the nanorod is infinitely long to ignore the end effects. However, in some cases, this approximation might not work for example when studying the field distribution in the vicinity of the poles or the interaction between two nanorods[1]. To take into account the end effects, we consider an infinitely thin nanorod which is a reasonable approximation for the high aspect ratio nanorods.


Figure 2.5 Coordinate system to define the position and orientation of nanorods. The long axis of the nanorod in is $z$-direction and $r_{0}$ is the position vector of the center of the nanorod.

As shown in Figure 2.5, the long axis of the infinitely thin nanorod is in $z$ direction and the position vector of the center of the nanorod is $\boldsymbol{r}_{0}$. Two poles will be sitting at $\boldsymbol{r}_{0} \pm l / 2 \hat{z}$, in which $l$ is the length of the nanorod and $\hat{z}$ is the unit vector in $z$ -
direction. Following this system of coordinates, the magnetization vector $\boldsymbol{M}(\boldsymbol{r})$ is defined as:

$$
\begin{equation*}
\boldsymbol{M}(\boldsymbol{r})=\int_{-l / 2}^{l / 2} \delta\left[\boldsymbol{r}-\left(\boldsymbol{r}_{0}+s \hat{z}\right)\right] Q \hat{z} d s \tag{2.19}
\end{equation*}
$$

where $\boldsymbol{r}$ is the position vector of the observation point in space. $Q$ is the linear density of magnetic moment i.e. the magnetic moment per unit length. $Q d s$ is the magnetic moment of infinitesimal magnetic dipole of length $d s$. We can substitute eq.(2.19) into eq.(2.2) and apply the relation $\boldsymbol{B}=\mu_{0}(\boldsymbol{H}+\boldsymbol{M})$ to derive the following equation:

$$
\begin{align*}
\nabla \cdot \boldsymbol{H} & =-\nabla \cdot \int_{-l / 2}^{l / 2} \delta\left[\boldsymbol{r}-\left(\boldsymbol{r}_{0}+s \hat{z}\right)\right] Q \hat{z} d s \\
& =-\nabla \cdot \int_{-l / 2}^{1 / 2} \delta\left(x-x_{0}\right) \delta\left(y-x_{0}\right) \delta\left(z-z_{0}-s\right) Q \hat{z} d s \tag{2.20}
\end{align*}
$$

where the relations $\boldsymbol{r}=(x, y, z), \boldsymbol{r}_{0}=\left(x_{0}, y_{0}, z_{0}\right)$ are applied. Since vector $\boldsymbol{M}(\boldsymbol{r})$ is directed along the $z$-axis, we replace the divergence operator with $\partial / \partial z$ on the right hand side of eq.(2.20):

$$
\begin{equation*}
\nabla \cdot \boldsymbol{H}=-\delta\left(x-x_{0}\right) \delta\left(y-x_{0}\right) \int_{-l / 2}^{l / 2} \frac{\partial}{\partial z} \delta\left(z-z_{0}-s\right) Q d s \tag{2.21}
\end{equation*}
$$

Defining a new variable $\xi=z-z_{0}-s$, and using the relations $d \xi=d z$ and $d \xi=-d s$, eq.(2.21) is rewritten as:

$$
\begin{align*}
\nabla \cdot \boldsymbol{H} & =\delta\left(x-x_{0}\right) \delta\left(y-x_{0}\right) \int_{z-z_{0}+l / 2}^{z-z_{0}-l / 2} \frac{\partial}{\partial \xi} Q \delta(\xi) d \xi \\
& =\delta\left(x-x_{0}\right) \delta\left(y-x_{0}\right)\left[\delta\left(z-z_{0}-l / 2\right)-\delta\left(z-z_{0}+l / 2\right)\right] Q  \tag{2.22}\\
& =Q \delta\left[\boldsymbol{r}-\left(\boldsymbol{r}_{0}+\frac{l}{2} \hat{z}\right)\right]-Q \delta\left[\boldsymbol{r}-\left(\boldsymbol{r}_{0}-\frac{l}{2} \hat{z}\right)\right]
\end{align*}
$$

Therefore, employing the electrostatics analogy, one can state that the magnetic field $\boldsymbol{H}$ generated by an infinitely thin magnetic nanorod is equivalent to the magnetic
field generated by two "magnetic charges" $\pm Q$, sitting at the two poles $r_{0} \pm / / 2 \hat{z}$. According to the definition of $Q d s$ as the magnetic moment of an infinitesimal magnetic dipole, one can obtain the relation between "magnetic charges" $Q$ and the magnetization $M$ of the magnetic nanorod with diameter $d: Q=M \pi d^{2} / 4$. In the system of coordinates with the origin taken at the nanorod center i.e. $\boldsymbol{r}_{0}=(0,0,0)$, the field is written as

$$
\boldsymbol{H}=\frac{M d^{2}}{16}\left(\frac{\hat{r}_{+}}{x^{2}+y^{2}+(z-l / 2)^{2}}-\frac{\hat{r}_{-}}{x^{2}+y^{2}+(z+l / 2)^{2}}\right) \quad\left\{\begin{array}{l}
\hat{r}_{+}=\frac{(x, y, z-l / 2)}{\sqrt{x^{2}+y^{2}+(z-l / 2)^{2}}}  \tag{2.23}\\
\hat{r}_{-}=\frac{(x, y, z+l / 2)}{\sqrt{x^{2}+y^{2}+(z+l / 2)^{2}}}
\end{array}\right.
$$



Figure 2.6 Magnetic field distribution of a uniformly magnetized nanorod with aspect ratio $/ / d=10$. The left part is simulated(Finite Element Method) using COMSOL 4.2 and the right part is the distribution is calculated using eq.(2.23)

Figure 2.6 illustrates that the magnetic field generated by a magnetic nanorod with magnetization $M$ and aspect ratio $l / d=10$ is well approximated by the field generated by two magnetic charges $\pm M \pi d^{2} / 4$ separated by distance $l$. The left half of Figure 2.6 is simulated using COMSOL4.2 assuming a uniform magnetization while the right half is
calculated using eq.(2.23). The magnitude of the magnetic field $H$ is normalized by the magnetization $M$. For a nanorod with finite diameter $d$, magnetic charges are distributed uniformly on the pole surface rather than concentrated at one point. Even though, for a nanorod with aspect ratio $l / d=10$, the right half of Figure 2.6 still matches very well with the left half. Therefore, for a magnetic nanorod with aspect ratio $l / d$ higher than 10 , it is safe to treat it as two magnetic charges $\pm M \pi d^{2} / 4$ separated by distance $l$. The physics behind this approximation can be explained as follows. One can divide the magnetic nanorod into many small dipoles, each dipole has the moment $m_{i}=Q \Delta l$ following the definition of electric dipole (Figure 2.7). If we sum up all the dipoles in the nanorod, all the charges inside will be cancelled out and the charge will only appear on two ends of the nanorod.


Figure 2.7 Schematic for magnetic charge model
To conclude, we solved the magnetostatic problems for both a single domain magnetic nanosphere and a nanorod. The field generated by a spherical nanoparticle is equivalent to the field generated by a magnetic dipole sitting at the center of the particle. For the magnetic nanorod, we found that the field generated by an infinitely thin
magnetic nanorod with magnetization along the long axis is equivalent to the field generated by two magnetic charges sitting at the nanorod ends.

### 2.2 Interaction between nanoparticles: nanospheres and nanorods

### 2.2.1 Spherical nanoparticles: dipole-dipole interactions

Following the previous section, the interactions between spherical nanoparticles correspond to the interactions between two point magnetic dipoles sitting at the centers of the particles. The energy of these interactions is written as[2]:

$$
\begin{equation*}
U=-\frac{\mu_{0}}{4 \pi r^{3}}\left[3\left(\boldsymbol{m}_{1} \cdot \frac{\boldsymbol{r}}{r}\right)\left(\boldsymbol{m}_{2} \cdot \frac{\boldsymbol{r}}{r}\right)-\boldsymbol{m}_{1} \cdot \boldsymbol{m}_{2}\right] \tag{2.24}
\end{equation*}
$$

where $\boldsymbol{r}$ is the vector connecting the centers of the two spherical nanoparticles, $\boldsymbol{m}_{1} \boldsymbol{m}_{2}$ are the two point magnetic dipoles, $\mu_{0}$ is the magnetic permeability of vacuum.


Figure 2.8 Schematic of two interacting dipoles
In 2D case, all the vectors can be defined by introducing a polar coordinate system as shown in Figure 2.8. $\theta_{1}$ and $\theta_{2}$ are the polar angles of the two magnetic dipoles $\boldsymbol{m}_{1}$ and $\boldsymbol{m}_{2} . \varphi$ is the polar angle of the connecting vector $\boldsymbol{r}$. Using the relations:
$\boldsymbol{m}_{1}=m_{1}\left(\cos \theta_{1}, \sin \theta_{1}\right), \boldsymbol{m}_{2}==m_{2}\left(\cos \theta_{2}, \sin \theta_{2}\right), \boldsymbol{r}=r(\cos \varphi, \sin \varphi)$, the energy of dipole-dipole interactions is rewritten in terms of $\theta_{1}, \theta_{2}$ and $\varphi$ as:

$$
\begin{equation*}
U=\frac{\mu_{0} m_{1} m_{2}}{4 \pi r^{3}} f\left(\theta_{1}, \theta_{2}, \varphi\right) ; f\left(\theta_{1}, \theta_{2}, \varphi\right)=\cos \left(\theta_{1}-\theta_{2}\right)-3 \cos \left(\theta_{1}-\varphi\right) \cos \left(\theta_{2}-\varphi\right) \tag{2.25}
\end{equation*}
$$

The energy dependences on the distance $(r)$ and orientations $\left(\theta_{1}, \theta_{2}, \varphi\right)$ are separated. If the orientation function is positive, $f\left(\theta_{1,}, \theta_{2}, \varphi\right)>0$, the distance $r$ has to be maximized to decrease the energy indicating a repulsion between two nanoparticles. In contrary, if $f\left(\theta_{1}, \theta_{2}, \varphi\right)<0$, the dipole-dipole attraction will try to bring two nanoparticles together.

Figure 2.9 shows the energy diagram characterizing the interaction between two spherical nanoparticles. Distance $r$ is fixed and only $f\left(\theta_{1,}, \theta_{2}, \varphi\right)$ is plotted. Black lines are the separatrices dividing the energy diagram into five regions. In region I, III and V, the function $f\left(\theta_{1}, \theta_{2}, \varphi\right)$ is negative implying that an attraction between particles. In region II and IV, the function $f\left(\theta_{1}, \theta_{2}, \varphi\right)$ is positive implying a repulsion between particles.


Figure 2.9 Energy diagram describing interactions between two dipoles. The distance between two nanoparticles is fixed and the dipole orientations $\theta_{1}$ and $\theta_{2}$ are variables.

In Figure 2.9, points 1 and 2 are the two energy minimas corresponding to the head to tail parallel configuration: two magnetic dipoles are either parallel or antiparallel to the connecting vector $\boldsymbol{r}$. Points 3 and 4 are the two energy maximas corresponding to the head to head antiparallel configuration: one magnetic dipole is parallel to the connecting vector $\boldsymbol{r}$ and the other one is antiparallel to it. The head to tail parallel configuration corresponds to the stable equilibrium state. Point 5 corresponds to the side by side antiparallel configuration and it's neither an energy minima nor maxima.

Magnetic force acting between two dipoles can be calculated by taking gradient of the interaction energy. The radial $F_{\mathrm{r}}$ and tangential $F_{\varphi}$ components of the magnetic force generated by particle 1 and acting on particle 2 are interpreted as:

$$
\left\{\begin{array}{l}
F_{\mathrm{r}}=-\frac{\partial U}{\partial r}=\frac{3 \mu_{0} m_{1} m_{2}}{4 \pi r^{4}}\left[\cos \left(\theta_{1}-\theta_{2}\right)-3 \cos \left(\theta_{1}-\varphi\right) \cos \left(\theta_{2}-\varphi\right)\right]  \tag{2.26}\\
F_{\varphi}=-\frac{1}{r} \frac{\partial U}{\partial \varphi}=\frac{3 \mu_{0} m_{1} m_{2}}{4 \pi r^{4}} \sin \left(\theta_{1}+\theta_{2}-2 \varphi\right)
\end{array}\right.
$$

The magnetic force acting on particle 1 will be of the same magnitude but in opposite direction. The torque acting on the two particles can be calculated by taking the derivative with respect to the polar angles $\theta_{1}$ or $\theta_{2}$ :

$$
\left\{\begin{array}{l}
\tau_{12}=-\frac{\partial U}{\partial \theta_{2}}=\frac{\mu_{0} m_{1} m_{2}}{4 \pi r^{3}}\left[\sin \left(\theta_{2}-\theta_{1}\right)-3 \cos \left(\theta_{1}-\varphi\right) \sin \left(\theta_{2}-\varphi\right)\right]  \tag{2.27}\\
\tau_{21}=-\frac{\partial U}{\partial \theta_{1}}=\frac{\mu_{0} m_{1} m_{2}}{4 \pi r^{3}}\left[\sin \left(\theta_{1}-\theta_{2}\right)-3 \sin \left(\theta_{1}-\varphi\right) \cos \left(\theta_{2}-\varphi\right)\right]
\end{array}\right.
$$

where $\tau_{12}$ is the torque generated by particle 1 and acting on particle 2 , $\tau_{21}$ is the torque generated by particle 2 and acting on particle 1 . Magnetic torques force the nanoparticles to rotate while magnetic forces result in translational motion of nanoparticles.

If a sufficiently strong magnetic field is present, two particles will be forced to orient in direction of the field, there will be no rotation of the particle but only translational motion. This scenario has great importance and is widely used for the field directed assembly of magnetic nanoparticles[3-5]. We'll study this problem more carefully.


Figure 2.10 Coordinate system for the two interacting magnetic nanoparticles with their magnetic moments in y-direction. Particle 1 is fixed, particle 2 is moving.

To simply the problem, we consider particle 1 fixed at the origin of the system of coordinates and particle 2 is free to move in the fluid (Figure 2.10). The external magnetic field is in y-direction. Two nanoparticles have the same radius $R_{1}=R_{2}=R$. The energy of dipole-dipole interactions is simplified to:

$$
\begin{equation*}
U=\frac{\mu_{0} m_{1} m_{2}}{4 \pi r^{3}}\left(1-3 \sin ^{2} \varphi\right) \tag{2.28}
\end{equation*}
$$

The magnetic force acting on particle 2 is interpreted as:

$$
\left\{\begin{array}{l}
F_{\mathrm{r}}=\frac{3 \mu_{0} m_{1} m_{2}}{4 \pi r^{4}}\left(1-3 \sin ^{2} \varphi\right)  \tag{2.29}\\
F_{\varphi}=\frac{3 \mu_{0} m_{1} m_{2}}{4 \pi r^{4}} \sin 2 \varphi
\end{array}\right.
$$



Figure 2.11 Energy of interactions between two magnetic nanoparticles. One is fixed at the origin, the other one is free to move. Color represents the level of the energy. Black arrows indicate the direction of the force. Blue lines corresponding to $U=0$ and $F_{\mathrm{r}}=0$ divide the diagram into attraction and repulsion zones.

Figure 2.11 shows the energy of interactions between two magnetic nanoparticles.
The white semicircle is the forbidden region for particle 2 because when particle 2 comes in contact with particle 1 , it can only roll over the particle surface. The center of particle 2 would draw the circle of radius $2 R$. The color represents the level of the energy and the black arrows indicate the direction of the magnetic force acting on particle 2. The energy miminum is achieved when the magnetic force forces particle 2 to stay on top of particle 1 forming the head to tail configuration: point 1 in Figure 2.9.

The blue line is the separatrix separating the attraction and repulsion regions. It corresponds to the contour line of $U=0$ ( $U>0$, repulsion, $U<0$ attraction). Using eq.(2.29), the separatrix can is specified as:

$$
\begin{equation*}
\sin \varphi= \pm \frac{1}{\sqrt{3}} \quad \text { or } \quad y= \pm \frac{x}{\sqrt{2}} \tag{2.30}
\end{equation*}
$$

According to eqs(2.28) and (2.29) this contour line also corresponds to $F_{\mathrm{r}}=0$ as well.
Assume that particle 2 is suspended in a simple Newtonian fluid with viscosity $\eta$. In the limit of low Reynolds number $(\operatorname{Re}=\rho V R / \eta \ll 1, \rho$ : density of fluid, $V$ : velocity of the particle) when the inertial force is much smaller than the viscous forces, the velocity of particle 2 will be[6]:

$$
\left\{\begin{array}{l}
V_{\mathrm{r}}=\dot{r}=\frac{F_{\mathrm{r}}}{6 \pi \eta R}  \tag{2.31}\\
V_{\varphi}=r \dot{\varphi}=\frac{F_{\varphi}}{6 \pi \eta R}
\end{array}\right.
$$

Eq.(2.31) indicates that the velocity of the nanoparticle is always pointing in the direction of magnetic force. As a result, the force field shown in Figure 2.11 is also the velocity field of particle 2.

### 2.2.2 Magnetic nanorods interacting by magnetic charges



Figure 2.12 Cartesian coordinate system to characterize the interaction between two nanorods
As shown in section 2.1.4, we should treat the magnetic nanorods with high aspect ratio as two separate magnetic charges. The interaction between two magnetic
nanorods should be written in terms of interactions between magnetic charges. We still consider a 2D case, i.e the two magnetic nanorods always stay in the same plane. To simply the notation, we build a Cartesian coordinate system (Figure 2.12) placing nanorod I in y-direction with its mass center at the origin.

Both nanorods have the same magnetization $M$, length $l$, diameter $d$ and the magnetic charge $Q=\pi M d^{2} / 4$. The total interaction between two nanorods can be calculated by summing up four interactions marked in Figure 2.12.

$$
\left.\begin{array}{l}
U(x, y, \theta)=\frac{\mu_{0} \pi M^{2} d^{4}}{64} \\
\left(\frac{1}{\sqrt{\left(x+\frac{l}{2} \cos \theta\right)^{2}+\left(y+\frac{l}{2} \sin \theta-\frac{l}{2}\right)^{2}}}-\frac{1}{\sqrt{\left(x-\frac{l}{2} \cos \theta\right)^{2}+\left(y-\frac{l}{2} \sin \theta-\frac{l}{2}\right)^{2}}}\right.  \tag{2.32}\\
-\frac{1}{\sqrt{\left(x+\frac{l}{2} \cos \theta\right)^{2}+\left(y+\frac{l}{2} \sin \theta+\frac{l}{2}\right)^{2}}}+\frac{1}{\sqrt{\left(x-\frac{l}{2} \cos \theta\right)^{2}+\left(y-\frac{l}{2} \sin \theta+\frac{l}{2}\right)^{2}}}
\end{array}\right)
$$

The magnetic force acting on nanorod II can be calculated as:

$$
\left\{\begin{array}{l}
F_{\mathrm{x}}=-\frac{\partial U(x, y, \theta)}{\partial x}  \tag{2.33}\\
F_{\mathrm{y}}=-\frac{\partial U(x, y, \theta)}{\partial y}
\end{array}\right.
$$

We assume nanorod I is fixed and nanorod II is free to move in a simple Newtonian fluid (constant viscosity $\eta$ ). Consider a sufficiently strong magnetic field pointing in $y$ direction so that nanrod II is always parallel to nanorod I $(\theta=\pi / 2)$.

In the limit of low Reynolds number, the translational velocity of nanorod 2 can be interpreted as[6]:

$$
\begin{align*}
& V_{\mathrm{x}}=F_{\mathrm{x}} \frac{\ln (2 l / d)+0.5}{4 \pi \eta l}  \tag{2.34}\\
& V_{\mathrm{y}}=F_{\mathrm{y}} \frac{\ln (2 l / d)-0.5}{2 \pi \eta l}
\end{align*}
$$

It follows that the velocity doesn't follow the direction of magnetic force due to different drag in $x$ and $y$ direction.


Figure 2.13 Energy diagram characterizing the interaction between two parallel nanorods. The white line $\left(F_{\mathrm{r}}=0\right)$ is the boundary separating the attraction from repulsion. The red line is the zero energy contour line $(U=0)$. The blue lines $(y= \pm x / \sqrt{2})$ are the boundary lines of attraction and repulsion zone for the dipole-dipole interactions.

Figure 2.13 shows the energy diagram for this special case. Point 1 is the energy minima and point 2 is the energy maxima. Point 1 corresponds to the stable equilibrium configuration: head to tail parallel orientation as shown in Figure 2.13. Nanorod II will always come to point 1 forming this equilibrium configuration. To define the attraction and repulsion region, we introduce the radial component of the magnetic force:

$$
\begin{equation*}
F_{\mathrm{r}}=F_{\mathrm{x}} \cos \varphi+F_{\mathrm{y}} \sin \varphi \tag{2.35}
\end{equation*}
$$

If $F_{\mathrm{r}}>0$, the magnetic force tends to increase the separation $r$ between the nanorods indicating a repulsion. If $F_{\mathrm{r}}<0$, the magnetic force tends to decrease the
saparation $r$ between the nanorods indicating an attraction. The boundary line separating the attraction and repulsion regions will be $F_{\mathrm{r}}=0$ (the white line in Figure 2.13). It is different from the contour line: $U=0$ (the red line in Figure 2.13). In contrast, in case of dipole-dipole interaction, the contour lines of $U=0$ and $F_{\mathrm{r}}=0$ are the same $(y= \pm x / \sqrt{2}$, the blue lines in Figure 2.13). These two straight lines are the asymptotes for both $F_{\mathrm{r}}=0$ and $U=0$ for the charge interaction model because in the limit: $x \gg l, y \gg l$ as the distance between nanorods is much greater than the length of nanords, two nanorods can be treated as point dipoles and the contour lines of $F_{r}=0$ and $U=0$ will match those of the dipole-dipole interaction case.


Figure 2.14 Energy diagram characterizing the interaction between two antiparallel nanorods. The white line $\left(F_{\mathrm{r}}=0\right)$ is the boundary separating the attraction from repulsion. The red line is the zero energy contour line $(U=0)$. Blue lines $(y= \pm x / \sqrt{2})$ are the boundary lines separating attraction from repulsion zones for the dipole-dipole interactions.

We can use the same method to construct the energy diagram and force field for two antiparallel nanorods $(\theta=-\pi / 2)$. As shown in Figure 2.14, point 1 becomes the energy maxima and point 2 is the energy minima corresponding to the antiparallel side by side configuration. Nanorod II will always come to point 2 to form this equilibrium
configuration. The boundary line distinguishing attraction and repulsion remains the same. The attraction zone for the parallel case becomes repulsion zone for antiparallel case and vice versa.

The energy of interaction for the two equilibrium configurations (point 1 for parallel case, point 2 for antiparallel case) can be calculated using eq.(2.32):

$$
\left\{\begin{array}{l}
U_{1}(0, l+\Delta l, \pi / 2)=\frac{\mu_{0} \pi M^{2} d^{4}}{64}\left(\frac{2}{l+\Delta l}-\frac{1}{2 l+\Delta l}-\frac{1}{\Delta l}\right) \approx-\frac{1}{\Delta l} \frac{\mu_{0} \pi M^{2} d^{4}}{64}  \tag{2.36}\\
U_{2}(\Delta l, 0,-\pi / 2)=\frac{\mu_{0} \pi M^{2} d^{4}}{64}\left(-\frac{2}{\Delta l}+\frac{2}{\sqrt{(\Delta l)^{2}+l^{2}}}\right) \approx-\frac{2}{\Delta l} \frac{\mu_{0} \pi M^{2} d^{4}}{64}
\end{array}\right.
$$

A small separation $\Delta l(\Delta l \ll l)$ is introduced to avoid singularity (infinite energy). It becomes clear that, the energy of interactions between two nanorods placed side by side antiparallel to each other (point 2 for the antiparallel case) is lower than the head to tail parallel configuration (point 1 for the parallel case). In the side by side antiparallel case, all the magnetic charges are neutralized. Therefore, this configuration corresponds to the lowest energy state and is the most stable configuration. When the external magnetic field is absent, two magnetic nanorods prefer to form the side by side antiparallel configuration.

### 2.3 Conclusions

In this chapter, we solved the magnetostatic problems for both single domain magnetic nanosphere and nanorod. The demagnetization factors for both nanosphere and nanorod were calculated using these solutions. Spherical nanoparticle is isotropic ( $N_{a}=N_{b}=N_{c}=1 / 3$ ) and magnetic nanorod is easier to be magnetized along its long axis $c$ $\left(N_{a}=N_{b}=1 / 2, N_{c}=0\right)$.

The field generated by a spherical nanoparticle was found to be equivalent to the field generated by a magnetic dipole positioned at the center of the particle. The field generated by an infinitely thin magnetic nanorod with magnetization along the long axis is equivalent to the field generated by two opposite magnetic charges sitting at the two poles.

Based on the solutions of magneostatics, we discussed the interactions between both spherical nanoparticles and nanorods. For the spherical nanoparticles the head to tail configuration is always the equilibrium configuration. For the magnetic nanorods the side by side placement with antiparallel magnetic moments is the most stable configuration when the external magnetic field is absent. If the external magnetic field is present, the head to tail configuration with parallel magnetic moments will be achieved. For both nanospheres and nanorods, attractive and repulsive interactions between two particles can be defined using the radial component of the magnetic force: $F_{\mathrm{r}}>0$ means repulsion and $F_{\mathrm{r}}<0$ means attraction. The separatrices $\left(F_{\mathrm{r}}=0\right)$ for the spherical nanoparticles and nanorods are different. For the spherical nanoparticles, the contour lines $F_{r}=0$ are two straight lines $y= \pm x / \sqrt{2}$ and they overlap with the contour line of $U=0$. In the case of magnetic nanorod, the contour line $U=0$ is different from that of $F_{\mathrm{r}}=0$, the separatrices $y= \pm x / \sqrt{2}$ are the asymptotes for the contour lines of both $U=0$ and $F_{\mathrm{r}}=0$, because when the distance between nanorods is much greater than the nanorod length, the nanorods behave as dipoles.

### 2.4 References

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## CHAPTER III

## SYNTHESIS AND CHARACTERIZATION OF MAGNETIC NANORODS

### 3.1 Synthesis of magnetic nanorods

There are several methods to make the rod-like magnetic nanoparticles, for example, the field directed assembly of magnetic nanobeads[1-3], filling nanotubes with magnetic nanoparticles[4], template based electrochemical deposition[5] as well as template free wet chemical synthesis[6]. In our research, we use the template based electrochemical growth of magnetic metal nanorods, which enables precise control of the size of nanorods.

The circular alumina membranes ( 25 mm diameter, Whatman 6809-6022) were used as templates for the synthesis of metallic nanorods. Parallel cylindrical pores perpendicular to the membrane surface run all the way through the membrane. The membranes are $60 \mu \mathrm{~m}$ in depth with 200 nm pores. The porosity $\varepsilon$ of the membrane is approximately 0.5 . The SEM images of such a membrane are shown in Figure 3.1. Pores are pretty uniform in diameter and the synthesized nanorods are expected to have a narrow size distribution.


Figure 3.1 SEM images (Hitachi S4800) of the alumina membrane used for the synthesis of magnetic nanorods: (a) top view, (b) side view of the fractured membrane.

We used a cotton swab to gently spread a Gallium-Indium alloy (Alfa Aesar) on the top side of the membrane to make it conductive. The membrane is placed on top of a clean copper plate (cathode) with the coated top side in contact with the plate. A rubber ring is placed on the membrane. The syringe is tightly clamped to the copper plate using two binder clips to prevent any leakage of the electrolyte. Then the electrolyte is poured into the syringe and a metallic wire (anode) is placed in the electrolyte. The experimental setup is shown in Figure 3.2(a).


Figure 3.2 (a)Experimental setup for the synthesis of metallic nanorods (b) Schematic showing the growth of metallic nanorod inside the porous membrane.

Using different metallic wires and electrolytes, we can grow different magnetic nanorods ( $\mathrm{Ni}, \mathrm{Co}, \mathrm{Fe}$, etc.) inside the membrane. We synthesized both Ni and Co magnetic nanorods. For the synthesis of Ni nanorods, we used a mixture of $\mathrm{NiSO}_{4} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ $(100 \mathrm{~g} / \mathrm{L}), \mathrm{NiCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(20 \mathrm{~g} / \mathrm{L})$, and $\mathrm{H}_{3} \mathrm{BO}_{3}(45 \mathrm{~g} / \mathrm{L})$ in water. The electrolyte for the synthesis of Co nanorods was made by mixing $\mathrm{CoSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}(100 \mathrm{~g} / \mathrm{L})$ and $\mathrm{H}_{3} \mathrm{BO}_{3}(45 \mathrm{~g} / \mathrm{L})$ aqueous solution in water. A 1.5 V voltage was applied by the DC regulated Power supply (GW Instek pss-2005, Instek) to initiate the electrochemical reaction. After the power was turned on, the metallic ions started to come inside the pores and deposit on the Cathode (Figure 3.2(b)). The deposition process was conducted for 12 minutes.

After the reaction was finished, the Gallium-Indium coating was removed using concentrated nitric acid $\left(\mathrm{HNO}_{3}\right)$. This step must be done with great caution otherwise the acid might dissolve the nickel nanorods inside the membrane as well. We took a cotton applicator and dipped it in the Nitric acid. Then we used this soaked cotton applicator to spread the acid onto the Gallium-Indium coating. Meanwhile another clean cotton applicator was used to remove the excessive nitric acid and prevent its penetration into the pores. After the coating was removed, the membrane was rinsed with water and placed into the 10 mL 6 M NaOH aqueous solution for at least 10 minutes until alumina was completely dissolved. The produced nanorods can be separated by decanting the solution and then transferred into the desired solvents (water, ethanol etc.) by several centrifugation /decanting /dispersion cycles. Ultrasound sonication was applied for about 1 minute to obtain a better dispersion of nanorods.


Figure 3.3 SEM images (Hitachi S4800) and the length distribution of nickel and cobalt nanorods synthzied using electrochemical deposition method. Frequency of the histogram is defined as $\Delta N / N . \Delta N$ is the number of nanorods in a certain length interval (e.g. $5 \mu \mathrm{~m}$ to $6 \mu \mathrm{~m}$ ), $N$ is the total number of nanorods. The applied voltage was 1.5 V and duration of reaction was 12 minutes for both cases.

The synthesized nanorods have a narrow length distribution as shown in Figure 3.3. Under the same conditions of chemical deposition (1.5 V voltage for 12 minutes), nickel nanorods were almost twice as long as cobalt nanorods. The length of nanorods was controlled by both the deposition time $T$ and current $I(t)$. In our experiment, the circular membrane has porosity $\varepsilon=0.5$ and the rubber ring has an inner diameter $D=17.5 \mathrm{~mm}$. The average length of the synthesized nanorods $L$ can be estimated through Faraday's law:

$$
\begin{equation*}
Q=\int_{0}^{T} I(t) d t=L \frac{\pi}{4} D^{2} \varepsilon \frac{\rho F}{M_{A}} z \tag{3.1}
\end{equation*}
$$

where $Q$ is the total charge, $\rho$ is the density of metal, $M_{A}$ is the molecular weight, $F=96485 \mathrm{C} / \mathrm{mol}$ is the Faraday constant and $z$ is the valence of metal ion. The current $I(t)$ was recorded during the experiment. For comparison, it is convenient to introduce an average current as $I_{a}=Q / T$. This parameter characterizes the average growth rate of the nanorods.

Table 3.1 Material parameters for nickel and cobalt and the estimated length of nanorod from Faraday's Law

| Material | Molecular <br> weight $M_{A}$ <br> $(\mathrm{~g} / \mathrm{mol})$ | Density $\rho$ <br> $\left(\mathrm{g} / \mathrm{cm}^{3}\right)$ | Valence $z$ |  | Average <br> current $I_{a}$ <br> $(\mathrm{~A})$ | Length $(\mu \mathrm{m})$ <br> Theory Experiment |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 58.7 | 8.91 | 2 | 0.028 | 5.72 | 5.83 |
|  | 58.9 | 8.90 | 2 | 0.015 | 3.08 | 3.14 |

Table 3.1 shows that the molecular weight $M_{A}$, density $\rho$ and valence $z$ are almost the same for nickel and cobalt. The difference in the rod length is mainly attributed to the different average current $I_{a}$. The average current appeared different because we were not able to control it and only voltage was controlled in the experiment. The theoretical value for the nanorod length calculated through the Faraday's law matches well with the value estimated from the SEM images.


Figure 3.4 SEM (Hitachi S4800) images and the size distribution of cobalt nanorods synthzied using electrochemical depsotion method. Voltage was 1.5 V and reaction time was 25 minutes and 60 minutes respectively.

On the other hand, the nanorod length will also depend on the duration of the electrochemical deposition. This dependence for nickel nanorods has been studied by our group and documented in Dr. Tokarev's Ph.D. Thesis[7]. We did the similar experiments for cobalt nanorods. During the synthesis, the applied voltage was kept constant and only the deposition time was varied. The deposition time was $12 \mathrm{mins}, 25 \mathrm{mins}$ and 60 mins respectively. As shown in Figure 3.3 and Figure 3.4, the length of cobalt nanorods increases monotonously $(3.14 \mu \mathrm{~m}, 8.07 \mu \mathrm{~m}, 19.2 \mu \mathrm{~m})$ as the reaction time increases gradually ( $12 \mathrm{mins}, 25 \mathrm{mins}, 60 \mathrm{mins}$ ).

To conclude, we developed the electrochemical deposition method to synthesize both nickel and cobalt nanorods. The diameters of nanorods can be varied by using
different membranes. Due to the lower average current $I_{a}$, the cobalt nanorods are almost twice shorter than the nickel nanorods under the same experimental conditions (the same voltage and reaction time). The length of nanorods can be controlled by changing deposition time $T$.

### 3.2 Characterization of magnetic nanorods

### 3.2.1 X-ray Diffraction


(b)


Figure 3.5 (a) Schematic of an X-ray diffractometer (b) Schematic of the Bragg diffraction
X-ray Diffraction (XRD) is widely used to characterize the crystal structure as well as the crystallite size of the material. Figure 3.5(a) shows schematically the working principle of an X-ray diffractometer. $\theta$ is the incident angle of the X-ray beam defined with respect to the sample surface. For the reflected beam, the detector is positioned at the same angle $\theta$. During the experiment, the angle $\theta$ is varied step by step in a certain range and the intensity $I(\theta)$ of the reflected beam is measured by the detector. Bragg's law is a simplified model of diffraction describing the diffraction of X-ray beam by crystals. As shown in Figure 3.5(b), two crystal planes are separated by distance $d$, and
the path difference between the two beams reflected by the two parallel planes is $2 d \sin \theta$. The Bragg angle $\theta$ is the same angle defined in Figure 3.5(a). Bragg proposed that when the phase difference is a multiple of the X-ray wavelength (constructive interference), a peak will appear in the intensity spectrum $I(\theta)$. This condition is expressed by Bragg's law[8]:

$$
\begin{equation*}
n \lambda=2 d \sin \theta \tag{3.2}
\end{equation*}
$$

where $n$ is a integer and $\lambda$ is the wavelength of the X-ray. For a certain crystal structure, the spacing $d$ between crystal planes is determined by the orientation of the plane defined by the Miller indices $h k l$. Therefore, different peaks in the spectrum $I(\theta)$ correspond to different crystal planes.


Figure 3.6 X-ray diffraction data for (a) cobalt and (b) nickel nanorod powders

Figure 3.6 shows the XRD data for nickel and cobalt nanorod powders obtained from the X-ray diffractometer (Rigaku, Ultima IV). The main peaks for the Co nanorods appear at $41.7^{\circ}, 44.6^{\circ}, 47.4^{\circ}, 75.9^{\circ}, 84.1^{\circ}$ which correspond to (100), (002), (101), (110), (103) planes for the hexagonal close packed crystal lattice. There are also some weak peaks in the spectrum marked by the dashed lines. These minor peaks are probably due to the presence of very small amount of cobalt hydroxide $\left(\mathrm{Co}(\mathrm{OH})_{2}\right)$. The main peaks for Ni nanorods appear at $44.6^{\circ}, 52.0^{\circ}, 76.5^{\circ}$ corresponding to (111), (200), (220) planes for the face centered cubic crystal structure. The additional peak at $83.0^{\circ}$ corresponds to the aluminum stage. There's no such a peak for cobalt, because a zero background stage was used for the experiment with cobalt nanorods.

The size of the crystallites $t$ can be estimated using the Scherrer equation[9]:

$$
\begin{equation*}
t=\frac{K \lambda}{\beta \cos \theta} \tag{3.3}
\end{equation*}
$$

where $K$ is the shape factor and $\beta$ (measured in radians) is the full width at half maximum (FWHM) for the peak. For a spherical crystallite with the cubic symmetry $K \approx 0.94[10]$. The rigorous derivation of eq.(3.3) can be found in Ref[9]. One can grab the idea of derivation of this equation by considering the following model. Assume that the crystal has $N+1$ crystalline planes, the size of crystallite $t$ will be $N d$. Bragg's equation (3.2) can be written in the form $n \lambda=N d \sin \theta=t \sin \theta$ for the two boundary planes of the crystallite. Taking derivative on both sides, one obtains:

$$
\begin{equation*}
\Delta n \lambda=t \cos \theta \Delta \theta \tag{3.4}
\end{equation*}
$$

If one takes $\Delta \theta=\beta, \Delta n=K$, eq.(3.4) is exactly the Scherrer equation.

The Scherrer equation also indicates that the greater FWHM $\beta$, the smaller the crystallite size is i.e. small crystallites broaden the peak. One way to understand this dependence is to consider the crystal as a diffraction grating. The size of the crystallite $t$ is proportional to the number of parallel planes $N+1$ that interact with the X-ray. The total reflection from the crystallite will be the superposition of the beam reflected by each individual planes. The phase difference between the two beams reflected by the plane \#1 and plane $\# N$ will be $2 \pi(N-1) d \sin \theta / \lambda$. Summing up the reflected beams by all the planes, we can write the intensity $I(\theta)$ as:

$$
\begin{equation*}
I(\theta) \propto\left|\sum_{n=1}^{N} e^{i n \gamma}\right|^{2} \propto\left|\frac{\sin (N \gamma)}{\sin \gamma}\right|^{2} \quad \gamma=\frac{2 \pi}{\lambda} d \sin \theta \tag{3.5}
\end{equation*}
$$



Figure 3.7 Dependence of the width of the peak on the number of crystalline planes based on the diffraction grating model.

Figure 3.7 shows how the function $I(\theta)$ varies for different $N$. We took $\gamma=\sin \theta$ for simplicity in the calculation. It clearly shows that with increasing number of crystalline planes $N$, the peak becomes shaper and shaper. The full width at half maximum $\beta$ is
smaller for larger $N$, i.e. for the larger crystallite. The crystallite size $t$ calculated with eq.(3.3) is summarized in the following table.

Table 3.2 Summary of the XRD data interpreted with the Scherrer equation with $\lambda=0.159 \mathrm{~nm}$, $K=0.94$

|  |  | Crystalline | FWHM |  |
| :---: | :---: | :---: | :---: | :---: |
| Plane |  |  |  |  |
| $(h k l)$ | $\beta$ (degree) | Crystallite Size <br> $t(\mathrm{~nm})$ |  |  |
|  | $41.7^{\circ}$ | $(100)$ | 0.27 | 32 |
| Co | $44.6^{\circ}$ | $(002)$ | 0.25 | 36 |
|  | $47.4^{\circ}$ | $(101)$ | 0.62 | 14 |
|  | $75.9^{\circ}$ | $(110)$ | 0.40 | 26 |
|  | $84.1^{\circ}$ | $(103)$ | - | - |
| Ni | $44.6^{\circ}$ | $(111)$ | 0.49 | 17 |
|  | $52.0^{\circ}$ | $(200)$ | 0.56 | 15 |
|  | $76.5^{\circ}$ | $(220)$ | - | - |

The estimated crystallite size is much smaller than the particle size ( 200 nm in diameter, several microns in length). Therefore, the synthesized cobalt and nickel nanorods are polycrystalline particles. Since each crystallite has at least one magnetic domain, the magnetic nanorods cannot form a single domain but have multidomain structures. It should be noted that, the Scherrer equation provides only the lower limit of the crystallite size and should be considered as the orders of magnitude estimation because there are other factors that will contribute to the peak broadening as well. The instrumental peak profile, defects, microstrain as well as temperature factor will all cause the peak broadening.

### 3.2.2 Magnetic Force Microscopy

The magnetic force microscopy (MFM) is a variation of atomic force microscopy (AFM). It is a powerful tool to characterize the magnetic nanostructure of the material. In the MFM, the AFM tip is coated with a thin (<50nm) magnetic film with very high coercivity, so that the magnetization of the probe does not change during the imaging. Figure 3.8 is the schematic of AFM as well as MFM. Forced by a piezoelectric element, the cantilever continuously oscillates about its equilibrium position. The laser beam is used to track the motion of the probe.


Figure 3.8 Schematic of action of the Atomic Force Microscope
In the MFM experiment, two consecutive scans were employed. First, the probe was moving along the sample surface and tapping the surface intermittently as shown in Figure 3.9(a). The height of the probe was adjusted to keep the amplitude of the oscillation constant during the scan. This way, the surface morphology of the sample surface was obtained. Then, the probe was lifted 50 nm above the surface level obtained in the first scan (Figure 3.9(b)). The probe wouldn't touch the surface during the characterization of magnetic interactions.
(a)

(b)


Figure 3.9 The two-step scan in the Magnetic Force Microscopy (a) Intermittent contact mode to obtain surface morphology of the sample (b) Noncontact mode to characterize the magnetic interactions.

The aim of this two-step scan for the MFM is to separate the magnetic interactions from other interactions. In the intermittent contact mode, when the probe is close to the sample surface, the mechanical contact force dominates[11]. Therefore, surface morphology can be correctly obtained. In the noncontact mode, the probe is suspended above the surface, the Van der Waals interactions are much weaker than the magnetostatic interactions, hence the magnetic nanostructure can be probed.


Figure 3.10 The phase shift caused by the magnetic interactions between the MFM tip and magnetic sample

The magnetic moment $\boldsymbol{m}$ of the MFM tip is always pointing in the z-direction (Figure 3.10). The orientation of magnetization in the sample can be parallel, antiparallel
and perpendicular relative to the magnetic moment of the MFM tip. The magnetic force $\boldsymbol{F}$ is written as: $\boldsymbol{F}=\mu_{0}(\boldsymbol{m} \cdot \nabla) \boldsymbol{H}=\mu_{0} m\left(\partial H_{\mathrm{x}} / \partial z, \partial H_{\mathrm{y}} / \partial z, \partial H_{\mathrm{z}} / \partial z\right) . \boldsymbol{H}$ is the magnetic field generated by the sample. $\boldsymbol{m} \cdot \nabla$ is replaced by $m \partial \partial z$ because $\boldsymbol{m}$ is directed in the zdirection. Only the z-component of the magnetic force $F_{Z}=\mu_{0} m \partial H_{z} / \partial z$ will be probed since the cantilever is oscillating in the z-direction. Close to the surface, the direction of the magnetic field $\boldsymbol{H}$ follows the direction of the magnetization $\boldsymbol{M}$ of the sample. The magnetic field is stronger when the tip is closer to the surface i.e. $\partial\left|H_{z}\right| / \partial z>0$. In case A , magnetization $\boldsymbol{M}$ as well as the magnetic field $\boldsymbol{H}$ are parallel to the magnetic moment $\boldsymbol{m}$ $\left(H_{z}>0\right)$. Therefore, the force between the probe and the sample is attractive $\left(\partial H_{z} / \partial z>0\right.$, $F_{z}>0$ ). In case B, both magnetization $\boldsymbol{M}$ and magnetic field $\boldsymbol{H}$ are perpendicular to $\boldsymbol{m}$ ( $H$ ${ }_{z}=0$ ). The z -component of the magnetic force will be zero $\left(F_{z}=0\right)$. Case C is exactly opposite to case A. The magnetization $\boldsymbol{M}$ is antiparallel to $\boldsymbol{m}$ leading to negative field and field gradient $\left(H_{z}<0, \partial H_{z} / \partial z<0\right)$. Force between the probe and the sample is repulsive $\left(F_{z}<0\right)$.

There will be a phase shift caused by the magnetic interactions between the MFM tip and magnetic sample as illustrated in Figure 3.10. This phase dependence can be explained by modeling the small oscillation of cantilever as a forced oscillation of harmonic oscillator:

$$
\begin{equation*}
\ddot{z}+2 \delta \dot{z}+\omega_{0}^{2} z=F_{0} \cos \omega t / m_{\mathrm{f}}+F_{\mathrm{z}}(z) / m_{\mathrm{f}} \tag{3.6}
\end{equation*}
$$

where $\delta>0$ is the damping coefficient, $\omega_{0}=\left(k / m_{\mathrm{f}}\right)^{1 / 2}$ is the natural frequency of the oscillator, $k$ is the effective stiffness of the cantilever and $m_{\mathrm{f}}$ is the effective mass. $F_{0}$ is the driving amplitude and $\omega$ is the driving frequency of the piezoelement. $F_{\mathrm{z}}(z)$ is the
magnetic force acting on the cantilever as discussed above. The magnetic force here is written as a function of the position of the cantilever. This force is stronger when the cantilever moves closer to the sample surface, i.e. $\mathrm{d}\left|F_{\mathrm{z}}(z)\right| / \mathrm{d} z>0$. For these three cases shown in Figure 3.10, Case A: $F_{\mathrm{z}}(z)>0, \mathrm{~d} F_{\mathrm{z}}(z) / \mathrm{d} z>0$, Case $\mathrm{B}: F_{\mathrm{z}}(z)=0, \mathrm{~d} F_{\mathrm{z}}(z) / \mathrm{d} z=0$, Case C: $F_{\mathrm{z}}(z)<0, \mathrm{~d} F_{\mathrm{z}}(z) / \mathrm{d} z<0$. For small oscillations, we can do a Taylor expansion for the magnetic force near the equilibrium position $z_{0}$ of the oscillator and keep only the first order term:

$$
\begin{equation*}
F_{z}(z) \approx F_{z}\left(z_{0}\right)+F_{z}^{\prime}\left(z-z_{0}\right)+\ldots, \quad F_{z}^{\prime}=\left.\frac{\mathrm{d} F_{z}(z)}{\mathrm{d} z}\right|_{z=z_{0}} \tag{3.7}
\end{equation*}
$$

The equilibrium position $z_{0}$ satisfies the relation: $k z_{0}=F_{\mathrm{z}}\left(z_{0}\right)$. The general solution for eq.(3.6) is written as:

$$
\begin{equation*}
z(t)=z_{0}+e^{-\delta t} z_{1}(t)+A_{\mathrm{m}} \cos (\omega t+\varphi) \tag{3.8}
\end{equation*}
$$

where $A_{\mathrm{m}}$ is the amplitude of the oscillation, $\varphi$ is the phase and they satisfy the following relation:

$$
\begin{align*}
A_{\mathrm{m}}= & \frac{F_{0} / m_{\mathrm{f}}}{\sqrt{\left[\left(k-F_{z}^{\prime}\right) / m_{\mathrm{f}}-\omega^{2}\right]^{2}+4 \delta^{2} \omega^{2}}}  \tag{3.9}\\
& \tan \varphi=\frac{2 \delta \omega}{\omega^{2}-\left(k-F_{z}^{\prime}\right) / m_{\mathrm{f}}} \tag{3.10}
\end{align*}
$$

As $t \rightarrow \infty$, the second term on the right hand side of eq.(3.8) disappears and only a harmonic oscillation is observed. Before the measurement, the piezoelement was tuned to operate at the natural frequency of the oscillator i.e. $\omega=\omega_{0}$. As a result, the amplitude and phase can be rewritten as:

$$
\begin{align*}
& A_{\mathrm{m}}=\frac{F_{0} / m_{\mathrm{f}}}{\sqrt{\left(F_{z}^{\prime} / m_{\mathrm{f}}\right)^{2}+4 \delta^{2} \omega_{0}^{2}}}  \tag{3.11}\\
& \tan \varphi=\frac{2 \delta \omega_{0}}{F_{z}^{\prime} / m_{\mathrm{f}}}
\end{align*}
$$

For case $\mathrm{B}, \mathrm{d} F_{\mathrm{z}}(z) / \mathrm{d} z=0, \varphi=\pi / 2$. For case $\mathrm{A}, \mathrm{d} F_{\mathrm{z}}(z) / \mathrm{d} z>0, \varphi<\pi / 2$ i.e. $\Delta \varphi<0$. For case $\mathrm{C}, \mathrm{d} F_{\mathrm{z}}(z) / \mathrm{d} z<0, \varphi>\pi / 2$ i.e. $\Delta \varphi>0$. By scanning over the sample surface, we can identify the orientation of the magnetization in different regions.


Figure 3.11 Magnetic Force Microscopy for the cobalt and nickel nanorods (a) surface morphology of the cobalt nanorod (b) magnetic structure of the cobalt nanorod (c) surface morphology of nickel (d) magnetic structure of the nickel nanorods.

Figure 3.11 shows the MFM image obtained from Atomic Force Microscope (Dimension 3100) for the cobalt and nickel nanorods. For cobalt, the phase image (Figure 3.11(b)) clearly shows the contrast between attractive (bright) and repulsive (dark) regions indicating different orientations of magnetization vector $\boldsymbol{M}$ in the constituting
crystallites. We can conclude that the cobalt nanorod has multi-domain structure in agreement with the results from the X-ray diffraction experiment. Furthermore, the width of each magnetic domain is about 100 nm which is close to the orders of magnitude estimation of the crystallite size for cobalt ( $\sim 40 \mathrm{~nm}$ ). On the other hand, the phase image for the nickel nanorods (Figure 3.11(d)) shows almost zero phase shifts everywhere except in the region close to the two poles. It can represent two nickel nanorods whose magnetic moments are directed along the axes and antiparallel to each other. Based on the MFM phase image, nickel nanorod appears to have a single domain structure, but the X-ray data for nickel already proved that nickel nanorod is polycrystalline and should have a multi-domain structure. This is explained by the weak magnetocrystalline anisotropy of nickel nanorod. The shape anisotropy is almost ten times stronger than the magnetocrystalline anisotropy for nickel as shown in Chapter I. As a result, the magnetic moment is weakly bonded to the crystal axis and would like to follow the long axis of the rod due to the shape anisotropy. The same phenomenon is not observed for cobalt since the shape anisotropy is comparable with crystalline anisotropy. However, for both nickel and cobalt nanorods, the grain boundary between crystallites will affect the magnetization process $[12,13]$.

### 3.2.3 Alternating Gradient Field Magnetometer (AGM)

The most important property for any ferromagnetic material is its magnetic hysteresis. We used the alternating gradient field magnetometer (AGM 2900 Princeton Measurement Inc.) to measure the hysteresis loops for the nickel and cobalt nanorods.


Figure 3.12 (a) The Alternating Gradient Field Magnetometer (AGM 2900) (b) close up for the probe region (c) Schematic, front view (d) Schematic, side view.

Figure 3.12 (a) and (b) are the real pictures of the instrument. The schematic of the probe placement is shown in Figure 3.12 (c) and (d). Two magnets generate a uniform magnetic field $B$ from 0 to 1 T directing along the x -axis. This field magnetizes the sample. Two coils produce the alternating field gradient which exerts an alternating magnetic force to the magnetized sample in the $x$-direction. The frequency of the alternating field gradient is tuned to match the natural frequency of the assembly (extension, sample carrier plus sample). Similar to the cantilever for the Magnetic Force Microscopy, we can also model the oscillation of the probe as a force oscillation of a harmonic oscillator. The deflection $A_{\mathrm{m}}$ of the probe can be written using eq. (3.11):

$$
\begin{equation*}
A_{\mathrm{m}}=\frac{F_{0} / m_{\mathrm{f}}}{2 \delta \omega_{0}} \tag{3.12}
\end{equation*}
$$

where $F_{0}$ is the amplitude of the alternating magnetic force, $m_{\mathrm{f}}$ is the effective mass of the assembly, $\delta$ is the damping coefficient and $\omega_{0}$ is natural frequency.

It follows that the deflection of the probe is proportional to the amplitude of the alternating magnetic force $\left(A_{\mathrm{m}} \propto F_{0}\right)$. This deflection is transmitted to a piezoelectric element. The output signal from the piezoelectric element is also detected at the natural frequency $\omega_{0}$. The amplitude of the field gradient (T/m) is fixed in each measurement and the magnetic force will be proportional to the magnetic moment of the sample ( $F_{0} \propto$ $m)$. Therefore, the magnetic moment of the sample can be determined from the output signal $\left(m \propto A_{\mathrm{m}}\right)$. The range of measurement is from $10^{-9} \mathrm{~A} / \mathrm{m}^{2}$ to $5 \times 10^{-3} \mathrm{~A} / \mathrm{m}^{2}$.


Figure 3.13 Magnetic hysteresis loop of the nickel and cobalt nanorods measured by the Alternating Gradient Field Magnetometer (AGM 2900 Princeton Measurements Inc.). Both nanorods were synthesized under 1.5 V for 12 minutes. (a) The full field range (b) close up for the low field range.

The hysteresis loops for both cobalt and nickel nanorods are shown in Figure 3.13. Both nanorods were synthesized under 1.5 V for 12 minutes (Figure 3.3). About 0.1 mg dry powder of the magnetic nanorods were placed on the probe for each measurement.

Figure 3.13 confirms that both types of nanoords are ferromagnetic with welldefined remanence $M_{\mathrm{r}}$ and coercivity $H_{\mathrm{c}}$. The saturation magnetization is close to the values for the bulk materials (nickel: $4.9 \times 10^{5} \mathrm{~A} / \mathrm{m}$, cobalt: $1.4 \times 10^{6} \mathrm{~A} / \mathrm{m}$ ). As discussed in section 3.2.1, the X-ray diffraction shows that the nickel and cobalt nanorods are both
polycrystalline materials. The model for the hysteresis of a single domain nanoparticle introduced in Chapter I will not be applicable for these nanorods.



Figure 3.14 Hysteresis loop (red solid curve) for an assembly of the single domain nanoparticles whose easy axes are randomly oriented. The blue dots are the experimental hysteresis loop. (a) nickel (b) cobalt.

Figure 3.14 shows that the theoretical curve (red curve) based on the single domain theory cannot fit the experimental data (blue dots) taking the anisotropy coefficient $K$ as the adjustable parameter. However, the single-domain model seems to match much better for nickel (Figure 3.14(a)) than for cobalt (Figure 3.14(b)). This tendency agrees with the MFM phase images (Figure 3.11(b) and (d)) which indicate that the nickel nanorod is much closer to a single domain structure than the cobalt nanorod.

The obtained anisotropy constant $K=22 \mathrm{~kJ} / \mathrm{m}^{3}$ is smaller than the value expected for a long nickel nanorod $K=75 \mathrm{~kJ} / \mathrm{m}^{3}$ (see Table 1.1) suggesting that the singled domain cylinder is a very approximate model.


Figure 3.15 (a) The sample zone with temperature variation (b) Schematic, front view (c) Schematic, side view.

The magnetometer also allows us to measure the hysteresis loops at different temperatures. Figure 3.15(a) shows the setup for the temperature variation. It is different from the room temperature measurement (Figure 3.12 (a) and (b)). Helium gas is running through the system and is heated to a desired temperature in the heating zone before reaching the sample zone. By controlling the flow rate and heating current, the temperature in the sample zone is controlled. This temperature can be varied from 10 K to 473 K . Four coils are used to provide an alternating field gradient in $z$ direction.

(b)


Figure 3.16 (a) Hysteresis loops of nickel nanorods taken at different temperatures. (b) Saturation $M_{\mathrm{s}}$, Remanence $M_{\mathrm{r}}$ and Coercivity $H_{\mathrm{c}}$ extracted from the hysteresis loops at different temperatures

Figure 3.16(a) shows how the hysteresis loop changes its form with temperature. The temperature was changed from 10 K to 400 K . The nickel nanorods were sitting inside a piece of the alumina membrane. The sample was first cooled at zero magnetic field to 10 K and then warmed up gradually. The magnetic moment was not normalized by either sample mass or volume. Figure 3.16(b) indicates that, saturation $M_{\mathrm{s}}$, remanence $M_{\mathrm{r}}$ and coercivity $H_{\mathrm{c}}$ all decrease as temperature increases. These magnetic properties do not change significantly with temperature. All these dependences on temperature cannot be explained by the theory for a single domain nanoparticle[14].

### 3.3 Conclusions

In this chapter, we explained the electrochemical deposition method designed to synthesize both nickel and cobalt nanorods. The diameters of nanorods can be controlled by the pore size of membrane and the length of nanorods can be controlled through both deposition time $T$ and average current $I_{a}$. Under the same experimental condition ( 1.5 volt, 12 min ), the produced cobalt nanorods is about half length of nickel due to the relative low average current $I_{a}$. Similar to nickel nanorods, the length of cobalt nanorods increases monotonously ( $3.14 \mu \mathrm{~m}, 8.07 \mu \mathrm{~m}, 19.2 \mu \mathrm{~m}$ ) as the reaction times increase gradually ( $12 \mathrm{mins}, 25 \mathrm{mins}, 60 \mathrm{mins}$ ).

The synthesized cobalt and nickel nanorods were characterized using X-ray diffraction, Magnetic Force Microscopy and Alternating Gradient Field Magnetometer. The X-ray diffraction experiment identified the crystal structure of the two materials: fcc
for nickel and hcp for cobalt. The crystallite size was also estimated using the Scherrer equation. The crystallite size for nickel is approximately 20 nm and 40 nm for cobalt indicating that both nickel and cobalt nanorods should be polycrystalline and multidomain material.

The Magnetic Force Microscopy confirmed the multi-domain structure for cobalt nanorods. The domain width was found to be of the same order of magnitude as crystallite size obtained by XRD. nickel nanorods appeared to be single domain according to the MFM image due to its weak crystalline anisotropy comparing to the shape anisotropy.

The hysteresis loops of the synthesized nanorods were also measured using Alternating Gradient Field Magnetometer. Both nickel and cobalt nanorods are ferromagnetic. We were not able to apply the single domain model to interpret the experimental data. The nickel nanorod showed better agreement than cobalt because its structure is much closer to the single domain structure than that of the cobalt nanorod. The hysteresis loops of nickel nanorods at different temperature were also obtained, saturation $M_{\mathrm{s}}$, remanence $M_{\mathrm{r}}$ and coericity $H_{\mathrm{c}}$ all slightly decreases as temperature increases.

### 3.4 References

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## CHAPTER IV

## COLLECTIVE ALIGNMENT OF MAGNETIC NANORODS IN THIN <br> FILMS

### 4.1 Introduction

In recent years, magnetic nanorods have caught great attention due to the breadth of applications their unique magnetic and geometrical features open for medicine[1, 2], sensors[3, 4], optofluidics[5, 6], and microrheology [7-10]. In particular, magnetic nanorods offer new opportunities in manufacturing of multifunctional composites with unprecedented magnetic and mechanical properties[11-13]. Composites with ordered nanorods are especially attractive for different high-tech applications[14, 15]. At the end of the last century, the problem of particle alignment in liquid media was actively discussed in applications to manufacturing of high-density recording films and discs[1618]. However, the strategy for nanorod alignment in macroscopic materials has not been developed and this remains the main challenge in materials engineering and processing. This problem requires understanding the kinetics of alignment of an assembly of nanorods. It also requires the development of advanced physicochemical methods of nanorod stabilization against agglomeration.

In this chapter, we address these problems using nickel nanorods as a model. To ensure uniformity of the dispersion, the surface of nickel nanorods was covered with polyvinylpyrrolidone (PVP). A $40-70 \mathrm{~nm}$ coating prevents aggregation of nanorods dispersed in a water-glycerol mixture. An orientational distribution function of nanorods is introduced and then studied both theoretically and experimentally for thin Newtonian film. We show that the kinetics of alignment of a nanorod assembly does not follow the predictions of the single-nanorod theory and significantly depends on the initial distribution of nanorods in the film. Then we apply the developed theory to analyze the time dependence of orientational distribution function for nanorods in solidifying films and reveals different regimes of nanorod alignment. We pay the main attention to the specification of a window of materials parameters where the nanorods can be completely aligned along the field during a specific time period.

### 4.2 Alignment of nanorods in Newtonian film

In the manufacturing of thin nanocomposite films, nanorods are aligned in the film plane by applying an external magnetic field parallel to the film surface. In this section, we only conside Newtonian liquids with constant viscosity $\eta$. We restrict ourselves to the case of dilute dispersions in which the interactions between nanorods are weak and can be ignored. To control the kinetics of nanorod alignment, one first needs to understand the kinetics of alignment of a single nanorod.

### 4.2.1 Kinetics of alignment of a single nanorod



Figure 4.1 Basic vectors associated with the magnetic nanorod and magnetic field
The orientation of a single nanorod in an external magnetic field can be described using Cartesian coordinates as shown in Figure 4.1, where $\boldsymbol{m}$ is the magnetic moment, which lies along the nanorod axis, and $\boldsymbol{B}$ is the external magnetic field. Vector $\boldsymbol{m}$ makes angle $\theta$ with vector $\boldsymbol{B}$, vector $\boldsymbol{B}$ makes angle $\alpha$ with the $x$-axis, and vector $\boldsymbol{m}$ makes angle $\varphi$ with the $x$-axis. Thereafter, nanorod orientation is defined by the orientation of its magnetic moment $\boldsymbol{m}$.

In most cases of composite manufacturing, inertial forces play a minor role in nanorod dynamics $[8,10]$. Therefore, balancing the magnetic torque by the viscous torque, one obtains the governing equation describing the nanorod rotation in the film plane [1922]:

$$
\begin{equation*}
\gamma \dot{\varphi}=m B \sin (\alpha-\varphi) \quad, \quad \gamma=\frac{\eta l^{3} \pi}{3 \ln (l / d)-A} \quad, \quad A \approx 2.4, \tag{4.1}
\end{equation*}
$$

where $\gamma$ is the drag coefficient, $l$ is the nanorod length, and $d$ is its diameter, $m$ is the magnetic moment of the nanorod and $B$ is the magnitude of applied field. The drag coefficient was calculated based on the model of an elongated ellipsoid with a high length-to-diameter ratio. In this asymptotic case, the end effects are not important[19].

The nanorod is assumed to revolve only in the film plane without spinning around its axis. Generalization of this model to a 3-D case would require introduction of additional drag coefficients[23]. Assuming that the magnetic field is directed along the $x$-axis, i.e., $\alpha=0$, and $\varphi_{0}$ is the initial orientation of the nanorod at $t=0$, one can solve eq.(4.1) analytically [19-22]:

$$
\begin{equation*}
t=-\frac{1}{\beta} \int_{\varphi_{0}}^{\varphi} \frac{d \varphi}{\sin \varphi}=\frac{1}{\beta} \ln \left|\frac{1-\cos \varphi_{0}}{1-\cos \varphi} \cdot \frac{\sin \varphi}{\sin \varphi_{0}}\right|, \quad\left(\beta=\frac{m B}{\gamma}\right) . \tag{4.2}
\end{equation*}
$$

Solution (4.2) suggests that the dimensionless time $T=\beta t$ for rotation of a nanorod toward its equilibrium orientation at $\varphi=0$ depends only on the initial orientation of the nanorod, $T=T\left(\varphi_{0}\right)$. Equation (4.2) cannot be directly used for estimation of the time needed for complete alignment of the nanorod with the field: direct substitution of $\varphi=0$ in eq.(4.2) results in a singularity, i.e., this time goes to infinity, $t \rightarrow \infty$.


Figure 4.2 Dimensionless time needed for a nanorod to reach its equilibrium orientation as a function of the initial orientation of the nanorod $\varphi_{0}$. The dashed lines help to understand the meaning of this master curve explaining the example in the text.

Therefore, for practical applications of eq.(4.2), one can set a criterion that almost complete co-alignment of a nanorod with the field will occur if its magnetic moment is
pointing toward the sector $-\Delta \varphi<\varphi<\Delta \varphi,|\Delta \varphi| \ll 1$. For example, taking $\Delta \varphi=0.01$, we obtain the behavior shown in Figure 4.2. The curve in Figure 4.2 specifies the dimensionless time $T$ needed for a nanorod that was initially oriented at an angle $\varphi_{0}$ with the $x$-axis, to get into the sector $-0.01<\varphi<0.01$. From this master curve, one can estimate the time needed for a particular nanorod to find its equilibrium orientation. For example, a nanorod at $\varphi_{0}= \pm \pi / 6$ to the $x$-axis will take about $T=4$ dimensionless units, see the dashed lines in Figure 4.2. This implies that the dimensional time to reach the equilibrium orientation $\varphi \cong 0$ will be equal to $t \cong 4 / \beta$ seconds ( $\beta$ is measured in $1 / \mathrm{s}$ ),

It is noteworthy that the required dimensionless time varies from zero to ten, implying that nanorods with magnetic moments antiparallel to the field would take almost ten times longer to reach the equilibrium position than nanorods whose magnetic moments start near the field direction. This observation explains the challenge of ordering an assembly of nanorods in the film: one needs to set up a criterion for nanorod alignment that will guarantee that all nanorods present will be captured and aligned along the field during nanocomposite processing.

### 4.2.2 Kinetics of alignment of nanorods assemblies

It is natural to follow the rotation of a nanorod assembly by introducing the orientational distribution function $F$ :

$$
\begin{equation*}
d N(\varphi)=N_{t} F(\varphi, t) d \varphi \tag{4.3}
\end{equation*}
$$

where $d N(\varphi)$ is the number of nanorods whose major axes are oriented within the angle $\varphi$ and $\varphi+d \varphi, N_{t}$ is the total number of nanorods in the film and $F(\varphi, t)$ is the distribution function. According to this definition, the distribution function describes the density of
nanorods sitting within the angle $\varphi$ and $\varphi+d \varphi$. If the nanorods are initially randomly distributed, the distribution function is constant, $F(\varphi, 0)=1 / 2 \pi$. If at a certain moment of time $t_{\|}$, all nanorods were to point in the direction of an external field oriented at angle $\alpha$ with the $x$-axis, the distribution function would transform into the delta function $F\left(\varphi, t_{\|}\right)=$ $\delta(\varphi-\alpha)$. Any distribution function distinct from these two limiting functions will describe a system of partially aligned nanorods.

(b) Partial alignment
(c) Complete alignment



Figure 4.3 Visualization of three different distribution functions describing (a) random orientation of nanorods $F(\varphi)=1 / 2 \pi$; (b) a normal distribution of nanorod orientations $F(\varphi)=\left(2 / \pi^{0.5}\right) \exp \left(-2 \varphi^{2}\right)$, exhibiting partial alignment of nanorods in the x -direction; (c) complete alignment of nanorods in the x-direction, $F(\varphi)=\delta(\varphi)$.

Figure 4.3 illustrates random, normal and delta distributions of nanorods in a field applied in the direction of the positive $x$-axis, $\alpha=0$. The centers of mass of all nanorods were fixed at the nodes of a two-dimensional square lattice.

To describe the evolution of the distribution function with time we employ the equation of particle conservation. The most general form of this equation reads $N_{t} \partial F / \partial t+\nabla \cdot \rho=0$. In our particular case, when the nanorods are allowed to spin only in the plane and are not engaged in translational movement, the divergence operator is reduced to $\nabla=\partial / \partial \varphi$ and the $\varphi$-component of the flux is defined as $J_{\varphi}=N_{t} F \mathrm{~d} \varphi / \mathrm{d} t$. Thus, the governing equation for the distribution function is written as:

$$
\begin{equation*}
\frac{\partial F(\varphi, t)}{\partial t}+\frac{\partial}{\partial \varphi}[F(\varphi, t) \dot{\varphi}]=0 \tag{4.4}
\end{equation*}
$$

Substituting eq.(4.1) into eq.(4.4), we obtain [24]:

$$
\begin{equation*}
\frac{\partial F(\varphi, t)}{\partial t}+\frac{\partial}{\partial \varphi}[F(\varphi, t) \beta \sin (\alpha-\varphi)]=0 . \tag{4.5}
\end{equation*}
$$

The differential eq.(4.5) describes the evolution of the distribution function under an external magnetic field directed at angle $\alpha$ with respect to the $x$-axis. The evolution of $F$ is specified by the initial condition $F(\varphi, 0)=1 / 2 \pi$ implying a random orientation of nanorods at the first moment of time. Numerical analysis of this equation has been performed in Ref. [24] for some particular examples. Here we show that eq.(4.5) can be solved analytically by the method of characteristics[25]. Following the trajectory determined by eq.(4.2), and choosing $\alpha=0$, the characteristic curve [25] for eq.(4.5) is written as:

$$
\begin{equation*}
d t=\frac{d \varphi}{-\beta \sin \varphi}=\frac{d F(\varphi, t)}{F(\varphi, t) \beta \cos \varphi} \tag{4.6}
\end{equation*}
$$

Integrating eq.(4.6) and taking into account the initial condition $F(\varphi, 0)=1 / 2 \pi$, we obtain:

$$
\begin{gather*}
F(\varphi, t)=\frac{1}{2 \pi} \frac{2 C}{\left(C^{2}-1\right) \cos \varphi+\left(C^{2}+1\right)}  \tag{4.7}\\
C=\exp (-\beta t) \tag{4.8}
\end{gather*}
$$

All physical parameters are collapsed into a single parameter $\beta$. Then, if one keeps the $\beta$ parameter constant, one should observe consistent kinetics. For example, if one changes the field $B$ and fluid viscosity $\eta$ keeping their ratio constant, the kinetics should not
change. As follows from eqs.(4.7)-(4.8), as time goes to infinity, all nanorods tend to align in the direction of the magnetic field, $F(\varphi, \infty)=\delta(0)$.


Figure 4.4 Dependences of $F(\pi / 8, t), F(\pi / 4, t), F(\pi / 2, t)$ and $F(3 \pi / 4, t)$ as functions of dimensionless time $T=\beta t$; b) Profile of distribution function $\mathrm{F}(\varphi, t)$ at three different time moments $t=0 \mathrm{~s}, t=$ $0.3 \mathrm{~s}, t=0.7 \mathrm{~s}$.

Figure 4.4(a) illustrates the dependence of $F(\pi / 8, t), F(\pi / 4, t), F(\pi / 2, t)$ and $F(3 \pi / 4, t)$ as functions of the dimensionless time $T$. Due to initial condition, these functions start from the same value, $F(\pi / 8,0)=F(\pi / 4,0)=F(\pi / 2,0)=F(3 \pi / 4,0)=1 / 2 \pi$. However, the evolution of these functions is very much different: we observe a non-monotonous behavior of the distribution function with a maximum for the nanorods positioned within a certain angle. One can specify this angle and time to reach this maximum concentration by using solution (4.7)-(4.8). The time at which the distribution function $F(\varphi, t)$ takes on its maximum value is determined as $\partial F(\varphi, t) / \partial t=0$, where $F$ is given by eqs.(4.7)-(4.8). Calculating this derivative, we obtain

$$
\begin{equation*}
\beta t=\frac{1}{2} \ln \left(\frac{1+\cos \varphi}{1-\cos \varphi}\right) \tag{4.9}
\end{equation*}
$$

Because $\beta t$ must be greater than zero, the argument under the logarithm must be greater than one, implying that the maximum is reached within the semi-plane $(-\pi / 2, \pi / 2)$.

As shown in Figure 4.4(a), the population of nanorods within this semi-plane first increases and then decreases; the maximum is observed within the time interval between $T=0$ and $T=4$. Figure 4.2 gives a hint for explaining this maximum. According to this master curve, the majority of nanorods require time $4<T<6$ to reach the equilibrium. The nanorods taking much longer time, $T>6$, and much shorter time, $T<4$ to reach the equilibrium are a minority. Therefore, the majority of nanorods starting outside the semiplane $(-\pi / 2, \pi / 2)$ would pass this semi-plane within the time interval $T<4$. Therefore, if an observer were to watch the nanorods passing by a certain sector $\varphi=\varphi_{\text {observer }}$ in the semi-plane $(-\pi / 2, \pi / 2)$, he should be looking for a majority of nanorods crossing this sector at a certain time $t$ corresponding to the maximum of $F\left(\varphi_{\text {observer }}, t\right)$.

Figure 4.4(b) illustrates the angular dependence of the function $F(\varphi, t)$ at different moments in time; three snapshots were taken at the times $t=0 \mathrm{~s}, t=0.3 \mathrm{~s}$ and $t=0.7 \mathrm{~s}$. The parameter $\beta$ was set as $\beta=12.1 \mathrm{~s}^{-1}$. One can see that the distribution function gradually changes from a constant to a delta function. These three distribution functions exactly correspond to the respective states (a), (b) and (c) in Fig.3.

In some applications, the full width at half maximum (FWHM) of the distribution function is of interest [24]. This function can be found analytically as follows. According to solution (4.7), the maximum correspond to $F(0, t)=1 /(2 \pi C)$. Therefore, the FWHM of the distribution is obtained as the solution to equation $\cos \varphi=\left(1-3 C^{2}\right) /\left(1-C^{2}\right)$, resulting in the formula for the FWHM as

$$
\begin{equation*}
w=2 \arccos \frac{1-3 \exp (-\beta t)}{1-\exp (-\beta t)} . \tag{4.10}
\end{equation*}
$$

This explicit formula relates the physical parameter $\beta$ with the FWHM at different time moments.

Analyzing the kinetics of alignment of an assembly of nanorods, it is more convenient to deal with the probability $P(\varphi, t)$ to find the nanorods positioned within a narrow angle, $[\varphi-\Delta \varphi, \varphi+\Delta \varphi]$. This probability $P(\varphi, t)$ is defined as

$$
\begin{equation*}
P(\varphi, t)=\int_{\varphi-\Delta \varphi}^{\varphi+\Delta \varphi} F\left(\varphi^{\prime}, t\right) d \varphi^{\prime}=\left.\frac{1}{\pi} \arctan \left[\frac{\tan \left(\varphi^{\prime} / 2\right)}{C}\right]\right|_{\varphi-\Delta \varphi} ^{\varphi+\Delta \varphi} \tag{4.11}
\end{equation*}
$$

Due to this definition, the probability $P(\varphi, 0)=\Delta \varphi / 2 \pi$ corresponds to the initial random orientation of nanorods. As time goes to infinity, the probability goes to one, $P(0, \infty)=1$ meaning that all the nanorods can be found within interval $[-\Delta \varphi, \Delta \varphi]$. One can examine a critical probability $P_{0}$ introducing it as follows: if $P(0, t)>P_{0}$, i.e. if the total number of nanorods positioned outside the interval $[-\Delta \varphi, \Delta \varphi]$ is negligibly small (1- $P_{0}$ ) $\ll 1$, one can say that almost all nanorods are aligned with the field. Using this alignment criterion, we can specify the time $\tau$ needed to reach this level of alignment. One can estimate this time by substituting $P_{0}$ into the left hand side of eq.(4.11) and solving for time $\tau$ :

$$
\begin{equation*}
\tau=\frac{1}{\beta} \ln \left[\frac{\tan \left(\pi P_{0} / 2\right)}{\tan (\Delta \varphi / 2)}\right] \tag{4.12}
\end{equation*}
$$

Inserts in Figure 4.4(b) specify the probability values showing that almost complete alignment was reached within $\tau<0.7$ seconds for the particular set of parameters $\beta=12.1 s^{-1}$ and $\Delta \varphi=\pi / 100$.

### 4.3 Experiments with nickel nanorods

### 4.3.1 Nanorod synthesis and surface modification

Nickel nanorods were synthesized inside pores of alumina membranes (Whatman Ltd.) by an electrodeposition technique described in detail in Chapter III. This experimental protocol enables one to produce nanorods with a narrow size distribution.


Figure 4.5 SEM image of nickel nanorods
Applying 1.5 DC voltage for 12 minutes, we obtained nanorods about $5 \mu \mathrm{~m}$ in length and less than 200 nm in diameter. The magnetic properties of these nanorods were analyzed using an alternating gradient magnetometer (AGM MicroMag 2900 by Princeton Measurements Inc.). These nanorods are ferromagnetic; magnetic hysteresis of a $50-\mu \mathrm{g}$ powder sample of electrodeposited nickel nanorods is shown in Figure 4.6(a). Figure 4.6(b), we plot the magnetization curve in the millitesla range of the magnetic
field, which is less than the coercive force. In this field range, the average magnetization is linearly dependent on the field.


Figure 4.6 (a) Full hysteresis loop obtained on the $50-\mu \mathrm{g}$ nanorod powder sample. (b) Magnetization curve in $0-10 \mathrm{mT}$ range showing linear magnetization behavior.

To improve the dispersibility of the nanorods, we formed an adsorption layer of polyvinylpyrrolidone (PVP) on their surfaces following the protocol in Ref.[26]. In brief, the alumina membrane holding the synthesized nanorods was placed in 1 M solution of sodium hydroxide containing $20 \mathrm{mg} / \mathrm{mL}$ of PVP ( 3500 Da ). After complete dissolution of the membrane, the nanorods were separated by decanting the solution and transferred into pure deionized water by several centrifugation/decanting/dispersion cycles. TEM images (STEM-Hitachi HD2000) confirm formation of the PVP polymer layer (Figure 4.7). The thickness of this layer varies in the range of $40-70 \mathrm{~nm}$.


Figure 4.7 TEM images of Ni nanorod covered with PVP layer (a) overall view and (b) close-up.
The functionalized nanorods were dispersed in water. The concentration of nanorods in water was $0.04 \mathrm{wt} \%$. One mL of a water-based dispersion was centrifuged for 1 min at $10,000 \mathrm{rpm}$. Then water was partially replaced with 0.1 mL of pure glycerol (Fisher Scientific Inc.). This dispersion was sonicated at $80^{\circ} \mathrm{C}$ for 15 minutes. Using a refractometer (Spectronic Instruments 336410) we measured the amount of water remaining in the vial. We centrifuge the sample again and measure refractive index of only the water-glycerol mixture. It was found to be 1.4634 at $23^{\circ} \mathrm{C}$, corresponding to a mixture of $93 \mathrm{wt} \%$ glycerol in water[27]. The weight concentration of nanorods of the resulting dispersion was then estimated as $0.3 \mathrm{wt} \%$. A $1-\mu \mathrm{L}$ drop of -glycerol-water mixture containing $0.3 \mathrm{wt} \%$ of nanorods was placed on a glass slide and immediately covered by another glass slide to prevent evaporation of water. Two glass slides were separated by two parallel $25-\mu \mathrm{m}$ fibers, which provided a liquid film thickness of $25 \mu \mathrm{~m}$. The visual appearance of polymer-stabilized nanorods in the glycerol-water mixture was significantly better. Observing in the dark field mode (Olympus BX 51) detected no aggregation of nanorods.

### 4.3.2 Alignment of nanorods in magnetic field

To generate a magnetic field, we used two magnetic coils placed parallel to each other and fixed under a BX-51 Olympus microscope equipped with a SPOT videocamera (SPOT Imaging Solutions, Inc.) The magnetic field was measured by a digital teslameter (133-DG GMW Inc.); and the field in the center of the optical cell was equal to 0.3 mT which is well weaker than the coercive force shown in Figure 4.6 (b). Therefore, the model with magnetic moment fixed at the easy axis seems to be adequate for description of the nanorod rotation. A schematic of the experimental setup is shown in Figure 4.8.


Figure 4.8 Schematic of the experimental setup
The video was recorded after switching on the coils. The field was switched off only when all the nanorods were completely aligned along the field direction. Nanorods start to rotate as soon as the field is turned on and stop spinning when the field is switched off. The final alignment of nanorods persists for a long time; small thermal fluctuations in the nanorod position and orientation do not destroy this orientation during the observation time.

To analyze the kinetics of alignment of the nanorod assemblies, the video was transformed into a sequence of frames using VirtualDub ( http://www.virtualdub.org ). The frames taken at time moments $t=0 \mathrm{~s}, 1 \mathrm{~s}, 2 \mathrm{~s}, 3 \mathrm{~s}$ and 4 s were saved for further
analysis, Figure 4.9. Analyzing five frames, we selected nanorods that were present in the observation plane in all five frames. Only nanorods having the same length ( $l \approx 5 \mu \mathrm{~m}$ ) were selected for the analysis. This selection allowed us to follow the theory not considering the effect of particle polydispersity. Nanorods coming into and/or leaving the observation plane during the observation period were not counted.


Figure 4.9 Five frames chosen for analysis of the distribution function; Circled nanorods were tracked during the analysis

Prior to the analysis of the distribution function, we determined the parameter $\beta$ by following the rotation of individual nanorods from the recorded video and fitted each trajectory using eq.(2) by adjusting the value of $\beta$. The experimental values of the angle $\varphi$ as a function of time for individual nanorods are shown in Fig. 10. The theoretical trajectory plotted with $\beta=0.75 \mathrm{~s}^{-1}$ closely follows the experimental dependence.


Figure 4.10 Nanorod trajectory (solid line) and the experimental points used for extraction of the $\beta$-parameter using eq.(4.2) ; b) $\beta$-parameters for ten nanorods.

Ten individual nanorods were tracked and the corresponding $\beta$-chart is shown in Figure 4.10 (b) providing an average value of $\beta=0.75 \pm 0.11 \mathrm{~s}^{-1}$. The standard deviation is caused by variation in the nanorod lengths and diameters; this can be inferred from the explicit expression for the $\beta$-parameter $\beta=M B[3 \ln (l / d)-A]\left[4 \eta(l / d)^{2}\right]$, where $M$ is the saturation magnetization of nickel. It is seen that the $\beta$-parameter is very sensitive to the aspect ratio $/ / d$. As the thickness of polymer coating and nanorod length vary from one nanorod to another, this parameter changes. Nevertheless, the standard deviation is small suggesting that the average value is reliable, and the interactions between nanorods are not significant. Observe that most nanorods in Figure 4.9 stay separated from each other confirming that the dispersion was stable and that interactions between the nanorods were negligible.

These observations and experimental results on alignment kinetics of individual nanorods support the hypothesis that the nanorod colloid should behave as a system of non-interacting nanorods. This hypothesis also agrees with Onsager's theory of isotropicnematic transition in a system of rigid nanorods[28, 29]. For the nanorods with diameters
of 200 nm and lengths of $5 \mu \mathrm{~m}$, the critical volume fraction for the isotropic phase is numerically estimated as $C_{\mathrm{iso}}=3.3 \times 0.2 / 5=0.132[29]$. The density of a glycerol-water mixture containing $93 \mathrm{wt} \%$ of glycerol at $23^{\circ} \mathrm{C}$ is $1.24 \mathrm{~g} / \mathrm{mL}[30]$. In a $0.3-\mathrm{wt} \%$ dispersion of nickel nanorods (density of nickel is $8.90 \mathrm{~g} / \mathrm{cm}^{3}$ ) the volume fraction of nickel nanorods is estimated as $4 \times 10^{-4}$, which is well below the Onsager limit. Therefore, the nanorods are not touching each other.

We further examined the hypothesis of non-interacting particles by quantitatively evaluating the distribution function and comparing it with the theoretically derived one. In the analysis, we examined five movies taking five frames corresponding to the same time moments as those shown in Figure 4.9. Then we tracked 14 nanorods present in each frame resulting in 70 nanorods per chart in Fig.11.



Figure 4.11 Orientation distribution for nickel nanorods at $t=0 \mathrm{~s}, 1 \mathrm{~s}, 2 \mathrm{~s}, 3 \mathrm{~s}$ and 4 s . Solid curves correspond to the theoretical curves.

Figure 4.11 summarizes the results of this analysis. The histograms represent experimental data given in terms of the probability function $P(\varphi, t)$ defined by eq.(4.11). Experimental histograms were constructed by counting the number of nanorods $N_{\varphi}$ present in each sector ( $\varphi-\Delta \varphi, \varphi+\Delta \varphi$ ) with $\Delta \varphi=\pi / 36$ and normalizing $N_{\varphi}$ by the total number of nanorods $N_{t}$ present in all five pictures. Then the histograms were fitted with eq.(4.11) by adjusting parameter $C$. For each frame, we have a unique parameter $C$ corresponding to the given shape of the probability function. As seen from Figure 4.11, the solid theoretical curves agree well with the experimental results.

It is worth recalling that the theoretical model assumes that the nanorods were randomly distributed in the first moment, $F(\varphi, 0)=1 / 2 \pi$. However, when the cover slide was placed on the droplet, it caused some flow orienting the nanorods in the film. Therefore, the nanorods were not randomly distributed in Frame 1, which we took as the initial moment. To satisfy the initial condition of the model, we shifted time to start at an arbitrary $t_{0}$ and followed the same form of $C$ defined by eq.(4.8):

$$
\begin{equation*}
C=\exp \left[-\beta\left(t+t_{0}\right)\right] . \tag{4.13}
\end{equation*}
$$



Figure 4.12 A set of the $C$-parameters extracted from Figure 4.11. The solid curve shows the exponential function (4.13).

With this definition of the $C$-function, the initial time moment corresponds to $t=$ $t_{0}$, a new adjustable parameter. Fig. 12 shows the $C$-parameters corresponding to the snapshots in Figure 4.11. These $C$-parameters appear to sit on the same curve defined by eq.(4.12) with parameters $\beta=0.77 \mathrm{~s}^{-1}$ and $t_{0}=2.3 \mathrm{~s}$. The value of the $\beta$-parameter is very close to the value obtained by tracking individual nanorods and using eq.(4.2) to fit the data, Figure 4.10. This confirms that the nanorods do not interact with each other.

Double checking the results, one can calculate the time needed to reach the equilibrium configuration setting the criterion $P_{0}=0.9$ and $\Delta \varphi=\pi / 36$ in eq.(4.11) and using Frame 5 in Figure 4.9 as the final state. For a colloid with parameters $\beta=0.77 s^{-1}$ and $t_{0}=2.3 \mathrm{~s}$, this time $\tau$ was calculated from eq.(4.11) as $\tau=6.5 \mathrm{~s}$. The duration of five frames is therefore estimated as $\tau-t_{0}=6.5-2.3=4.2 \mathrm{~s}$, which matches the experimental value of 4 s . Thus, the proposed theory describes the experimental observations fairly well, suggesting that the nanorods do not interact with each other and that their alignment kinetics depends on the initial distribution.

### 4.4 Alignment of nanorods in solidifying film

In the processing of magnetic films, one important step lacking understanding of the behavior of nanorods is related to the complexity of rheological behavior of solidifying film during the sol-gel processing. Many liquids used for sol-gel processing rapidly react on the environmental conditions by changing their rheological properties[31, 32]. The time dependent viscosity of many practically important carriers is typically described by the following equation $\eta(t)=\eta_{0} \exp \left(t / \tau_{0}\right)$, where $\eta_{0}$ is the initial viscosity of the carrier, $t$ is the time and $\tau_{0}$ is the characteristic time of polymerization[31, 32]. Recent experiments showed that the spinning behavior of a single nanorod in a film with this type of viscosity variation is drastically different from the spinning behavior of nanorods in fluids with constant viscosity[8]. Alignment of an assembly of magnetic nanorods in a solidifying film has not been discussed in the literature.

### 4.4.1 Rotation of a single nanorod in a solidifying film

Eq.(4.1) is still applicable for the rotation of a single nanorod in a solidifying film. Introducing new variable $U=\eta_{0} l^{3} \pi \exp \left(t / \tau_{0}\right) /\left(\tau_{0} m B[3 \ln (/ / d)-A]\right)$ and taking $\alpha=0$, eq.(4.1) is rewritten in the dimensionless form as:

$$
\begin{equation*}
\frac{\mathrm{d} \varphi}{\mathrm{~d} U}=-\frac{\sin \varphi}{U^{2}} \tag{4.14}
\end{equation*}
$$

Integrating eq.(4.14), one obtains its explicit solution as:

$$
\begin{equation*}
\tan \left(\frac{\varphi}{2}\right)=\exp \left(\frac{1}{U}-\frac{1}{U_{0}}\right) \tan \left(\frac{\varphi_{0}}{2}\right), U_{0}=\frac{\tau_{\eta}}{\tau_{0}}=\frac{\eta_{0}}{\tau_{0}} \frac{4(l / d)^{2}}{M B[3 \ln (l / d)-A]} \tag{4.15}
\end{equation*}
$$

where $\varphi_{0}$ is the initial orientation of the magnetic moment. We introduced the saturation magnetization of the material $M$ and expressed the magnetic moment as $m=\pi d^{2} l M / 4$. The characteristic time $\tau_{\eta}$ corresponds to the time needed for a nanorod to find its equilibrium configuration in a liquid with constant viscosity $\eta_{0}$. In solution (4.15), all physical parameters collapse into a single dimensionless parameter $U_{0}=\tau_{\eta} / \tau_{0}$.

The limiting solution as $U$ goes to infinity, $\tan (\varphi / 2)=\exp \left(-\tau_{0} / \tau_{\eta}\right) \tan \left(\varphi_{0} / 2\right)$, illustrates the effect of different time scales $\tau_{\eta}$ and $\tau_{0}$. If time $\tau_{\eta}$ is much greater than the characteristic time of film polymerization $\tau_{0}, \tau_{0} / \tau_{\eta} \ll 1$, the limiting rotation angle $\varphi$ does not change appreciably, $\varphi \sim \varphi_{0}$, i.e.one expects that the nanorod will stay frozen with magnetic moment pointing in the same initial direction $\varphi_{0}$. In the opposite case, when $\tau_{0} / \tau_{\eta} \gg 1$, exponent $\exp \left(-\tau_{0} / \tau_{\eta}\right)$ tends to zero implying that the nanorod will be able to find its equilibrium configuration $\varphi=0$ within time $\tau_{0}$. The quantitative analysis of all possible cases is shown in Figure 4.13(a). To avoid singularity, $\varphi_{0}$ is restricted in the sector [$0.99 \pi, 0.99 \pi]$.


Figure 4.13 (a) The equilibrium direction of magnetic moment, $\varphi$, as a function of the initial orientation $\varphi_{0}$ plotted for four different $U_{0}$ (b) Classification of different dynamic regimes of nanorod spinning. Initial conditions $\varphi_{0}$ and $U_{0}$ for different trajectories are shown as open circles.

For practical applications of eq.(4.15), one can set a criterion that almost complete co-alignment of a nanorod with the field will occur if its magnetic moment is pointing toward the sector $-\Delta \varphi<\varphi<\Delta \varphi|\Delta \varphi| \ll 1$. For example, taking $\Delta \varphi=\pi / 100$, we obtain diagram shown in Figure $4.13(\mathrm{~b})$. The arrowed lines correspond to the nanorod trajectories emanating from different initial conditions specified by the open circles. The shaded region bounded by the black solid line defines the initial conditions leading to complete co-alignment of nanorods with the field. The final destinations of all trajectories passing through this shaded region satisfy the criterion $-\pi / 100<\varphi<\pi / 100$. Thus, the nanorods with the initial condition confined in the shaded region will hit the angle [$\pi / 100, \pi / 100]$ as time goes to infinity. For example, in fluids with a constant viscosity where $\tau_{0}=\infty$, the initial conditions fill the whole interval $[-\pi, \pi]$ of the vertical axis $U_{0}=0$. All these nanorods will be aligned along the field as time goes to infinity. As the time ratio $\tau_{0} / \tau_{\eta}$ increases, less and less initial angles $\varphi_{0}$ will lead to the complete alignment of the nanorods as time goes to infinity. This observation implies that not all nanorods can be captured by the field prior to the film solidification.

### 4.4.2 Alignment of an assembly of nanorods in the field

To study the kinetics of ordering of an assembly of non-interacting nanorods in the field, the same orientational distribution function $F(\varphi, t)$ is introduced following eq.(4.3). The differential eq.(4.5) still describes the evolution of the distribution function under an external magnetic field directed at angle $\alpha$ with respect to the $x$-axis. The solution still has the same form as eq.(4.7), but with a different $C$ parameter.

$$
\begin{equation*}
C=\exp \left[-\left(1-e^{-t / \tau_{0}}\right) / U_{0}\right] \tag{4.16}
\end{equation*}
$$



Figure $4.14 F(\pi / 8, t), F(\pi / 4, t), F(\pi / 2, t), F(3 \pi / 4, t)$ as functions of the dimensionless time $T=t / \tau_{\eta}$ at different $U_{0}$

Figure 4.14 illustrates the dependence of $F(\pi / 8, t), F(\pi / 4, t), F(\pi / 2, t), F(3 \pi / 4, t)$ as functions of the dimensionless time $T=t / \tau_{\eta}$ at different $U_{0}$. In the analysis, we assumed that $\tau_{\eta}$ is a constant and $U_{0}$ is varied only through $\tau_{0}$ which is inversely proportional to $U_{0}$. These functions start from the same value, $F(\pi / 8,0)=F(\pi / 4,0)=F(\pi / 2,0)=F(3 \pi / 4,0)=1 / 2 \pi$. The limiting case $U_{0}=0$ shown in Figure 4.14 (a) is the same as Figure 4.4(a) for the Newtonian fluid case. Another limiting case $U_{0}=\infty$ corresponds to a case when the film solidifies faster than neither nanorod can make any turn. Taking this limit, we see from Figure 4.14 (d) that the distribution function does not change with time, $F(\varphi, t)=1 / 2 \pi$, implying that the nanorods will keep their random distribution during the time of field
application. Figure 4.14(b) and (c) show that the equilibrium values $F(\pi / 8, \infty), F(\pi / 4, \infty)$, $F(\pi / 2, \infty), F(3 \pi / 4, \infty)$ are different. Increasing $U_{0}$, the equilibrium is achieved at an earlier moment of time because viscosity increases significantly faster than any nanorod movement. Contrary to Figure 4.14(a) and (b) the distribution function for $U_{0}=5$ does not have any maximum; all nanorods are just drifting around their initial positions.

The equilibrium distribution function $F(\varphi, \infty)$ is obtained by taking the limit $t=\infty$ in Eq.(4.7) and (4.16)

$$
\begin{equation*}
F(\varphi, \infty)=\frac{1}{2 \pi} \frac{1}{\cosh \left(1 / U_{0}\right)-\sinh \left(1 / U_{0}\right) \cos \varphi} \tag{4.17}
\end{equation*}
$$

This function $F(\varphi, \infty)$ has a maximum at $\varphi=0$ indicating that the majority of nanorods still have a tendency to align along the field direction. However, a considerable amount of nanorods cannot be captured by the field; the number of non-aligned nanorods depends on parameter $U_{0}$. To quantify the rate of ordering of the nanorods, it is convenient to analyze the probability $P(t, \Delta \varphi)$ to find nanorods within angle $[-\Delta \varphi, \Delta \varphi]$ at time $t$. This probability is defined as:

$$
\begin{equation*}
P(t, \Delta \varphi)=\int_{-\Delta \varphi}^{\Delta \varphi} F(\varphi, t) d \varphi=\frac{2}{\pi} \arctan \left[\frac{\tan (\Delta \varphi / 2)}{C}\right] \tag{4.18}
\end{equation*}
$$



Figure 4.15 (a) Profile of limiting distribution functions $F(\varphi, \infty)$ for four different parameters $U_{0}$; (b) The peak values of the limiting distribution function $F(0, \infty)$ and probability $P(\infty, \pi / 100)$ as functions of $U_{0}$

The behavior of the limiting distribution function $F(\varphi, \infty)$ is shown in Figure 4.15(a) for four different $U_{0}$. The corresponding probability $P(\infty, \pi / 100)$ is provided for each value $U_{0}$. The peak value of the limiting distribution function $F(\varphi, \infty)$ decreases as $U_{0}$ increases indicating that less and less nanorods can be captured by the field as parameter $U_{0}$ increases.

As follows from Figure $4.15(\mathrm{~b})$ the peak value $F(0, \infty)$ decreases by three orders of magnitude when $U_{0}$ increases from 0.12 to 0.5 . When $U_{0}$ goes to infinity, the peak $F(0, \infty)$ hits the asymptotic value $1 / 2 \pi$. The upper line in Figure $4.15(b)$ shows the behavior of the probability to find nanorods within angle $[-\pi / 100, \pi / 100]$ as a function of parameter $U_{0}$. This probability also decreases as parameter $U_{0}$ increases. Substituting eq.(4.16) into eq.(4.18), one can obtain the asymptotic value $P(\infty, \Delta \varphi)$ as

$$
\begin{equation*}
P(\infty, \Delta \varphi)=\frac{2}{\pi} \arctan \left[\tan \left(\frac{\Delta \varphi}{2}\right) \exp \left(\frac{1}{U_{0}}\right)\right] \tag{4.19}
\end{equation*}
$$

For example, in fluids with constant viscosity parameter $U_{0}$ is equal to zero, $U_{0}=0$. From Figure 4.15(b) we infer that the probability is equal to one, $P(\infty, \Delta \varphi)=1$, i.e. all nanorods are expected to find their equilibrium alignment parallel to the field direction. As parameter $U_{0}$ goes to infinity and the film solidifies very fast, the probability to find nanorods aligned along the field diminishes approaching $P(\infty, \Delta \varphi)=\Delta \varphi / \pi$. This is the probability to find nanorods within angle $[-\Delta \varphi, \Delta \varphi]$ corresponding to the random distribution of nanorods. For a particular value $\Delta \varphi=\pi / 100$, this probability is equal to 0.01 as shown in Figure 4.15(b).

### 4.4.3 Alignment criterion

In order to specify the range of physical parameters ensuring complete alignment of the nanorods along the prescribed direction prior to the film solidification, we introduce a quantitative criterion choosing a specific value for the probability, $P(\infty, \Delta \varphi)=P_{0}$. We say that the complete alignment is attainable if and only if the inequality $P(\infty, \Delta \varphi)>P_{0}$ holds true. One can solve eq.(4.19) for $U_{0}$ plugging $P_{0}$ on the left hand side. The solution $U_{0}\left(P_{0}\right)=U_{\mathrm{c}}$ is:

$$
\begin{equation*}
\frac{1}{U_{\mathrm{c}}}=\ln \left[\frac{\tan \left(\pi P_{0} / 2\right)}{\tan (\Delta \varphi / 2)}\right] \tag{4.20}
\end{equation*}
$$

If parameter $U_{0}$ is greater than this critical value, $U_{0}>U_{\mathrm{c}}$, one infers that the probability to find the nanorod pointing in the direction parallel to the field is less than $P_{0}$. Therefore, for the semi-axis $U_{0}>U_{\mathrm{c}}$, one cannot achieve complete alignment of the nanorods along the field direction. In order to align nanorods parallel to the field direction, the physical parameters must be taken from the semi-axis $U_{0} \leq U_{\mathrm{c}}$. According
to this criterion, for fast ordering, one would prefer to have liquids with low initial viscosity $\eta_{0}$, longer solidification time $\tau_{0}$, and nanorods with high saturation magnetization $M$, and small aspect ratio $l / d$. Strong fields are also favorable for fabrication of ordered magnetic coatings.

As a practical example of using this criterion, we analyze nanorods made of four different materials: $\gamma-\mathrm{Fe}_{2} \mathrm{O}_{3}, \mathrm{Ni}, \mathrm{Co}$, and Fe . These materials are listed in the increasing order of values of their saturation magnetizations: $M_{\mathrm{Fe} 2 \mathrm{O} 3}=4.3 \times 10^{5} \mathrm{~A} / \mathrm{m}, M_{\mathrm{Ni}}=4.9 \times 10^{5}$ $\mathrm{A} / \mathrm{m}, M_{\mathrm{Co}}=1.44 \times 10^{6} \mathrm{~A} / \mathrm{m}, M_{\mathrm{Fe}}=1.77 \times 10^{6} \mathrm{~A} / \mathrm{m}[33]$. Taking $P_{0}=0.99$ and $\Delta \varphi=\pi / 100$ as the criteria, the right hand side of eq.(4.20) is completely defined. Rearranging eq.(4.20), one can solve it for the ratio $\left(\eta_{0} / \tau_{0} B\right)$ as a function of the nanorod aspect ratio $l / d$ for all listed materials.


Figure 4.16 Phase diagrams specifying the range of parameters leading to the complete ordering of nanorods in solidifying films.

Figure 4.16 shows the resulting phase diagrams; the ordered phases are separated from the non-ordered phases by the shown boundaries. The lower region where the
inequality $U_{0} \leq U_{\mathrm{c}}$ holds, corresponds to the range of parameters leading to the complete alignment of nanorods in the film prior to its solidification. In the upper region $U_{0}>U_{\mathrm{c}}$ one should be able to find a sufficient amount of nanorods which are not pointing in the field direction after film solidification.

The phase diagrams in Figure 4.16 can be further enriched with different magnetic materials. These diagrams enable to find the ratios $\eta_{0} / \tau_{0} B$ and $l / d$, or saturation magnetization $M$ which would ensure the complete ordering of nanorods in the field direction.

On the other hand, by choosing different $U_{0}$ one can control the resulting magnetization of the film. Indeed, the film magnetization $m_{\text {eff }}$ is defined as:

$$
\begin{equation*}
m_{\mathrm{eff}}=m N_{t} \int_{-\pi}^{\pi} \cos \varphi F(\varphi, \infty) d \varphi=m N_{t}\left[\operatorname{coth}\left(1 / U_{0}\right)-\frac{1}{\sinh \left(1 / U_{0}\right)}\right] \tag{4.21}
\end{equation*}
$$



Figure 4.17 Dimensionless magnetization of the film as a function of $U_{0}$ and corresponding distributions of magnetic moments in the film at three different magnetizations.

Figure 4.17 shows the dependence of dimensionless magnetization, $m_{\text {eff }} /\left(m N_{t}\right)$ as a function of parameter $U_{0}$. As expected, parameter $U_{0}$ completely determines the level of film magnetization. The final orientational configurations of magnetic moments are shown for three different parameters $U_{0}: U_{0}=0.1, U_{0}=1, U_{0}=10$. Only fluids with very small parameter $U_{0}$ provide almost ideal alignment of nanorods. As $U_{0}$ increases, more and more nanorods are quenched in the solidifying field half way to their equilibrium configuration parallel to the field. Accordingly, as parameter $U_{0}$ increases, the film magnetization sharply decreases. When parameter $U_{0}$ goes to infinity, the nanorods remain "frozen" in the initial positions; hence their orientation remains random resulting in zero magnetization of the film.

In many practical applications, nanorods have different sizes and their magnetic properties vary from one nanorod to another. In the proposed model, all physical parameters collapse into a single parameter $U_{0}$. Therefore, the effect of nanorod polydispersity can be further analyzed considering an average over parameter $U_{0}$ provided that the nanorod dispersions over sizes and magnetization are known. Since the kinetics of nanorods assembly with a particular $U_{0}$ is defined by eq.(4.7) and (4.16), one can average this distribution function using the known dispersions. Thus, the derived eq.(4.7) and (4.16) constitute the basic kinetic equations applicable for different cases, but one needs to average these equations with a specific distribution function taking into account a particular polydispersity of nanorods in the system.

### 4.5 Conclusion

In this chapter we describe the alignment kinetics of an assembly of noninteracting magnetic nanorods suspended in different fluid.

We first studied an assembly of magnetic nanorods suspended in a Newtonian fluid with constant viscosity $\eta$ and subject to an external magnetic field $B$. It has been shown that the alignment kinetics is controlled by a single parameter $\beta$. We theoretically predicted and experimentally confirmed that one can control the alignment of an assembly of nanorods by choosing the parameter $\beta$ and time of application of the external field. Experiments with nickel nanorods covered with PVP in a glycerol-water mixture supported the theory.

Next, we describe we theoretically studied the kinetics of ordering of an assembly of nanorods suspended in a solidifying liquid film. The process of solidification was
modeled by assuming that the film viscosity increases with time exponentially fast and nanorods are randomly distributed in the films prior to the application of external magnetic field. We showed that the nanorods would not always align parallel to the external magnetic field; some of them will be quenched halfway to the equilibrium orientation prior to the film solidification. Different regimes of ordering were revealed and classified and the time required for the nanorods to align along the field direction was analyzed depending on the physical parameters of the liquids and nanorod materials. Fortunately, all physical parameters were collapsed in a single dimensionless parameter $U_{0}$ defined by eq.(4.15). This parameter controls the alignment kinetics and limiting distribution of nanorods in the film and resulting magnetization of the film. We introduced a criterion of the nanorod ordering and constructed phase diagrams shown in Figure 4.16. These phase diagrams predict the physical conditions ensuring the complete order of nanorods in the film providing maximum possible magnetization.

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## CHAPTER V

## VISCOSITY CHANGE OF MULLITE PRECURSOR DURING EVAPORATION

As shown in the previous chapter, the alignment of magnetic nanorods in a solidifying film significantly depends on the fluid viscosity. In the composite processing when the solvent evaporates, viscosity changes significantly. Therefore, in order to control the nanorod alignment during solvent evaporation it is crucial to understand the effect of evaporation on viscosity. In this chapter, we will first study the evaporation kinetics of the mullite precursor droplet and then use the magnetic rotational spectroscopy (MRS) to measure the time-dependent viscosity. A correlation between the viscosity and concentration of mullite in the precursor drop was analized in detail and the Eyiring model was employed to explain the observed dependency.

### 5.1 Evaporation of water droplet

In order to study the evaporation of mullite precursor, we remind the basic physics of evaporation using water droplets as an example [1, 2]. We will closely follow ref[3], where the evaporation of a sessile water droplet with a pinned contact line was studied. The water droplet was considered as a semispherical cap sitting on the substrate as shown in Figure 5.1. Two parameters, the contact angle $\theta$ and the radius of droplet
base, $R$, completely define the droplet shape. Since the contact line of the droplet was not moving, the radius of droplet base $R$ does not change with time while the contact angle $\theta$ does.


Figure 5.1 Sessile water droplet on the substrate with a contact angle $\theta$ and the radius of droplet base, $R$.

At the surface of the water droplet, the water vapor concentration equals to the saturated vapor concentration $c_{\mathrm{v}}$. Far away from the droplet, the vapor concentration is smaller than the saturation vapor concentration approaching $H c_{v}$ where $H$ is the relative humidity in the ambient air $(H<1)$. As a result, the water vapor diffuses from the droplet surface where the vapor concentration is greater to the periphery thus causing the shrinkage of the droplet volume.

The water vapor concentration $c$ is a function of both position $(r, z)$ and time $t$. The temporal and spatial variation of the vapor concentration is governed by the diffusion equation:

$$
\begin{equation*}
\frac{\partial c}{\partial t}=D \Delta c, \tag{5.1}
\end{equation*}
$$

where $D$ is the diffusivity of the water vapor in the air. Since the substrate is impermeable to the vapor, the vapor flux at the droplet edge is singular. This flux singularity complicates the diffusion problem[3].

There are two time scales associated with diffusion. The first time scale provides a rough estimate of how fast the vapor diffuses away from the drop. The rate of vapor diffusion depends on the size of the object causing a concentration gradient to occur. In this case, the water droplet sets the spatial scale, $R$, hence this time scale is estimated as: $\tau_{\mathrm{d}} \sim R^{2} / D$. Another time scale gives a rough estimate of time for the droplet disappearance, $\tau_{\mathrm{f}}$. To find $\tau_{\mathrm{f}}$, we estimate the rate of droplet evaporation by balancing the rate of change of the volume with the rate of mass change. The latter is limited by diffusion from the droplet surface to the air.

The evaporation flux is estimated as $J=D|\nabla c| \sim D(1-H) c_{\mathrm{v}} / R$. Using this estimate, the mass loss per unit time is written as $\mathrm{d} m / \mathrm{d} t \sim J \cdot A \sim R^{2} D(1-H) c_{\mathrm{v}} / R$, where $A$ is the area of the droplet surface. The total mass of the droplet $m$ at the time moment $t$ can be estimated as $\rho R^{3}$, where $\rho$ is the density of water. As a result, the characteristic time of droplet disappearance is estimated as $\tau_{\mathrm{f}} \sim m /(J \cdot A) \sim \rho R^{2} /\left(D(1-H) c_{\mathrm{v}}\right)$. The ratio of these two times scales, $\tau_{\mathrm{d}} / \tau_{\mathrm{f}} \sim(1-H) c_{\mathrm{v}} / \rho$, does not depend on the droplet size and sets up a criterion for selection of different kinetics of drop evaporation. If this ratio is much greater than 1 , one expects to observe a diffusion limited kinetics when the drop disappearance is mostly controlled by how fast the water vapor diffuses away from the drop surface. In the opposite case, when the ratio $\tau_{\mathrm{d}} / \tau_{\mathrm{f}}$ is much smaller than 1 , one
expects to see a slow kinetics when the concentration field around the drop sets up momentarily at the time scale of droplet shrinkage.

In order to estimate this ratio for water droplets, we take the following physical constants: ambient relative humidity $H=30 \%$, saturated vapor concentration $c_{\mathrm{v}}=$ $2.18 \times 10^{-5} \mathrm{~g} / \mathrm{cm}^{3}$ [4] and density of water $\rho=1 \mathrm{~g} / \mathrm{cm}^{3}$. With these parameters, the ratio $\tau_{\mathrm{d}} /$ $\tau_{\mathrm{f}}$ is estimated as $\tau_{\mathrm{d}} / \tau_{\mathrm{f}} \sim 1.53 \times 10^{-5} \ll 1$. Therefore, the time needed for the establishment of a steady state vapor diffusion is much smaller than the time of droplet disappearance. Consequently, the water evaporation can be considered as a quasi-static process, i.e. the temporal variation of vapor concentration in the left hand side of eq. (5.1) can be neglected. As a result, to obtain the spatial distribution of vapor, we only need to solve the Laplace equation

$$
\begin{equation*}
\Delta c=0 \tag{5.2}
\end{equation*}
$$

with the boundary condition at the droplet surface $\left(c=c_{v}\right)$, the condition on substrate impermeability to vapor, $\partial c / \partial z=0$ at $z=0$, and condition at infinity where $c=H c_{\mathrm{v}}$. Once the concentration is obtained, the rate of mass loss can be obtained by integrating the vapor flux over the droplet surface as

$$
\begin{equation*}
\dot{m}(t)=-\int(D \nabla c) \cdot d \boldsymbol{s} . \tag{5.3}
\end{equation*}
$$

There is no analytical solution to problem (5.2)-(5.3) but Hu and Larson found an approximate solution [3]:

$$
\begin{equation*}
\dot{m}(t)=-\pi R D(1-H) c_{\mathrm{v}}\left(0.27 \theta^{2}+1.30\right), \tag{5.4}
\end{equation*}
$$

where the contact angle $\theta$ is measured in radians. If contact angle $\theta$ changes from 0 to $\pi / 2$, the contact angle dependent term changes from 1.30 to 1.97 implying that the evaporation
rate has a weak dependence on contact angle $\theta$. This angle is almost constant for a pinned droplet when $\theta$ is small. To accurately determine the evaporation rate, we have to relate $\theta$ with the droplet mass:

$$
\begin{equation*}
m(t)=\rho \pi R^{3} \frac{2-3 \cos \theta(t)+\cos ^{3} \theta(t)}{3 \sin ^{3} \theta(t)} \tag{5.5}
\end{equation*}
$$

Therefore, eq.(5.5) provides an implicit relation $\theta=\theta(m)$. We numerically analyzed eq.(5.5), to construct a forth order polynomial approximation:

$$
\begin{equation*}
\theta^{2}=17.96 \alpha^{4}-33.08 \alpha^{3}+19.86 \alpha^{2}-0.14 \alpha \quad \alpha=\frac{m(t)}{\rho \pi R^{3}} \tag{5.6}
\end{equation*}
$$

After substitution this approximation into eq. (5.4), we simplified the kinetic equation as

$$
\begin{equation*}
\dot{m}(t)=-\pi R D(1-H) c_{\mathrm{v}}\left(4.848 \alpha^{4}-8.933 \alpha^{3}+5.361 \alpha^{2}-0.039 \alpha+1.300\right) \tag{5.7}
\end{equation*}
$$



Figure 5.2 The evaporation of a $1.2 \mu \mathrm{~L}$ water droplet in air (ambient relative humidity $H=38 \%$, temperature $T=24^{\circ} \mathrm{C}$ ). The experimental mass loss (blue circle) was obtained using Cahn DCA322 analyzer. The theoretical curve is calculated using eq.(5.7) with $c_{\mathrm{v}}=2.18 \times 10^{-5} \mathrm{mg} / \mu \mathrm{L}, D=24.9$ $\mathrm{mm}^{2} / \mathrm{s}, R=1.02 \mathrm{~mm}, m(0)=1.2 \mathrm{mg}$.

To check the validity of eq.(5.7), we conducted a series of experiments on evaporation of water droplets in air under the ambient relative humidity $H=38 \%$ and
temperature $T=24^{\circ} \mathrm{C}$. The experimental mass loss (blue circles in Figure 5.2) of a $1.2 \mu \mathrm{~L}$ water droplet was acquired using Cahn DCA-322 analyzer. Parameters used in eq. (5.7) are given in the figure caption. The initial contact angle $\theta=65^{\circ}$ was measured using KRUSS DSA10 and the radius of droplet base $R=1.02 \mathrm{~mm}$ was then calculated using eq.(5.5). The saturation vapor concentration and diffusion coefficient of water vapor in the air were taken at $T=24^{\circ} \mathrm{C}$ from Refs. [4, 5]. The theoretical curve (the red line in Figure 5.2) was calculated directly using these parameters without introducing any additional fitting parameters! The theoretical curve shows excellent agreement with the experimental data. Figure 5.2 also features an almost linear decrease of the sample mass indicating that the evaporation rate of a water droplet is almost constant within such a range of contact angles $\left(0^{\circ} \sim 65^{\circ}\right)$.

Since both the saturation vapor concentration $c_{\mathrm{v}}$ nd diffusion coefficient $D$ depend on temperature, it would be helpful to obtain an empirical relation taking into account the effect of temperature. This relation would allow one to calculate the rate of water evaporation at different temperatures.


Figure 5.3 (a) Diffusion coefficient of water vapor in air as a function of temperature (b) the saturation water vapor concentration as a function of temperature.

The data on diffusion coefficient in Figure 5.3(a) was taken from ref.[4] and was approximated as:

$$
\begin{equation*}
D(T)=0.171 T+20.8 \tag{5.8}
\end{equation*}
$$

where temperature is measured in Celsius and diffusion coefficient $D$ is measured in $\mathrm{mm}^{2} / \mathrm{s}$. The data on the saturation vapor concentration in Figure 5.3(b) was taken from ref.[6] and was approximated as:

$$
\begin{equation*}
c_{\mathrm{V}}(T)=3.65 \times 10^{-4} T^{3}+4.93 \times 10^{-3} T^{2}+0.377 T+4.81 \tag{5.9}
\end{equation*}
$$

where temperature is measured in Celsius and vapor concentration $c_{\mathrm{v}}$ is measured in $\mathrm{mg} / \mathrm{m}^{3}$.

With this analytical description of the evaporation kinetics of water droplets, one can move further to describe evaporation of more complex aqueous solutions. As seen from this analysis, the evaporation kinetics depends on the materials parameters only through the saturation vapor concentration and density of the material. Therefore, in order to study the evaporation kinetics of complex compounds, one needs to specify these parameters.

### 5.2 Evaporation of mullite precursor droplet

### 5.2.1 Materials

Mullite $\left(3 \mathrm{Al}_{2} \mathrm{O}_{3} \cdot 2 \mathrm{SiO}_{2}\right)$ is a ceramics refractory materials widely used in different applications thanks to its thermal resistance, toughness and exceptional physical, chemical stability at high temperature[7, 8]. Aluminum isopropoxide (AIP, $\mathrm{Al}\left(\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{O}\right)_{3}$, $98 \%$, , aluminum nitrate nonahydrate ( $\mathrm{ANN}, \mathrm{Al}\left(\mathrm{NO}_{3}\right)_{3} \cdot 9 \mathrm{H}_{2} \mathrm{O}, 98 \%$, Alfa Aesar, MA,

USA) and tetraethyl orthosilicate (TEOS, $\mathrm{Si}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{4}, 98 \%$, Acros Organics, NJ, USA) were used to synthesize the precursor. For these studies, the mullite precursor sol was synthesized in the Dr. F.Peng group at Clemson University. The synthesis procedure can be found in Ref.[9]. Briefly, the mole ratio of AIP, ANN, TEOS and water were kept at $0.58: 0.02: 0.2: 5$. The ANN was dissolved in the deionized water at room temperature with vigorously stirring the solution for 30 min . Then AIP and TEOS were added into the solution and stirred for 20 hours. AIP and TEOS were dissolved completely, and clear solution was obtained. The solution was then refluxed at $80^{\circ} \mathrm{C}$ for 5 hours. Approximately $2 / 3$ part of the solvent was removed using a rotary evaporator (IKA RV 10 digital, IKA, China). The obtained solutions were then set bake into an oven at $80^{\circ} \mathrm{C}$ until viscous sols were formed. The synthesized sol was very viscous and it was very difficult to withdraw certain amount of sol consistently using a micropipette. Therefore, we diluted the sol with the same amount (mass) of the DI water i.e. the mass concentration $w$ was one half of that of the sol right after the reflux. This diluted sol was used in the evaporation study.

### 5.2.2 Correction of the model

The main difference between the pure water and mullite precursor is that the vapor concentration at the droplet surface is no longer equal to the saturation vapor concentration $c_{v}$ but it depends on the mass concentration $w$ of mullite in the droplet. This vapor concentration $c$ is expected to be a function of the mass concentration of mullite $c(w)$ and is set equals to the equilibrium relative humidity $H(w)$ times the saturation vapor concentration: $c(w)=H(w) c_{\mathrm{v}}$ [10]. When water evaporates, the sol
becomes more and more concentrated and the equilibrium relative humidity changes correspondingly. In order to describe the evaporation of a mullite precursor droplet, eq. (5.7) should be modified as:

$$
\begin{align*}
\dot{m}(t)= & -\pi R D[H(w)-H] c_{\mathrm{v}}  \tag{5.10}\\
& \left(4.848 \alpha^{4}-8.933 \alpha^{3}+5.361 \alpha^{2}-0.039 \alpha+1.300\right)
\end{align*}
$$

In order to solve this differential equation, we have to find the equilibrium humidity $H(w)$ and density of the solution $\rho(w)$ as a function of mass concentration of mullite. The mass concentration of mullite $w$ at each time moment $t$ is defined through the following relation:

$$
\begin{equation*}
w(m)=m_{0} w_{0} / m, \tag{5.11}
\end{equation*}
$$

where $m_{0}$ is the initial mass of the droplet, $w_{0}$ is the initial mass concentration of mullite, $m(t)$ is the current mass of the evaporating droplet at time moment $t$. Therefore, the analysis of eq. (5.9) requires the knowledge of one more parameter, the initial mass concentration of mullite, $w_{0}$

### 5.2.3 Effect of the mullite concentration on the saturation vapor concentration

The mass concentration of mullite in the diluted sol was found using the TGA experiment (Hi-Res TGA 2950, TA Instrument). The heating rate was set $5^{\circ} \mathrm{C} / \mathrm{min}$ and temperature was held at $100^{\circ} \mathrm{C}$ for ten minutes before finishing the run to ensure the complete evaporation of water. The mass concentration of mullite was found to be $w_{0}=$ $38.0 \%$.

To ensure that the temperature induced drying led to the same chemical composition of mullite, we repeated the experiment by drying the droplet under vacuum.

A droplet of the diluted sol was placed in a vacuum desiccator and the vacuum was applied for 30min at room temperature. By comparing the initial and final masses of the sample, the mass concentration of mullite was found to be $w_{0}=38.2 \%$ which is very close to the value obtained from the TGA experiment. The difference was probably due to the water absorption during the transfer of sample from the desiccator to a microbalance. We consider the mullite concentration obtained from the TGA experiment as the reference and use this value in further calculations.


Figure 5.4 Experimental setup for measurement of equilibrium relative humidity of the mullite sol
With the determined mass concentration $w(m)$, we can start analyzing the dependence of equilibrium humidity $H(w)$ and density $\rho(w)$ on mullite concentration. Figure 5.4 depicts the experimental setup to measure the equilibrium relative humidity of the mullite sol. The capacity of the container is about 20 mL ; it was filled with the 15 mL diluted mullite sol. A humidity sensor (HS-2000D, Kele Precision Manufacturing) was threaded through the cap and sealed with epoxy. The container was then closed using the cap and wrapped tightly using para-film to prevent any leakage of water vapor. The humidity sensor was connected to PC and a Labview program was written for data acquisition.

The total mass of the sol is greater than 10 g and the possible mass change during the experiment is less than $c_{\mathrm{v}} \times 20 \mathrm{ml}=2.36 \times 10^{-4} \mathrm{~g}$. As a result, the mass concentration of the sample can be considered constant during the experiment.

To achieve equilibrium, we waited at least one hour for each measurement. After one hour, the data points were acquired every second for about one minute and the average humidity and its standard deviation were assigned based on this set of data points. The mass concentration of mullite is varied by evaporating a certain amount of water before closing the cap. The blue circles in Figure 5.5 are the experimental data obtained using this set of experiments. The two end points (without error bars) are the two limiting cases: $H(0)=1$ for the pure water, $H(1)=0$ for the pure solute.


Figure 5.5 Equilibrium relative humidity as a function of mass concentration of mullite sol The experimental curve was approximated using an exponential function as

$$
\begin{equation*}
H(w)=1.0085-0.0085 \exp (4.7588 w) \tag{5.12}
\end{equation*}
$$

The red line in Figure 5.5 matches well with the experimental data and hence eq.(5.12) can be applied to solve eq.(5.10).

### 5.2.4 Effect of the mullite concentration on droplet density

In order to obtain the density of the mullite sols at different dilution levels, we measured both droplet volume and mass during the evaporation. Two droplets with the same initial volume were used: one was placed on Cahn DCA-322 to obtain the mass change, the other on KRUSS DSA10 to obtain the shape of the droplet so that volume can be calculated. Two droplets were evaporating under the same condition (humidity and temperature). Each pair of mass and volume was obtained at the same moment during the evaporation. Figure 5.6 shows the density of mullite sol as a function of mass concentration of mullite. The images of droplets for the corresponding data point are also included. Density of mullite sol has an almost linear dependence on the mass concentration.


Figure 5.6 Density of mullite sol as a function of mass concentration. A linear function was used for fitting the experimental data:

$$
\begin{equation*}
\rho(w)=A w+B . \tag{5.13}
\end{equation*}
$$

where $A=2.28 \mathrm{~g} / \mathrm{mL}$ and $B=0.30 \mathrm{~g} / \mathrm{mL}$. Eq. (5.13) is only applicable for the solution with mass concentration greater than $30 \%$ ( $w>0.3$ ). As follows from eq.(5.9), the density influences the evaporation rate through the change of parameter $\alpha$. This dependence is not very strong, hence the density variation of the evaporating droplet is not the controlling factor in these experiments. The most important parameter controlling the evaporation kinetics is the equilibrium relative humidity $H(w)$.

### 5.2.5 Evaporation kinetics

Figure 5.7 summarizes the results of the experiments on evaporation of the mullite precursors. The initial mass of the droplet was $m(0)=2.66 \mathrm{mg}$. Its mass loss during evaporation was monitored using Cahn DCA-322 analyzer. During experiments, the droplets lost about $2.3 \mu \mathrm{~L}$ (the black circles in Figure 5.7). The experiment was conducted at temperature $T=22{ }^{\circ} \mathrm{C}$ and ambient relative humidity $H=25 \%$. The saturation vapor concentration $c_{\mathrm{v}}=1.96 \times 10^{-5} \mathrm{~g} / \mathrm{mL}$ and diffusion coefficient $D=24.6$ $\mathrm{mm}^{2} / \mathrm{s}$ were calculated using eqs.(5.8) and (5.9), respectively. The radius of the droplet base $R=1.33 \mathrm{~mm}$ was obtained directly from the image of the residual after evaporation.

Substituting eqs.(5.11), (5.12) and (5.13) into eq. (5.10), we can solved eq. (5.10) numerically with all the parameters defined above. Without introducing any adjustable parameters, the calculated theoretical curve (the blue line in in Figure 5.7) shows good agreement with the experimental data.


Figure 5.7 The evaporation of a $2.3 \mu \mathrm{~L}$ mullite precursor droplet in air (ambient relative humidity $H=25 \%$, temperature $T=22^{\circ} \mathrm{C}$ ). The mass loss (the black circles) was obtained using Cahn DCA322 analyzer. The theoretical curve was calculated using eq. (5.10) with $c_{\mathrm{v}}=1.94 \times 10^{-5} \mathrm{~g} / \mathrm{mL}$, $D=24.6 \mathrm{~mm}^{2} / \mathrm{s}, R=1.33 \mathrm{~mm}, m(0)=2.66 \mathrm{mg}$. The dashed green line represents the equilibrium relative humidity as a function of time.

Comparing Figure 5.7 with Figure 5.2, it becomes clear that the evaporation kinetics of the mullite precursor droplet is different from that of water droplet. For the water droplet, the evaporation rate is almost constant until complete evaporation. For the mullite precursor droplet, a gradual change of evaporation rate is observed. The change of equilibrium relative humidity (the dashed green line in Figure 5.7) is the major cause for this difference in evaporation kinetics.

At the early stage ( $t<500 \mathrm{~s}$ ), the equilibrium relative humidity is greater than $80 \%$ and is much higher than the ambient humidity $H=25 \%$. As a result, a fast evaporation rate is observed. Since the equilibrium humidity changes very slowly with time owing to very low concentration of mullite in the droplet, the evaporation rate is almost constant. Within the next time window $500 \mathrm{~s}<\mathrm{t}<1200 \mathrm{~s}$, the equilibrium relative humidity
decreases very fast, consequently, the evaporation rate slows down. We expect gelation to occur within this time interval, i.e. the sol should undergo a transformation from a water-like liquid state to a very viscous gel state. At the late stage, $t>1200 \mathrm{~s}$, the equilibrium relative humidity is very close to the ambient humidity: the droplet transforms to a solid. Therefore, the evaporation is very slow with the rate approaching zero. The final mass concentration of the droplet is determined by the ambient humidity.

To summarize the findings we conclude that the evaporation kinetics is divided into three regions, I: a water-like fast evaporation; II: gelation transition; III: slow evaporation of a solid. In order to confirm the hypothesis that the solution undergoes a transition from a liquid to a gel state in region II, we studied the viscosity change during evaporation.

### 5.3 Change of viscosity during evaporation

### 5.3.1 Experimental setup and calibration

In order to measure the time dependent viscosity of an evaporating droplet, we use the magnetic rotational spectroscopy (MRS) with magnetic nanorods. The detailed design of the instrument can be found in Ref.[11]. Briefly, an optical cell equipped with magnetic coils producing a rotating magnetic field was employed in these experiments. Introducing a $90^{\circ}$ phase difference between the magnetic coils 1,3 and 2,4 in Figure 5.8, one can control the rate of spinning of the magnetic field vector in the xy-plane. Magnetic nanorods were suspended in the mullite precursor. The fluid sample was placed in the
area depicted in Figure 5.8 and the whole setup was placed under microscope (Olympus, BX 51) for the observation of magnetic nanorods.


Figure 5.8 The stage used for the MRS experiment. Magnets 1,3 and 2,4 produce magnetic field at the same frequency but with the $90^{\circ}$ phase difference.


Figure 5.9 A series of microscope images obtained with a rotating magnetic nanorod. The red arrows show the direction of a 1 Hz rotating magnetic field and the black arrows indicate the direction of the magnetization vector of the nanorod.

A digital camera (BASLER acA2040) was attached to the microscope for video acquisition. The highest frame rate provided by the camera was about 188 fps . A series of captured images are shown in Figure 5.9. The angle $\varphi$ is the angle formed by magnetization vector $\boldsymbol{M}$ with the $x$-axis. The magnetization vector is co-aligned with the long axis of the nanorod. The angle $\alpha=\alpha_{0}+\omega t$ corresponds to the orientation of the external magnetic field $\boldsymbol{B}$, where $\alpha_{0}$ is the initial orientation of magnetic field with respect to the x -axis and $\omega$ is the angular frequency of the rotating magnetic field. The angle $\alpha_{0}$ was determined by the initial phase of the signal. For the signal shown in Figure 5.8, we had $\alpha_{0}=0$. It is convenient to introduce angle $\theta=\alpha-\varphi$ specifying the direction of the applied magnetic field with respect to the direction of magnetization vector. In our experiments, only nanorods rotating in the $x y$ plane were analyzed, therefore, both $\boldsymbol{M}$ and $\boldsymbol{B}$ vectors are confined in the same plane. The rotation of magnetic nanorod is governed by the following equation [1, 12]:

$$
\begin{equation*}
\dot{\varphi}=\omega_{c} \sin \theta=\omega_{c} \sin \left(\alpha_{0}+\omega t-\varphi\right), \tag{5.14}
\end{equation*}
$$

where $\omega_{\mathrm{c}}$ is the critical angular frequency introduced as

$$
\begin{gather*}
\omega_{c}=\frac{1}{\tau} \frac{3 \ln (l / d)-2.4}{(l / d)^{2}}  \tag{5.15}\\
\tau=\frac{4 \eta}{M B} \tag{5.16}
\end{gather*}
$$

where $\eta$ is viscosity of the fluid, $l / d$ is the aspect ratio of the nanorod, $l$ is the nanorod length and $d$ is the nanorod diameter. With the known initial orientation of the nanorod, $\varphi_{0}$, and time evolution of the magnetic field, $\alpha=\alpha_{0}+\omega t$, the orientation of magnetic nanorod as a function of time can be completely determined by solving eq.(5.14) for a
certain $\omega_{c}[13,14]$. We can determine $\omega_{c}$ by fitting the nanorod trajectory extracted from numerical solution of eq.(5.14) with the one obtained from the video.


Figure 5.10 Calibration of the experimental setup (a) 90 degree rotation of the magnetic nanorod under a constant magnetic field. (b) The critical angular frequency $\omega_{\mathrm{c}}$ for nanorods with different lengths.

In our experiment, we always use 200nm thick nickel nanorods; the nanorod lengths $l$ were determined from the microscope images. Therefore, the characteristic time $\tau$ defined by eq.(5.16) can be calculated using eq.(5.15). Viscosity $\eta$ can be determined as soon as the magnetostatic energy term $M B$ is known.

To determine this term, we performed a calibration experiment using $75.8 \mathrm{wt} \%$ water-glycerol mixture ( $75.8 \%$ glycerol). A $2 \mu \mathrm{~L}$ water-glycerol droplet was placed on the glass slide and covered by a cover slide immediately after the drop placement to prevent it from evaporation. Two pieces of the $50 \mu \mathrm{~m}$ thick double sided tape were placed between the two slides and used as spacers. The calibration experiment was performed at $25.4 \mathrm{C}^{\circ}$ and viscosity of the mixture at this temperature was obtained as $\eta=29.3 \mathrm{mPa} \cdot \mathrm{s}$.

To simply the experiment and image tracking procedure, we applied a DC signal to the magnets. Magnets 2 and 4 (Figure 5.8) were turned on to align nanorods in the $x$
direction $\left(\varphi_{0}=0\right)$. Then these magnets 2,4 were turned off and at the same time magnets 1 , 3 were turned on to align the nanorods in the $y$-direction. The nanorod rotations were recorded by the camera at its highest frame rate (188fps). Analyzing the video with a Matlab-based tracking algorithm [14, 15], we obtained the nanorod trajectory, i.e. angle $\varphi$ as a function of time. In Figure 5.10 (a) these experimental points are denoted by the blue circles. The theoretical curve was built by using eq.(5.14) with $\alpha_{0}=\pi / 2, \omega=0$ and $\varphi_{0}=0$ and taking $\omega_{\mathrm{c}}$ as an adjustable parameter. The comparison shows an excellent agreement with the experimental data and the critical angular frequency was found to be $\omega_{\mathrm{c}}=21.1 \mathrm{~s}^{-1}$ for this $13.8 \mu \mathrm{~m}$ long nanorod.

We performed the same experiment following the dynamics of ten nanorods having different lengths and calculated $\omega_{\mathrm{c}}$ for each of them. Then we plotted the critical frequency $\omega_{\mathrm{c}}$ as a function of aspect ratio $l / d$ as shown in Figure 5.10 (b). Taking $\tau$ as the adjustable parameter, we were able to fit the experimental data with eq.(5.15). Under this particular experimental condition we obtained $\tau=0.11 \mathrm{~ms}$. Since viscosity $\eta$ was known, $\eta$ $=29.3 \mathrm{mPa} \cdot \mathrm{s}$, the $M B$ term was found to be $1066 \mathrm{~J} / \mathrm{m}^{3}$.

### 5.3.2 Measuring the time dependent viscosity

In an evaporating mullite droplet, the viscosity was expected to constantly change with time. In order to probe the time dependent viscosity, we have to apply the AC signal to the magnets creating a continuous rotating field. The amplitude of the AC signal was the same as that of the DC signal in the calibration experiment so that the same value for the $M B$ term can be used.


Figure 5.11 Rotation of magnetic nanorods under spinning magnetic field. (a) synchronous (b) asynchronous rotations. The angle $\alpha=\omega t$ specifyes the direction of magnetic field, angle $\varphi$ defines the orientation of magnetic nanorods and angle $\theta$ provides the phase difference between the field vector and magnetization vector.

For a nanorod rotating in a simple Newtonian fluid, its spinning regimes are classified as synchronous and asynchronous regimes [1]. When the angular frequency of the magnetic field is smaller than the critical angular frequency, $\omega<\omega_{\mathrm{c}}$, the nanorod spins at the same frequency as that of the magnetic field keeping a constant phase difference $\theta_{0}$ as shown in Figure 5.11(a). This phase difference is determined by the ratio of the two frequencies: $\sin \theta_{0}=\omega / \omega_{c}$. When the angular frequency of the external field becomes greater than the critical frequency, $\omega>\omega_{\mathrm{c}}$, the viscous drag becomes so strong that the nanorod is no longer able to keep in pace with the field and spins asynchronously at a lower average frequency compared to the field.

The phase difference $\theta$ is constantly changing with time as shown in Figure 5.11(b) $[1,11-13,15]$. The direction of the magnetic moment also changes periodically when $\theta=(2 k+1) \pi(k=0,1,2,3 \ldots)$. Taking advantage of this phenomenon, we can increase the angular frequency $\omega$ of the magnetic field gradually and find out the angular frequency at which the nanorod just starts to rotate asynchronously [16]. This angular
frequency coincides with the critical angular frequency $\omega_{\mathrm{c}}$ and the fluid viscosity $\eta$ can be determined from this measured value using the calibrated $M B$ value.

However, this method does not work for a fluid with the time-dependent viscosity. Therefore, the full trajectory of the nanorod has to be analyzed. For the evaporating mullite droplet, one would expect the viscosity to increase with time as the concentration of mullite increases. We can still use eq. (5.14) to describe the rotation kinetics of the nanorod. The difference from the Newtonian case will be that the critical frequency $\omega_{\mathrm{c}}$ will also be a function of time for the evaporating droplet. To find this dependence, an analytical dependence of viscosity on time is commonly assumed and the nanorod trajectory is analyzed numerically and matched with the experiment to find the necessary phenomenological constants [13].

We would like to approach this problem in a different way, namely by measuring the fluid viscosity directly at different moments of time during the drop evaporation. The idea is not to assume any particular dependence of viscosity on time, but experimentally find this dependence. As shown earlier in our evaporation experiments, the evaporation kinetics of mullite precursor is sufficiently slow. Therefore, viscosity is almost constant within some time window. This time interval can be determined experimentally requiring that the solution of eq.(5.14) should match the experimental data with a constant $\omega_{c}$.

The experimental protocol is as follows: at a certain moment of time $t$ and associated interval $[t-\Delta t / 2, t+\Delta t / 2]$, one has to analyze the behavior of the nanorods following the steps developed for the Newtonian fluids. Then the calculated viscosity will
be considered as the viscosity of mullite precursor at the moment $t$. Scanning viscosity over time, we can reconstruct the dependence of viscosity on time, $\eta=\eta(t)$

Since we are mostly interested in the viscosity change during the mullite gelation when the solution is already very viscous, we will focus on the analysis of asynchronous rotation of nanorods. A $2 \mu \mathrm{~L}$ mullite droplet was placed on a cover slide and the dynamics of nanorod was captured during evaporation at 30 frames per second. The angular frequency $\omega$ of the magnetic field was set $\omega=2 \pi \mathrm{~s}^{-1}$. An illustration of the nanorod behavior in this very thick fluid is shown in Figure 5.12.


Figure 5.12 A gallery of images showing the oscillation of the nanorod inside the evaporating mullite sol.


Figure 5.13 The time evolution of the magnetization vector spinning inside evaporating mullite droplet. The angular frequency of the magnetic field is $\omega=2 \pi \mathrm{~s}^{-1}$. The blue circles are the experimental data points extracted from the video and the red lines are the theoretical curves calculated using eq.(5.14).

The dependence of the angle $\varphi$ on time was extracted from the video and it is shown in Figure 5.13. The nanorod for this particular experiment was $9.2 \mu \mathrm{~m}$ long. The time $t=0$ was chosen as the moment when the droplet was placed on the substrate. It is clear that the average rotation rate of the nanorod gradually decreases with time. We analyzed the change of the nanorod orientation within a 3 s time interval. In this video with about 100s time span, we collected more than 30 data points. The insets in Figure 5.13 are four examples of them and the theoretical curves all fit well with the experimental data taking $\omega_{\mathrm{c}}$ as the adjustable parameter.

Initially, the nanorod rotated at a relatively fast rate and its orientation changed by about 6 rad from 606 s to 609 s . In the 633 s to 636 s time interval, the orientation changed only by about 2 rad. In the 687 s to 690 s time interval, the average rotating rate was
almost zero and the nanorod oscillated only around a certain direction. We finished the analysis when the amplitude of the nanorod oscillations was comparable with the angular resolution of the images.


Figure 5.14 Exponential increase of viscosity of mullite droplets during evaporation.
From the calculated critical frequency, $\omega_{\mathrm{c}}$, the viscosity can be calculated for each 3 s interval using eq.(5.15) with the calibrated $M B$ value. We conducted experiments with five mullite droplets with similar sizes. In all cases, we found that the time dependence of mullite viscosity can be nicely approximated by the exponential function $\eta=\eta_{0} \exp \left(t / \tau_{\eta}\right)$ with two characteristic parameters, $\eta_{0}$ - characteristic viscosity of the droplet at the initial instant of time, and $\tau_{\eta}$ is the characteristic time of mullite gelation. In Figure 5.14 we show the results of a series of experiments confirming this exponential dependence of viscosity on time.

It is noticeable that the characteristic time of mullite gelation $\tau_{\eta}$ does not vary significantly from droplet to droplet. Within the 100s time window, viscosity changes by
two orders of magnitude (from $10^{1}$ to $10^{3} \mathrm{mPa} \cdot \mathrm{s}$ ). However, at the same moment of time, the viscosity seems to vary a lot from droplet to droplet. This variation might be caused by distinct evaporation kinetics of different droplets. Indeed, as seen from eq. (5.10), the evaporation kinetics depends on temperature $T$, ambient humidity $H$, as well as the radius of droplet base, $R$. These parameters may vary from droplet to droplet. In order to correlate the viscosity dependence on time with the change of mullite concentration in the drop, we propose to compare the viscosity dependence with the evaporation kinetics.

### 5.3.3 Dependence of viscosity on mullite concentration

Using eq. (5.10), we can build the mass loss curve for each droplet with the defined temperature $T$, ambient humidity $H$ and the radius of droplet base $R$. Temperature and ambient humidity were measured using a hygrometer and the radius of droplet base was determined using the image of the residual print after droplet evaporation.


Figure 5.15 The evaporation kinetics of five mullite droplets used for the viscosity measurement. The mass loss curves were built using eq. (5.10). The solid lines correspond to the time interval in which the viscosity was measured.

The evaporation kinetics for five droplets are shown in Figure 5.15. The time intervals in Figure 5.14 when the measurements of the fluid viscosity were taken are marked by the solid lines. It is clearly seen that, although the experimental conditions vary from droplet to droplet, the significant increase of viscosity was observed in the transition region where the evaporation rate showed a drastic change. From Figure 5.15, we can calculate the mass concentration at the corresponding moment of time. Together with Figure 5.14, one can build a relation between the viscosity and the mass concentration of mullite. All the data points were brought to the similar mass concentration region as shown in Figure 5.16. A theoretical curve was built to fit the experimental data.


Figure 5.16 Viscosity of the mullite solution as a function of mass concentration of mullite
It appears that the viscosity also exponentially increases with the mullite concentration in the droplet:

$$
\begin{equation*}
\eta(w)=501 \exp [62.7(w-0.75)] \tag{5.17}
\end{equation*}
$$

Eq.(5.17) is only applicable for the particular concentration range $(0.72<w<0.80)$ shown in Figure 5.16. In this period of time ( $\sim 100 \mathrm{~s}$ ), the mass concentration of mullite, $w$, changes with time almost linearly. This linear relation is obtained as follows: the evaporation rate within this time window can be considered to be almost constant, hence $m(t)=m\left(t_{0}\right)-\beta\left(t-t_{0}\right)$ where, $m\left(t_{0}\right)$ is the mass at the initial moment $t_{0}$ when the viscosity data was firstly acquired (Figure 5.14), $\beta$ is the evaporation rate. Using eq.(5.11), an approximate linear relation can be obtained when the mass change $\beta\left(t-t_{0}\right)$ is much smaller than the mass at time $t_{0}$.

$$
\begin{equation*}
w=\frac{m_{0} w_{0}}{m\left(t_{0}\right)-\beta\left(t-t_{0}\right)} \approx \frac{m_{0} w_{0}}{m\left(t_{0}\right)}\left[1+\frac{\beta\left(t-t_{0}\right)}{m\left(t_{0}\right)}\right] . \tag{5.18}
\end{equation*}
$$

This analysis sheds a light on the mechanism of viscosity change: an exponential dependence of viscosity on mullite concentration can be put within the framework of the Eyring theory of vacancies in liquids [17].

### 5.3.4 The mechanism of viscosity change

In Eyring's theory, viscosity $\eta$ depends on the volume ratio $\delta$ between the solidlike molecules and the gas-like molecules (vacancies):

$$
\begin{equation*}
\eta \propto \delta \exp (\kappa \delta) \tag{5.19}
\end{equation*}
$$

where $\kappa$ is the parameter proportional to the activation energy. For the mullite sol (mixture of water and mullite solid), we take mullite molecules as the solid-like molecules and water as the vacancies. Mullite molecules are considered to be packed in a certain lattice and water molecules will act as the vacancy (or defect). The activation
energy will be the energy needed for the mullite molecule to escape from the potential well formed by its neighbor.

For the mullite sol at a certain mass concentration, the total volume $V_{\mathrm{t}}$ of the sol is $m / \rho(w)$ where $m$ is the total mass and $\rho(w)$ is the density given by eq.(5.13). The volume of the mullite molecules $V_{m}$ is $m w / \rho_{\mathrm{s}}$, where $\rho_{\mathrm{s}}=2.58 \mathrm{~g} / \mathrm{cm}^{3}$ is the density of mullite solid obtained by substituting $w=1$ in eq. (5.13). Therefore, the volume ratio between mullite molecules and water is:

$$
\begin{equation*}
\delta=\frac{V_{\mathrm{s}}}{V_{\mathrm{t}}-V_{\mathrm{s}}}=\frac{m w / \rho_{\mathrm{s}}}{m / \rho(w)-m w / \rho_{\mathrm{s}}}=\frac{(2.28 w+0.3) w}{2.58-(2.28 w+0.3) w} . \tag{5.20}
\end{equation*}
$$

One can expand eq.(5.20) asymptotically in the vicinity of $w=0.75$ concentration as

$$
\begin{equation*}
\delta \approx 1.41+8.38(w-0.75) \tag{5.21}
\end{equation*}
$$

Eq.(5.21) is only applicable when ( $w-0.75$ ) $\ll 1$. Substituting eq.(5.21) into eq.(5.19) yields:

$$
\begin{equation*}
\eta \propto \exp [8.83 \kappa(w-0.75)], \tag{5.22}
\end{equation*}
$$

where the terms proportional to ( $w-0.75$ ) are neglected because the linear dependence is much weaker than the exponential one. Eq.(5.22) shows the required $w$ dependence offered by eq.(5.17). Thus the Eyring theory is able to explain the physics behind this dependence.

As the mulite concentration $w$ increases, the volume ratio $\delta$ (mullite molecules to water molecules) also increases indicating that it is more probable for a mullite molecule to have mullite molecule in its neighbor rather than a water molecule (vacancy). As a
result, it would cost more energy for the mullite molecules to escape from the lattice. Therefore, a larger external force $f$ is needed to put the the mullite molecules in motion. This is an indication of the gel formation.

Hence, region II on the kinetic graphs is associated with the gel formation in mullite droplets manifested through an exponential increase of the droplet viscosity.

### 5.4 Conclusion

In this chapter, we studied both the evaporation kinetics and the time-dependent viscosity of an evaporating mullite droplet.

Starting with the evaporation of a water droplet, we proved that the quasi-static approximation was appropriate for description of the evaporation of water droplet. Using equation(5.7), we calculated the mass loss curve which agreed well with the experimental data. No extra fitting parameters were introduced.

Next, we studied the evaporation of a mullite precursor droplet following a similar relation by introducing a concentration dependent equilibrium relative humidity and density. Both of these two quantities were experimentally measured at different mass concentrations of mullite. Using eq. (5.10), the theoretical curve was constructed and matched well with the experimental data. The evaporation kinetics is divided into three regions: region I assumes a water-like fast evaporation; region II shows significant decrease of evaporation rate; region III was associated with a slow evaporation of solid materials. Knowing the initial mass $m_{0}$, radius of droplet base $R$, temperature $T$ and ambient relative humidity $H$, we were able to accurately predict the evaporation kinetics.

At last, the time-dependent viscosity of an evaporating mullite droplet was measured. Using the magnetic rotational spectroscopy with magnetic nanorods, we found that the viscosity exponentially increases with time within region II associated with significant decrease of the evaporation kinetics. Using eq. (5.10) and the time dependent viscosity, we built a master curve of viscosity as a function of mass concentration $w$. We found that viscosity also exponentially increases with concentration $w$ in a certain range. Such dependence was successfully explained using the Eyring theory of vacancies in liquids. With the increasing mass concentration of mullite, the mobility of mullite molecules decrease leading to an exponential increase of viscosity. This theory confirms that region II corresponds to the gelation transition region where the evaporation rate shows drastic decrease.

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## CHAPTER VI

## A GRADIENT FIELD DEFEATS THE INHERENT REPULSION BETWEEN MAGNETIC NANORODS

### 6.1 Introduction

In the past decade, one-dimensional magnetic nanostructures, such as magnetic nanorods, chains of magnetic nanoparticles, and nanotubes filled with magnetic nanoparticles have offered great opportunities for design of multifunctional devices and for manufacturing of anisotropic nano and microstructures[1-4]. These applications include, for example, optofluidics[5-9], microrheology[10-14], magnetic swimming [1520], photonics[21], drug delivery [22] and electromagnetic shielding[23]. Particularly, in the manufacturing of composite materials, different configurations of magnetic fields are usually applied to obtain the desired pattern of magnetic rods or chains [2, 4, 24-27]. A uniform magnetic field is usually used to align the nanorods in one direction or to form self-assembled chains from magnetic nanoparticles. Recently, the strategies for aligning an assembly of non-interacting magnetic nanorods in both Newtonian and nonNewtonian fluids under a uniform magnetic field have been proposed and developed [28, 29]. However, in many cases, one needs to deal with a concentrated colloid of magnetic
nanorods where the interactions between nanorods are crucial for the patterning of the microstructures[30-36].

The main challenge to control the assembly of magnetic nanorods is to bring them together and place next to each other [7, 35, 36]. Indeed, when two identical magnetic nanorods come together side by side, they are prone to move away due to their inherent repulsion. A uniform magnetic field keeps them parallel to each other but they are intended to form a tandem with a head-to-tail ordering. Phase diagram for the long nanorods demonstrates a significant enlargement of the region of repulsion compared to the point dipoles [7,37]. Therefore, one needs to develop a new strategy in order to defeat this inherent repulsion.

One possible strategy is to use a non-uniform magnetic field with a special field gradient [30, 33, 35, 38]. In a non-uniform magnetic field generated by a magnet, the magnetic force acting on a nanorod with magnetization vector $\boldsymbol{M}$ is written as $\boldsymbol{F}_{\mathrm{m}}=V(\boldsymbol{M} \cdot \nabla) \boldsymbol{B}$, where $\boldsymbol{B}$ is the magnetic field vector, $V$ is the volume of the nanorod. As follows from this formula, generating a special field gradient, magnetic nanorods can be pushed toward each other thus maintaining the desired distance between them. For example, using a cylindrical magnet with the $y$-axis directed along the axis of the cylinder, one can orient all nanorods in the $y$-direction and generate the force $\boldsymbol{F}_{\mathrm{m}}=V(M \partial / \partial y) \boldsymbol{B}$, where $M$ is the absolute value of the nanorod magnetization. For a cylindrical magnet shown in FIG. 1 (a) and (b), the radial component of magnetic field is directed outward the central axis, i.e. it is positive. This component fades away as the $y$ coordinate increases. Accordingly, the radial component of magnetic force is negative
pushing the nanorods to cluster at the central axis. These arguments show that the placement of magnetic nanorods next to each other can be done by applying a nonuniform magnetic field with a strong axial gradient of the radial component of magnetic field [39].

However, when one needs to gather nanorods at the micrometer scale, such strong gradients are difficult to produce. Therefore, it is natural to question: would it be possible to vary only an axial component of the magnetic field to defeat the nanorod repulsion and place them next to each other?

The behavior of nanorods in a non-uniform magnetic field with a strong variation of its strength only in one direction is poorly understood and is rarely discussed in the literature [2, 9, 40]. The interest to form different microstructures using a field gradient is growing [3, 9, 30, 33, 34, 41-43], however the lack of understanding of the behavior of nanorods and unidentified strategy to control the placement of nanorods side by side hinders the progress in this field.

In this chapter, we describe the behavior of a pair of magnetic nanorods in a nonuniform magnetic field with a strong gradient along the axis of magnetization of nanorods. Nickel nanorods are suspended in a 2D Newtonian film and their dynamics is filmed using the dark field microscopy. We develop a particle tracking algorithm to follow the nanorod movement and analyze their trajectories. In the model, we take into account magnetostatic and viscous drag forces. The analysis of experiments shows that the model adequately describes the behavior of interacting magnetic nanorods. We therefore employed this model to construct a phase portrait of the dynamic system
describing the moving nanorods. The effect of the field gradient on realization of either head-to-tail or side-by-side configurations was investigated. The conditions for controlled placement of magnetic nanorods side by side were revealed.

### 6.2 Experiments

### 6.2.1 Preparation of a dispersion of Ni nanorods

To make nickel nanorods we employed electrochemical template synthesis [44, 45]. Nanorods were synthesized inside 200nm pores of alumina membranes (Watman Ltd.) following the procedure described in Chapter III. This experimental protocol enables one to produce nanorods of about $6 \mu \mathrm{~m}$ in length and less than 200 nm in diameter. Following the protocol of Refs. [28, 41], we stabilized the nanorods with a layer of polyvinylpyrrolidone (PVP). The PVP coated nickel nanorods were dispersed in a 76 wt $\%$ water-glycerol mixture ( $76 \%$ glycerol, $24 \%$ water). In experiments, dispersion of nickel nanorods of low concentration ( $0.005 \mathrm{wt} \%$ ) was used. A $1 \mu \mathrm{~L}$ droplet of such dispersion was placed on a glass slide (VWR International, LLC) and immediately covered by another glass cover slide (VWR International, LLC). Two $26 \mu \mathrm{~m}$ thick Nylon fibers were placed as spacers between slides. This gap thickness was sufficient to avoid the movement of nanorods in the direction perpendicular to the substrates yet thick enough to neglect the effect of hydrodynamic interactions of the nanorods with the substrates. In our earlier publication [28] we confirmed this statement by measuring viscosity of different standard liquids using Magnetic Rotational Spectroscopy [11, 46] .

### 6.2.2 Optical cell

Schematic of the optical cell is shown in Figure 6.1(a). Two cylindrical magnets were employed in this experiment. The rear face of the smaller magnet was attached to the front face of the larger one so that both magnets had a common axis as shown in Figure $6.1(\mathrm{~b})$. The smaller magnet was 1.6 mm in diameter and 1.6 mm in length, and the larger magnet was 12.7 mm in diameter and 12.7 mm in length (Grade N52, K\&J Magnetics). This construction allowed us to apply a sufficiently strong field of the order of one Tesla. The gradient changes by as much as two orders of magnitude within the distance of about 5 mm from the front face of the smaller magnet as illustrated in Figure 6.1(c). The field distribution was simulated using COMSOL taking magnetization as $1.48 \times 10^{6} \mathrm{~A} / \mathrm{m}$ for both magnets and placing the origin of coordinates at the free surface of the small magnet 2 .


Figure 6.1 (a) Schematic of the experimental setup. A sample with the nanorod dispersion is placed under the objective and magnetic field is varied by moving the stage with the attached
magnets along the $y$-axis back and forth. (b) The system of two magnets used in experiments (c) Magnetic field and its gradient calculated along the $y$-axis of the system.

This construct was positioned under the microscope (Olympus BX 51) with the common axis parallel to the optical stage. The position of the construct was controlled by a linear stage (VT-21, MICOS). The Olympus BX 51 microscope was equipped with a digital camera (SPOT Imaging Solutions, Inc.) enabling us to apply the dark field imaging. The sample was positioned under the microscope in front of the smaller cylindrical magnet as shown in Figure 6.1(a) and the behavior of nanorods was studied by focusing camera on four different spots along the common axis of the magnets at the following positions with respect to the smaller magnet: $5 \mathrm{~mm}, 3 \mathrm{~mm}, 2 \mathrm{~mm}, 1.5 \mathrm{~mm}$.

### 6.2.3 Experimental protocol

The main challenge to study the interactions between nanorods subject to a nonuniform field is that the nanorods are always moving in the fluid. The nanorods keep moving toward the region of a stronger field until they reach a boundary, for example, the liquid-air interface. When a nanorod hits the boundary, it does not move anymore and stays pinned to boundary. Experimentally, when the dispersion is dilute, it is very difficult to catch two nanorods in the focus and then follow their movement. It is therefore convenient to focus the camera to a pinned nanorod and watch the behavior of incoming nanorods, Figure 6.2(b).


Figure 6.2 (a) Illustration of the model of "magnetic charges" applied to a nanorod with magnetization $M$, length $l$, and diameter $d$. The nanorod can be subdivided onto a system of elementary cylinders of length $\Delta l$ each carrying magnetic moment $m_{i}$. Only end cylinders have non-compensated "charges" $Q$ generated at their faces. (b) Illustration of the system of two nanorods. The center of local Cartesian system of coordinates $(X, Y)$ is attached to the center of mass of the nanorod that is pinned to the boundary shown at the bottom of this picture. The position of the incoming nanorod is identified by the coordinates of its center mass ( $X, Y$ ). (c) Distribution of the field lines generated by two magnets 1 and 2. Different colors are used to distinguish the strength of magnetic field at different places. The red box marks the position of the spot where the Figure (b) was taken.

Initially, the magnets were placed far away from the sample to eliminate any translational motion of the nanorods. The recording started when the magnets were brought closer to the sample. Figure 6.3 shows two sequences of images illustrating different scenarios of the nanorod landing: (a) landing on top of the pinned nanord; (b) landing next to each other.


Figure 6.3 Two series of images illustrating different scenarios of the nanorod landing. (a) The incoming nanorod lands on top of the pinned one. (b) The incoming nanorod lands side by side next to the pinned one.

### 6.3 Magnetostatic interactions between nanorods and external field

### 6.3.1 Energy landscape

In the focal plane of observation it is convenient to introduce the local Cartesian system of coordinates $(X, Y)$ with the $Y$-axis aligned along the common axis of the magnets. The origin of the local system of coordinates is taken at the center of mass of the pinned nanorod as illustrated in Figure 6.2(b). The position of the incoming nanorod is denoted by the coordinates of its center of mass $(X, Y)$. It is not necessary that the incoming and pinned nanorods would have the same length. Therefore we introduce two lengths: $L$ is for the pinned one and $l$ for the incoming nanorod.

The observations were taken at the points located along the common axis of the magnets. As illustrated in Figure 6.2(c), the $x$-component of magnetic field $\boldsymbol{B}$ is almost zero at these points. Therefore, magnetization $\boldsymbol{M}$ of all nanorods is expected to point in the $y$-direction. If the nanorods were non-interacting, they would move only in the $y$ -
direction. Within the small field of view $(\sim 20 \mu \mathrm{~m} \times 20 \mu \mathrm{~m})$ shown in Figure 6.2(b), the gradient $\mathrm{d} B / \mathrm{d} y$ can be considered constant $\mathrm{d} B / \mathrm{d} y=\alpha$. The variation of magnetic field in this small spot is sufficiently small. Therefore, we assume that magnetization of nanorods is constant. We also assume that two neighbor nanorods have the same magnetization $M$. In experiments, the applied magnetic field was sufficiently strong to ensure that the nanorods were not able to change their orientations even in a close proximity to each other.

Since the distance between nanorods is comparable with their lengths, the nanorods cannot be treated as point dipoles [7]. We therefore employ the model of "magnetic charges" $[7,47,48]$. To determine the charge $Q$, we divide the magnetic nanorod onto a chain of infinitesimally small magnets as shown in Figure 6.2(a). Each elementary magnet has the moment $m_{i}=Q \Delta l$ with an elementary "magnetic charge" $Q$. If we sum up all elementary magnets within the nanorod, all internal poles of the opposite sign will be cancelled out and "magnetic charges" of the opposite sign will remain only at the ends of the nanorod. For a nanorod with diameter $d$ and magnetization $M$, "magnetic charge" $Q$ can be therefore calculated as: $Q=\pi d^{2} M / 4$.

Following the chosen system of coordinates, Figure 6.2(b), the energy of the nanorod subject to an external field can be calculated by introducing magnetostatic potential $\varphi(X, Y)$. It has to satisfy the Laplace equation written in cylindrical coordinates as: $\partial^{2} \varphi / \partial x^{2}+(1 / x)(\partial \varphi / \partial x)+\partial^{2} \varphi / \partial y^{2}=0$. In the vicinity of the central axis, the potential is represented as: $\varphi=-B_{0} Y+\alpha\left(X^{2}-2 Y^{2}\right) / 4$, where $B_{0}$ is the constant component of a nonuniform external magnetic field taken at the center of mass of the pinned nanorod $(0,0)$.

In our experiments, the gradient $\alpha=\mathrm{d} B_{y} / \mathrm{d} y$ is always negative. This implies that the nanorods tend to move to the boundary $(X,-L / 2)$ as illustrated in Figure 6.2(b).

With the given potential, the magnetic field is obtained as $\boldsymbol{B}=-\nabla \varphi=(-\alpha X / 2$, $B_{0}+\alpha Y$ ). The magnetostatic energy of the incoming nanorod in the external magnetic field is calculated as: $\varphi(X, Y+l / 2) Q-\varphi(X, Y-l / 2) Q=-Q l y \alpha-Q l B_{0}$. The second term is independent on the position of the incoming nanorod and hence it does not contribute to the force balance. The total magnetostatic energy of two interacting magnetic nanorods under the field gradient is therefore written as:

$$
\begin{align*}
& U(X, Y)=\frac{\mu_{0} Q^{2}}{4 \pi}\left(\frac{1}{\sqrt{X^{2}+(Y+l / 2-L / 2)^{2}}}-\frac{1}{\sqrt{X^{2}+(Y-l / 2-L / 2)^{2}}}\right.  \tag{6.1}\\
& \left.-\frac{1}{\sqrt{X^{2}+(Y+l / 2+L / 2)^{2}}}+\frac{1}{\sqrt{X^{2}+(Y-l / 2+L / 2)^{2}}}\right)-Q l Y \alpha,
\end{align*}
$$

where $\mu_{0}$ is permeability of vacuum. As follows from Eq.(6.1), magnetostatic energy scales as $U \propto \mu_{0} Q^{2} /(4 \pi L)$. We can make Eq.(6.1) dimensionless by dividing it by $\mu_{0} Q^{2} /(4 \pi L)$, provided that all coordinates $(X, Y)$ are normalized by the length of the pinned nanorod $L$ :

$$
\begin{align*}
& \frac{4 \pi L U(X, Y)}{\mu_{0} Q^{2}}=-\frac{4 \pi l L^{2} \alpha}{\mu_{0} Q} \frac{Y}{L}+ \\
& \left(\frac{1}{\sqrt{(X / L)^{2}+(Y / L+(l / 2 L)-1 / 2)^{2}}}-\frac{1}{\sqrt{(X / L)^{2}+(Y / L-(l / 2 L)-1 / 2)^{2}}}\right.  \tag{6.2}\\
& \left.-\frac{1}{\sqrt{(X / L)^{2}+(Y / L+(l / 2 L)+1 / 2)^{2}}}+\frac{1}{\sqrt{(X / L)^{2}+(Y / L-(l / 2 L)+1 / 2)^{2}}}\right) .
\end{align*}
$$

The factor $\beta=4 \pi l L^{2} \alpha / \mu_{0} Q$ measures the strength of the field gradient with respect to the mutual magnetostatic interactions between two nanorods. If this parameter is small,
$\beta \ll 1$, the field gradient has almost no effect on the incoming nanorod: two nanorods interact as there would be no any field gradient. If this parameter is large, $\beta \gg 1$, the incoming nanorod should not feel any presence of the neighbor nanorod hence it should be able to land on the boundary.

Figure 6.4 shows the energy landscape generated by the incoming nanorod in the presence of the pinned nanorod and external magnetic field $\boldsymbol{B}=\left(-\alpha X / 2, B_{0}+\alpha Y\right)$. In calculations we assumed that the pinned nanorod has the same length $L=l$. Different colors correspond to the different energy levels.

### 6.3.2 Magnetic force

Using this energy landscape, one can calculate the force acting on the incoming nanorod. The magnetic force is obtained through the gradient of the total magnetostatic energy $U(X, Y)$ as:

$$
\begin{equation*}
F_{X}=-\partial U(X, Y) / \partial X, F_{Y}=-\partial U(X, Y) / \partial Y \tag{6.3}
\end{equation*}
$$

The black arrows in Figure 6.4 show the direction of magnetic force acting on the incoming nanorod.

In the absence of external magnetic field gradient $\beta=0$, the nanorods tend to come together forming a head-to-tail configuration Figure 6.4(a). This case corresponds to points $1(0,1)$ and $2(0,-1)$ in Figure $6.4(\mathrm{~d})$ providing the same energy level. Due to the impermeable boundary, the incoming nanorod cannot reach point 2 . Therefore, point 1 is the energetically favorable because two opposite "magnetic charges" cancel each other at the junction point.


Figure 6.4 The energy landscape for an incoming nanorod positioned at $(X, Y)$. The pinned nanorod has the same magnetization, length, and diameter. (a) The energy landscape for a nanorod subject to the field generated by the pinned nanorod when the external field is not applied, $\beta=0$. (b) Deformation of the energy landscape caused by the field gradient corresponding to $\beta=2.5$ (c) Effect of a strong gradient $\beta=25$. Different colors represent different energy levels. The black arrows show the direction of magnetic force acting on the incoming nanorod. The dashed purple line shows the impermeable boundary. (d) Configurations 1 and 2 correspond to the energy minima. and configuration 3 corresponds to the energy maximum when the nanorods interact in the absence of external field.

In the absence of magnetic field gradient, when two nanorods are placed side by side next to each other, point $3(0,0)$ in Figure $6.4(\mathrm{~d})$, they produce the energy maximum. Strong repulsion between the nearest "magnetic charges" of the same sign, forces the nanorods to run away from this configuration 3 .

In magnetic field gradient, the energy landscape deforms and one finds new minima. These minima appear as a result of topological transformations of the energy
surface as illustrated in Figure 6.4(b) and (c). When the field gradient is not very strong and parameter $\beta$ is of the order of 1 the deformation of the energy surface is insignificant, yet the topography changes to decrease the region with a strong $x$-component of the magnetic force. This change occurs in regions $X / L>1$ and $X / L<-1$, where the magnetic force undergoes significant change. The arrows in Figure 6.4(b), $\beta=2.5$, show that the $x$ component of the force goes to zero in these regions. Therefore, in these regions the incoming nanorod is expected to land at the boundary not on top of the pinned nanorod. Points 1 and 2 are still the energy minima and point 3 is the energy maximum. The field gradient causes the energy level at point 2 to decrease relative to point 1 .

When the field gradient is strong and parameter $\beta$ is much greater than 1 , the energy surface deforms significantly. For example, in Figure 6.4(c) corresponding to $\beta=25$, the energy surface in the vicinity of point 1 forms a funnel-like singularity. Thus, with a slim chance of success the incoming nanorod would land on top of the pinned one. The region where the field gradient governs the positioning of the incoming nanorod spreads over the larger region where the arrows in Figure 6.4(c). are pointing straight down.

This analysis of the energy landscape favors a possibility of placement of the incoming nanorod side by side next to the pinned one. In applications, it is important to control the nanorod placement, hence it is necessary to specify the range of initial positions of the incoming nanorod $(X, Y)$ leading to its landing on the boundary or on top of the pinned nanorod.

### 6.4 Dynamics of magnetic nanorods: phase portrait

Assume that the nanorods are suspended in a simple Newtonian fluid with viscosity $\eta$. In the limit of low Reynolds numbers when the inertial force is much smaller than the viscous force, the velocity field of the incoming nanorod is described by the following dynamic system [49]:

$$
\begin{align*}
& \frac{d X}{d t}=-\frac{1}{\gamma_{X}} \frac{\partial U(X, Y)}{\partial X}, \gamma_{X}=\frac{4 \pi \eta l}{\ln (2 l / d)+0.5}  \tag{6.4}\\
& \frac{d Y}{d t}=-\frac{1}{\gamma_{Y}} \frac{\partial U(X, Y)}{\partial Y}, \quad \gamma_{Y}=\frac{2 \pi \eta l}{\ln (2 l / d)-0.5}
\end{align*}
$$

Where $\gamma_{\mathrm{X}}$ and $\gamma_{\mathrm{Y}}$ are the translational drag coefficients of the nanorods moving in the $X$ and $Y$ directions, respectively [49], and $t$ is time. The dynamic system (6.4) was analyzed numerically: each pair of initial conditions ( $X_{0}, Y_{0}$ ) generated a trajectory. Two nanorods with the same length $(L=l)$, diameter $d$, and magnetization $M$ were used in these calculations. Since the center of coordinates was chosen at the center of mass of the pinned nanorod, the substrate was located the $L / 2$ distance below the center of coordinates. Therefore, when the incoming nanorod reached position $Y / L=0$ the calculations stopped indicating that the nanorod has landed on the boundary. In Figure $6.5(\mathrm{a})$, (b) and (c), the blue lines solutions describe the trajectories $(X(t), Y(t))$ of the incoming nanorods. In order to distinguish the scenarios of the nanorod landing, we have to analyze all initial conditions and classify the trajectories on the phase portrait of Eq. (6.4).


Figure 6.5 The phase portrait of dynamic system (4) for different parameters $\beta$. (a) $\beta=2.5$, (b) $\beta=11.1$, (c) $\beta=15$. In figures (a), (b) and (c), the blue lines are the trajectories of the center of mass of the incoming nanorods. The impermeable boundary is located at $Y / L=-0.5$ which is not shown in the graphs. The pink region is forbidden for the incoming nanorod implying that the nanorod would never land in this region. The purple lines are separatrices for this two dimensional dynamic system. The solid purple lines divide the phase portrait into two regions (I and II). If the nanorod starts its motion from region I, it will come to the boundary. The nanorod starting in region II will land on top of the pinned nanorod. The black dot $(0,1)$ is the energy minimum corresponding to point 1 in Figure 6.4. This point is the attractor of this dynamic system. The empty blue circle $(0,0)$ is the energy maximum corresponding to point 3 in Figure 6.4. It is an unstable stationary point for this dynamic system. The empty black circles are the saddle points and are the interceptions of the separatrices. (d) The plot of the minimum distance separated the incoming nanorod and the pinned nanorod as a function of $\beta$ for the pair of nanorods with different length ratios $/ / L$.

We first look at the $Y$-axis of the phase portrait. Along this axis, the following equality $F_{X}(0, Y)=0$ holds true. This equality implies that magnetic force is always
directed along the $Y$-axis and the nanorods starting at any point $\left(0, Y_{0}\right)$ will move along the $Y$-axis.

There are two singular points of this system where the $Y$-component of magnetic force $F_{Y}$ goes to infinity. The first singular point shown as the black dot with coordinates $(0,1)$ in Figure 6.5(a),(b) and (c), corresponds to the energy minimum. It is the attractor of the dynamic system: the pinned nanorod attracts the incoming one and forces it to land on top. The local trajectories converge towards this attractor and the arrows show the velocity vectors of the incoming nanorods.

The second singular point is the center of coordinates attached to the center of mass of the pinned nanorod, point $(0,0)$. This point corresponds to the energy maximum: two nanorods which are brought together and placed side by side next to each other cannot stay in equilibrium. The local trajectories emanate from this unstable stationary point.

Besides these two singular points, there are two more stationary points of the dynamic system (4) satisfying the following equations: $F_{X}=0, F_{Y}=0$. These stationary points are the saddle points of the dynamic system. Along some bundles of local trajectories the velocity vectors are always directed toward these stationary points and along some other set of trajectories the velocity vectors are always directed outward them. These two stationary points are marked as the empty black circles in Figure 6.5(a), (b) and (c). In Figure 6.5(b) these two saddle points merge at the $Y$-axis.

The separatrices, the solid purple lines, are defined as the trajectories of nanorods emanating from the saddle points. The details of their calculations are given in the Appendix.

### 6.5 Classification of the landing scenarios for the nanorods

With the aid of this analysis of the phase portrait of dynamic system(6.4), we can classify the scenarios of the nanorod landing. The solid purple separatrices in Figure 6.5(a), (b) and (c) divide the phase portrait onto three regions: region I (dark green), II (dark yellow) and the forbidden region (pink) where nanorod cannot land in. The nanorods are pushed away from the forbidden region by the strong magnetic field of the pinned nanorod.

When the nanorod starts its motion in region I, it is mostly pushed by the external field gradient and the magnetic force generated by the pinned nanorod is much weaker. Therefore, this nanorod will always land on the boundary next to the pinned nanorod.

In region II, the field generated by the pinned nanorod is strong and is able to push the incoming nanorod to land on top.

The boundaries of regions I, II and the forbidden region are sensitive to the applied magnetic field gradient $\alpha$ since $\beta$ is proportional to $\alpha$. In the limiting case $\beta=0$, when the external field is uniform, two saddle points are infinitely far from each other and region II occupies an infinitely large area. This implies that the incoming nanorod will always land on top of the pinned one. This statement is supported by the energy map shown in Figure 6.4(a).

Increasing the field gradient, i.e. parameter $\beta$, one opens the possibility to land the incoming nanorod next to the pinned one. In the phase portrait, two saddle points are pushed to come from infinity closer to the $Y$-axis: Therefore, the area of region II shrinks and the area of region I increases to offer the incoming nanorod a possibility to land next to the pinned one.

There is a critical field gradient when two saddle points merge at the $Y$-axis. In Figure $6.5(\mathrm{~b})$ this case corresponds to $\beta_{\mathrm{cr}}=11.1$. The critical field gradient separates two topologically different portraits: when $\beta<\beta_{\text {cr }}$, the expansion of region I and contraction of region II and the forbidden region occur mainly in the $x$-direction. In the opposite case when $\beta>\beta_{\text {cr }}$, two saddle points move along the $Y$-axis separating region II from the forbidden region. Region I expands mainly in the $Y$-direction.

In the limit $\beta$ tends to infinity, when the field gradient is much stronger than the field of the pinned nanorod, one saddle point moves to coincide with the energy maximum at $(0,0)$ and the other merges with the energy minimum at $(0,1)$. In this limit, the areas of region II and the forbidden region shrink to zero, implying that the incoming nanorod will always land on the boundary side by side to the pinned nanorod.


Figure 6.6 Coordinates of the two saddle points as functions of $\beta$. (a) $X$-coordinate (b) $Y$ coordinate.

Figure 6.6 summarizes the topological change of the phase portrait. When $\beta<\beta_{\text {cr }}$, two saddle points are symmetric with respect to the $Y$-axis. As $\beta$ increases, two saddles points come closer to the $Y$-axis implying the expansion of region I and shrinkage of region II and the forbidden region. When $\beta=\beta_{\mathrm{cr}}$ two saddle points merge at the $Y$-axis and stay there as $\beta$ further increases. When $\beta$ goes to infinity, one saddle point moves along the $Y$-axis toward point $(0,0)$, the other moves along the $Y$-axis toward point $(0,1)$. Simultaneously, region II and the forbidden region disappear. This topological change of the phase portrait is illustrated with the supplementary movie (S1).

For the practical applications, it is instructive to analyze the change of the half width of the forbidden region, $X_{\min }$, as a function of $\beta$. This parameter $X_{\min }$, corresponds to the minimum spacing between two nanorods landed at the boundary. In Figure 6.5(d) we plot this minimum spacing as a function of $\beta$ for the nanorods with different length ratios $l / L$. In all cases, the minimum spacing decreases as $\beta$ increases. It appears that the minimum spacing $X_{\min }$ decreases to zero as the field gradient increases. Thus, the
nanorods of different lengths can be placed side by side next to each other by increasing the $\beta$-parameter.

### 6.6 Experimental verification of different scenarios of nanorod landing

Experimental reproduction of the phase portrait requires tracking of the multiple pairs of incoming and pinned nanorods with the same length ratios $l / L$ as well as with the same dimensionless parameter $\beta$. Therefore, Figure 6.5(a), (b) and (c) are difficult to reproduce experimentally. However, the trajectories of the incoming nanorods are traceable. The length ratio $l / L$ can be measured directly from the images and only one unknown parameter $\beta$ is needed determination from the experiments. Since the $\beta$ parameter has a strong dependence on the diameter of the pinned nanorod $\beta \propto 1 / d^{2}$, but the dark field images do not allow one to accurately measure the nanorod diameters, we determined this parameter by fitting the experimental trajectories with the numerical solutions of Eqs.(6.4).

Several frames including the initial and final frames were first extracted from each video and the initial frame was then overlaid with all the following frames. Therefore, we can form an image showing the trajectory of the incoming nanorod. In Figure 6.7 we demonstrate five composite images. These pictures illustrate different scenarios of the nanorod landing. The center of mass of the incoming nanorod is denoted by the purple circle and the pinned nanorod is marked by the red rectangle.


Figure 6.7 Experiments with nickel nanorods. The purple circles denote the centers of mass of the incoming nanorods. The red rectangles mark the pinned nanorods. The blue lines are the theoretical curves. The initial position of the incoming nanorod is represented by the normalized coordinates given in the parentheses.

Using parameter $\beta$ as the adjustable parameter, in each case we obtained the best fits for the experimental trajectories. This best fits are shown in FIG 4 as the blue lines. The theoretical curves demonstrate an excellent agreement with the experimental trajectories. This confirms the validity of the proposed model.

In Figure 6.7 (a) - (e), the dimensionless parameter $\beta$ increases gradually from 5 to 98. In Figure 6.7 (a) where parameter $\beta$ is the smallest, the field gradient is considered weak. According to the model predictions, the incoming nanorod lands directly on top of the pinned one. In Figure 6.7 (b), parameter $\beta$ is greater than that in Figure 6.7 (a) and the incoming nanorod also starts movement from a more distant position. Hence, at the initial moment of time the interactions between nanorods are weaker as compared to those in FIG. 6(a). As a result, the trajectory of the incoming nanorod is distinct: the incoming nanorod first passes the pinned one tempting to land next to it. But when its head almost
passes the pole of the pinned nanorod where the local field is stronger than the external one, its $Y$-component of velocity reverses the sign reflecting the change in the force field. The incoming nanorod first moves downward then drifts upward and finally jumps on top of the pinned one. These maneuvers are illustrated by the last three purple points in Figure 6.7 (b).

In Figure 6.7 (c), we show a similar behavior of a nanorod which was initially positioned closer to the pinned one and was subject to a stronger field gradient. Again, this nanorod demonstrated similar maneuvers and landed on top of the pinned one.

In the small Reynolds number flows, this kind of maneuvers of incoming nanorods overshooting the pinned one is counterintuitive [49,50]: since inertia plays no role, one would not expect the nanorod to change the flow direction. However, this overshooting is not related to inertia but is completely governed by the non-uniform magnetic field. It can be understood by considering the interaction between the head of the incoming nanorod ( $-Q$ ) and the tail of the pinned one $(+Q)$ and neglecting the interactions between other distant poles. Following this assumption, the $Y$-component of the magnetic force between these two poles can be interpreted using eqs.(6.1) and (6.3) as

$$
\begin{equation*}
F_{Y}=-\partial U(X, Y) / \partial Y=-\frac{\mu_{0} Q^{2}}{4 \pi} \frac{Y-l / 2-L / 2}{\left[X^{2}+(Y-l / 2-L / 2)^{2}\right]^{3 / 2}}+Q l \alpha \tag{6.5}
\end{equation*}
$$

The field gradient $\alpha$ is always negative. When the head of incoming nanorod is above the tail of the pinned one and the inequality $Y-L / 2-L / 2>0$ holds true, the force $F_{Y}$ is always negative indicating that the nanorod moves always downwards. If the incoming nanorod passes the pinned nanorod by an infinitesimally small distance as shown in

Figure 6.7 (b) and (c), the first term in Eq. (5) becomes negative. As the incoming nanorod keeps moving downwards, the force $F_{Y}$ may decrease to zero and then flip the direction at some critical point. After this moment, the incoming nanorod will drift upwards and finally jumps on top of the pinned one. Thus, the model completely captures the effect of the field non-uniformity and describes new phenomenon of overshooting which has never been observed and discussed in the literature on small Reynolds number swimmers [2, 51-54].

The nanorods in Figure 6.7 (d) and (e) had the same initial $X$-coordinate $(X / L=0.1)$ However, since the field gradient for the case in Figure 6.7 (d) is smaller relative to that in Figure 6.7 (e), the smaller gradient was not able to defeat the force field of the pinned nanorod and the incoming nanorod landed on top of the pinned one. In contrast, at the dimensionless field gradient $\beta=98$, we were able to place the nanorods side by side next to each other. Thus, the proposed theory completely explains the experimental observations and can guide the remote controlled placement of the nanorods [35].

### 6.7 Conclusion

In this Chapter, We present a complete analysis of the dynamics of interacting magnetic nanorods subject to non-uniform external magnetic field. The magnetostatic interactions between long magnetic nanorods are described through the interactions of their poles carrying "magnetic charges". The energy landscape was studied theoretically and all minima and maxima of the energy surface were specified.

Then we described the 2D dynamics of magnetic nanorods when their resistance is controlled by the viscous drag. Using the phase portrait of this dynamic system we
described the regions of initial positions from which the free nanorod can be placed side by side next to the pinned one.

This theory was then confirmed in experiments with nickel nanorods. We showed that a strong repulsion between nanorods can be defeated by applying a non-uniform magnetic field with a strong gradient in the direction of nanorod alignment. The effect of a spontaneous change of the flow direction of the incoming nanorod "overshooting" the pinned one was observed for the first time and explained by the proposed model. This effect is quite unusual for a low Reynolds number flow, and is explained by a specific distribution of the magnetic field around the pinned nanorod. With the aid of the proposed theory, one can build different lattices with the spacing dependent on the field gradient and magnetic properties of nanorods.

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## CHAPTER VII

## FERROMAGNETIC RESONANCE FOR THE SINGLE DOMAIN NANOPARTICLES

### 7.1 Background

Microwave absorption by ferromagnetic nanoparticles has attracted great attention in recent years due to the broad potential applications in medicine and different technologies [1-5]. There are several advantages of using ferromagnetic nanoparticles as microwave absorbers. A ferromagnetic single domain nanoparticle demonstrates an enhanced absorption of the microwave electromagnetic (EM) irradiation at the ferromagnetic resonance (FMR) frequency when the magnetic moment of nanoparticle starts vigorous procession about its easy axis[6, 7]. The ferromagnetic resonance frequency and associated absorption of the EM irradiation can be easily controlled by varying the particle shape, size and their concentration in a composite.

The wavelength of the radio frequency (RF) wave is much larger than the size of the nanoparticles. In many cases, when the inter particle distance in the nanocomposites is much smaller than the RF wavelength. For example, a 10 GHz frequency EM wave in vacuum has the wavelength $\lambda$ of about $3 \times 10^{-2} \mathrm{~m}$, which is much greater than the size of nanoparticles ranging between $10^{-9} \mathrm{~m}$ to $10^{-8} \mathrm{~m}$. Therefore, each wave period covers
thousands and thousands of nanoparticles in the nanocomposites and the wave cannot recognize them, propagating through the material as it would be a continuum. Description of this continuum typically employs an effective medium approximation resulting in the concentration dependent permeability and permittivity [8-15].

The basic mechanisms of interactions of the EM waves with magnetic nanoparticles have been studied and developed in the last century[6, 16]. However, the analysis of interactions of EM waves with nanocomposites has received much less attention and these interactions remain poorly understood [17-19]. At the same time, the current understanding of interactions of nonmagnetic metal nanocomposites with the EM waves has been significantly advanced and enabled new exciting engineering applications [20, 21].

Microwaves propagating through ferromagnetic materials show strong circular birefringence suggesting that these materials are anisotropic[22]. Hence, the theory developed for non-magnetic metal nanocomposites which are isotropic, cannot be directly applied to magnetic nanocomposites. In order to study the FMR phenomena in nanocomposites, one has to generalize the effective medium theory on magnetic nanocomposites.

As a natural first step in this development, we start with the analysis of the ferromagnetic resonance of a single domain nanoparticle embedded in a matrix. Closely following the classical works of Landau and Lifshitz [23] and Kittel[24], we derived the constitutive equation for the magnetic induction $\boldsymbol{B}$ in a nanoparticle subject to the AC field. The difference is that we set up the FMR theory considering the corresponding
boundary value problem of electrodynamics. This approach will allow us to generalize the obtained solution on a composite using the averaging technique developed for nonmagnetic nanocomposites [11, 13, 25].

### 7.2 Ferromagnetic resonance in a single domain nanoparticle



Figure 7.1 (a) Schematic of the ferromagnetic resonance experiment. A bias DC field, $\boldsymbol{H}_{\mathrm{ex}}$ is applied to a composite film and an EM wave with the wave vector $\boldsymbol{k}$ and the magnetic field vector $\boldsymbol{h}_{1}$ oscillating perpendicular to the bias field propagates through the material. Detector analyzes the exiting wave with the magnetic component $\boldsymbol{h}_{2}$. (b) Schematic of the precession of the magnetization vector about the easy axis of a spherical nanoparticle. The easy axis of a nanoparticle is assumed parallel to the internal DC field, $\boldsymbol{H}_{\mathrm{in}}$. Inside the materials, the AC component of magnetic field, $\overline{\boldsymbol{h}}$, is perpendicular to the internal bias field $\boldsymbol{H}_{i \mathrm{i}}$. Both these fields are perturbed by the nanoparticle magnetization generating forces the magnetization vector $\boldsymbol{M}$ to spin around the easy axis. In the picture, the end of magnetization vector moves over the circular orbit, where $\boldsymbol{m}$ is the xy-projection of magnetization vector.

A FMR experiment is schematically shown in Figure 7.1. The ferromagnetic material is placed in a static magnetic field $\boldsymbol{H}_{\mathrm{ex}}$ and a microwave is applied to the material. The magnetic component $\boldsymbol{h}_{1}$ of the microwave is perpendicular to the static
magnetic field, $\boldsymbol{h}_{1} \perp \boldsymbol{H}_{\text {ex }}$. This applied irradiation is partially absorbed by the material ( $h_{2}$ $<h_{1}$ ). In the conventional FMR experiments[16], the microwave absorption by the sample is measured by changing the strength of the bias magnetic field $\boldsymbol{H}_{\mathrm{ex}}$ keeping the frequency $f$ of the AC field non-changed. The FMR is detected when a maximum absorption is observed at a certain magnetic field $\boldsymbol{H}_{\mathrm{c}}$ [16, 22-24]. One can also fix $\boldsymbol{H}_{\mathrm{ex}}$ and scan over the frequency to observe an absorption peak [16].

Conventional FMR experiments are conducted on the ferromagnetic samples for which the constitutive equations are known. In the case of composites containing ferromagnetic single domain nanoroparticles, the field inside the sample is perturbed and even the field in the non-magnetic host would be perturbed and different from the external applied field $\boldsymbol{H}_{\mathrm{ex}}$. Therefore, the constitutive equation for such a material has to be corrected. To simplify the problem, we assume that the nanocomposite is prepared in a special way to set the easy axes of the nanoparticles parallel to the direction of external field $\boldsymbol{H}_{\mathrm{ex}}$, the z-direction in Figure 7.1. This assumption is not strong and, as shown in Refs. [26-28], this type of alignment can be realized in practice. Upon application of the external magnetic field, the film with the volume fraction of nanoparticles $\chi$ perturbs this field. Thus, the field inside the film changes as $\boldsymbol{H}_{\mathrm{in}}=\boldsymbol{H}_{\mathrm{ex}}-\chi \boldsymbol{M}$, where $\boldsymbol{M}$ is the magnetization of a single nanoparticle. This internal bias field acts on each nanoparticle to align all magnetic moments of the nanoparticles parallel to this field. For each single nanoparticle embedded in the material this field is external. In order to find the permeability of a composite film, we have to look at the reaction of a single nanoparticle on the applied field $\boldsymbol{H}_{\text {in }}$.

### 7.2.1 Landau-Lifshitz-Gilbert dispersion of magnetic permeability of a

 nanoparticleIn a single domain nanoparticle, the magnetization vector is "frozen" in the direction of the particle easy axis. When an EM wave penetrates the nanoparticle, the magnetization vector $\boldsymbol{M}$ is forced to deflect from the easy axis. As a result, the magnetization vector spins around that direction. This precession is schematically depicted in Figure 7.1. In continuum electrodynamics, the dynamics of magnetization vector is described by the Landau-Lifshitz-Gilbert (LLG) equation[11, 16].

$$
\begin{equation*}
\frac{d \boldsymbol{M}}{d t}=-\gamma \mu_{0}\left[\boldsymbol{M} \times\left(\boldsymbol{H}_{\mathrm{s}}+\boldsymbol{h}\right)\right]+\frac{\alpha}{|\boldsymbol{M}|}\left(\boldsymbol{M} \times \frac{d \boldsymbol{M}}{d t}\right), \tag{7.1}
\end{equation*}
$$

where $\gamma$ is the gyromagnetic ratio, $\mu_{0}$ is the permeability of vacuum and $\alpha$ is the phenomenological damping coefficient, and $\boldsymbol{h}$ is an AC field inside the nanoparticle. The bias static field inside the nanoparticle, $\boldsymbol{H}_{\mathrm{s}}$, depends on the effective field caused by the crystalline magnetic anisotropy in the particle, $\boldsymbol{H}_{\mathrm{a}}$, the demagnetization field introduced in Chapter I and II, $\boldsymbol{H}_{\mathrm{d}}$, and internal field $\boldsymbol{H}_{\text {in. }}$. The field $\boldsymbol{H}_{\mathrm{a}}$ depends on the interaction between spins and the crystal lattice [24]. For a uniaxial magnetocrystalline anisotropy, this field $\boldsymbol{H}_{\mathrm{a}}$ is parallel to the easy axis and it strength is calculated as $H_{\mathrm{a}}=2 K_{1} / \mu_{0} M$ [16] where $K_{1}$ is the anisotropy coefficient as introduced in Chapter I. Assume that the nanoparticles are spherical. As shown in Chapter II, by solving a magnetostatic problem, the demagnetization field $\boldsymbol{H}_{\mathrm{d}}$ for a spherical nanoparticle is obtained as $\boldsymbol{H}_{\mathrm{d}}=-\boldsymbol{M} / 3$. Taking into account all these components, the bias static field inside the nanoparticle is introduced as:

$$
\begin{equation*}
\boldsymbol{H}_{\mathrm{s}}=\boldsymbol{H}_{\mathrm{in}}+\boldsymbol{H}_{\mathrm{a}}+\boldsymbol{H}_{\mathrm{d}} \tag{7.2}
\end{equation*}
$$

The magnetization vector $\boldsymbol{M}$ can be also divided into static $\boldsymbol{M}_{0}$ and dynamic $\boldsymbol{m}$ components. In the FMR experiment, the dynamic components of magnetization and the field are usually much smaller than the static components ( $h \ll H_{\mathrm{s}}, m \ll M_{0}, M \cong M_{0}$ ). Therefore, eq.(7.1) can be linearized and written in the first approximation as [16]:

$$
\left\{\begin{array}{l}
\boldsymbol{M}_{0} \times \boldsymbol{H}_{s}=0  \tag{7.3}\\
\frac{d \boldsymbol{m}}{d t}=-\gamma \mu_{0}\left[\boldsymbol{m} \times \boldsymbol{H}_{s}+\left(\boldsymbol{M}_{0} \times \boldsymbol{h}\right)\right]+\frac{\alpha}{\left|\boldsymbol{M}_{0}\right|}\left(\boldsymbol{M}_{0} \times \frac{d \boldsymbol{m}}{d t}\right)
\end{array}\right.
$$

The first equation indicates that the static magnetization $\boldsymbol{M}_{0}$ is always parallel to the static magnetic field, $\boldsymbol{H}_{\mathrm{s}}$, hence the dynamic component of magnetization, $\boldsymbol{m}$, spins in the $x y$ plane. The second equation governs the precession of the magnetization vector $\boldsymbol{m}$. The dynamic magnetization $\boldsymbol{m}$ is induced by the magnetic field $\boldsymbol{h}$. Assuming the following form of the external field $\boldsymbol{h}: \boldsymbol{h}=\boldsymbol{h}_{0} \mathrm{e}^{\mathrm{i} \omega t}$, the second eq.(7.3) can be solved for $\boldsymbol{m}$ explicitly and hence the dynamic magnetic induction $\boldsymbol{b}=\mu_{0}(\boldsymbol{m}+\boldsymbol{h})$ can be found as:

$$
\begin{gather*}
\boldsymbol{b}=\mu_{0} \mu \boldsymbol{h}+\mu_{0} i g(\boldsymbol{h} \times \hat{z}), \quad \boldsymbol{h}=\boldsymbol{h}_{0} e^{i \omega t}  \tag{7.4}\\
\mu=1+\gamma \mu_{0} M \frac{\omega_{r}+i \alpha \omega}{\left(\omega_{r}+i \alpha \omega\right)^{2}-\omega^{2}}, \quad g=\gamma \mu_{0} M \frac{\omega}{\left(\omega_{r}+i \alpha \omega\right)^{2}-\omega^{2}},  \tag{7.5}\\
\omega_{r}=\gamma \mu_{0} H_{s}, \tag{7.6}
\end{gather*}
$$

where $\mu_{0}$ is the permeability of vacuum. The constitutive equation (7.4) and dispersion of magnetic permeability (7.5) are applicable for any ferromagnetic material and these relations are not specific for the nanoparticles[16]. Specifics of the nanomaterial comes from the definition of $\boldsymbol{H}_{\mathrm{s}}$. Therewith, the frequency $\omega_{\mathrm{r}}$ introduced by eq. (7.6) carries all
information on the materials properties and nature of the nanoparticle. However, the dispersion of permeability of ferromagnetic materials expressed in eqs.(7.5) demonstrating non-monotonous behavior deserves an explanation.

### 7.2.2 Ferromagnetic resonance as the materials property

Since magnetic field $\boldsymbol{h}$, and magnetic induction $\boldsymbol{b}$ are the 2D-vectors oscillating in the xy-plane, constitutive equation (1.4) can be written in a tensor form through its $x$ and $y$ components as

$$
\binom{b_{x}}{b_{y}}=\mu_{0}\left(\begin{array}{cc}
\mu & i g  \tag{7.7}\\
-i g & \mu
\end{array}\right)\binom{h_{x}}{h_{y}} \text { or } b_{i}=\mu_{0} \mu_{i j} h_{j}
$$

where $\mu_{i j}$ is the magnetic permeability tensor.
Minus-wave: Right-handed Plus-wave: left-handed circularly polarized wave circularly polarized wave


$$
\boldsymbol{h}_{ \pm}=\left(h_{0} \mathbf{e}_{\mathbf{x}} \pm i h_{0} \mathbf{e}_{\mathbf{y}}\right) e^{i \omega t}
$$

Figure 7.2 Rotation of magnetic field in the circularly polarized waves and the induced precessions of the magnetization vector $\boldsymbol{M}$. The right-handed wave is defined as that spinning in the anti-clockwise direction if the z-axis is pointed upward. The left-handed wave spins in the clock-wise direction.

The 2D $\boldsymbol{h}$-field in a circularly polarized EM wave can be considered as a complex-values 2 D vector $\boldsymbol{h}_{ \pm}=\left(h_{0} \mathbf{e}_{\mathrm{x}} \pm i h_{0} \mathbf{e}_{\mathrm{y}}\right) \exp (i \omega t)$ [11]. The unit vectors $\mathbf{e}_{\mathrm{x}}$ and $\mathbf{e}_{\mathrm{y}}$
point in the $x$ and $y$ directions respectively. We will call the wave $\boldsymbol{h}_{+}=\left(h_{0} \mathbf{e}_{\mathrm{x}}+\right.$ $\left.i h_{0} \mathbf{e}_{\mathrm{y}}\right) \exp (i \omega t)$ the "plus"-wave, and the wave $\boldsymbol{h}_{-}=\left(h_{0} \mathbf{e}_{\mathrm{x}}-i h_{0} \mathbf{e}_{\mathrm{y}}\right) \exp (i \omega t)$ the "minus"-wave.

When a circularly polarized wave propagates through the material along the wave vector $\boldsymbol{k}$, magnetic field $\boldsymbol{h}$ spins around this vector perpendicularly to it, $\boldsymbol{h} \perp \boldsymbol{k}$. This rotation of vector $\boldsymbol{h}$ is schematically shown in Figure 7.2. where the plus wave with subscript ' + ' and the minus wave with subscript ' - ' are defined as the left- and righthanded circularly polarized waves, respectively.

In this representation of circularly polarized waves, eqs.(7.4) and (7.5) can be simplified by introducing the right- and left-handed magnetic inductions $\boldsymbol{b}_{ \pm}=\left(b_{0} \mathbf{e}_{\mathrm{x}} \pm\right.$ $\left.i b_{0} \mathbf{e}_{\mathrm{y}}\right) \exp (i \omega t)$ as,

$$
\begin{equation*}
\boldsymbol{b}_{ \pm}=\mu_{0}(\mu \mp g) \boldsymbol{h}_{ \pm} \quad \mu \mp g=1+\frac{\gamma \mu_{0} M}{\omega_{r} \pm \omega+i \alpha \omega} \tag{7.8}
\end{equation*}
$$

Figure 7.3 illustrates the characteristic features of the relative permeabilities of a ferromagnetic material seeing by the two distinctly polarized waves. As follows from eq.(7.8), the resonance peak appears only for the minus-wave for which the $\boldsymbol{m}$-vector spins in the anti-clockwise direction in Figure 7.2. When the microwave frequency $\omega$ approaches the natural precession frequency $\omega_{r}=\gamma \mu_{0} H_{\mathrm{s}}$, the denominator in eq. (7.8) tends to zero and the effective permeability $(\mu-g)$ significantly increases. Close to this natural frequency, the permeability significantly varies with the frequency and can become negative (Figure 7.3). In the limit $\omega \gg \omega_{\mathrm{r}}$, the permeability approaches 1 and the ferromagnetic material behaves as a nonmagnetic material.

For a bulk material, the negative permeability implies that the EM wave cannot penetrate the material. When the EM penetrates the distance $d$ below its surface, the amplitude of the EM wave will exponentially decay, $h \propto \exp (-2 \pi d / \lambda)$ [11]. Therefore, when an EM wave hits a ferromagnetic film, the absorption significantly increases at the resonance frequency $\omega_{\mathrm{r}}$ and finally the material becomes almost impermeable for the waves when the frequency is further increased. This is a signature of the ferromagnetic resonance in the bulk materials.

However, if the diameter of a ferromagnetic nanoparticle is much smaller than the wavelength $\lambda$, the EM wave will be able to penetrate the nanoparticle. This effect is specific for the nanoparticles and it deserves a special attention.



Figure 7.3 Typical behavior of the permeability $\mu \pm g$. (a) minus-wave $\mu+g$, (b) plus wave $\mu-g$. Calculations are given for a ferromagnetic nanoparticle using the following parameters: $\mu_{0} H_{\mathrm{s}}=$ $0.31 \mathrm{~T}, M=4.3 \times 10^{5} \mathrm{~A} / \mathrm{m}$ and $\alpha=0.05$

### 7.2.3 Frequency dependence of the field distribution inside and outside the nanoparticle

Knowing the magnetic permeability of the ferromagnetic nanoparticle, we can analyze the interaction between the microwave and the particle. For a gigahertz wave, the wavelength $\lambda$ is measured in centimeters. The characteristic time scale for the wave penetration is $\tau=d / c$, where $d$ is the particle diameter and $c$ is the speed of light. Taking $d=10^{-8} \mathrm{~m}$, we have $\tau \sim 10^{-9} / 10^{8}=10^{-17} \mathrm{~s}$. The characteristic time for the flip of magnetization in the gigahertz wave is $\tau_{\omega} \sim 10^{-9} \mathrm{~s}$. Therefore, the nanoparticle is subject to a quasi-static magnetic field, because in the time scale of the magnetization change the field sets up almost instantaneously. With the aid of this estimate, all terms in the Maxwell equations that are time-dependent can be safely dropped and the model for the field distribution around and inside the nanoparticle is reduced to the equations of magnetostatics [11]:

$$
\begin{equation*}
\nabla \cdot \boldsymbol{b}^{i}=0, \quad \nabla \times \boldsymbol{h}^{i}=0 \quad(i=l, m) \tag{7.9}
\end{equation*}
$$

The superscripts $l, m$ stands for the host material and magnetic nanoparticle, respectively. As known from magnetostatics [11], the magnetization inside an ellipsoidal particles can be constant. Hence assuming this constancy of $\boldsymbol{M}$, the equation for induction $\nabla \cdot \boldsymbol{b}^{i}=0$ is reduced to $\nabla \cdot \boldsymbol{h}^{i}=0$. The second equation $\nabla \times \boldsymbol{h}^{i}=0$ is always satisfied by introducing magneto-static potential $\varphi^{i}$ as $\boldsymbol{h}^{i}=-\nabla \varphi^{i}$. Substituting this relation into the first equation $\nabla \cdot \boldsymbol{h}^{i}=0$, we obtain the Laplace equation for the potential:

$$
\begin{equation*}
\nabla^{2} \varphi^{i}=0 \tag{7.10}
\end{equation*}
$$

subject to the boundary conditions at the nanoparticle surface $r=R$ :

$$
\left\{\begin{array}{l}
\varphi^{l}(R)=\varphi^{m}(R)  \tag{7.11}\\
\boldsymbol{b}^{l}(R) \cdot \frac{\boldsymbol{R}}{R}=\boldsymbol{b}^{m}(R) \cdot \frac{\boldsymbol{R}}{R}
\end{array}\right.
$$

Far away from the nanoparticle, the field must be equal to the average field $\overline{\boldsymbol{h}}$ in the composites, $\nabla \varphi^{i}=-\overline{\boldsymbol{h}}$ as $r$ tends to $\infty$. The solution to eqs.(7.10) and (7.11) for a spherical nanoparticles is sought in the form[11]

$$
\begin{equation*}
\varphi^{i}=-\alpha^{i}(\overline{\boldsymbol{h}} \cdot \boldsymbol{r})-\beta^{i} \frac{(\overline{\boldsymbol{h}} \cdot \boldsymbol{r})}{r^{3}} \tag{7.12}
\end{equation*}
$$

where $\boldsymbol{r}=(r, \theta)$ is the position vector with the origin at the nanoparticle center. Using the boundary condition at infinity, $\nabla \varphi^{i}=-\overline{\boldsymbol{h}}(r \rightarrow \infty)$, we immediately obtain $\alpha=1$. To avoid singularity of the magnetic potential $\varphi^{m}$ at $r=0$, the constant $\beta^{m}$ should be set as zero, $\beta^{m}$ $=0$. Thus, the field inside the particle is uniform and this field constant $\alpha^{m}$ has to be found from the remaining boundary conditions. Substituting constitutive equation (7.8) into eq.(7.11), and assuming that the host matrix satisfies the following constitutive equation $\boldsymbol{b}^{l}=\mu_{0} \boldsymbol{h}^{l}$, the two coefficients $\alpha^{m}, \beta^{l}$ for left- and right-handed circularly polarized waves are obtained as[25]:

$$
\left\{\begin{array}{l}
\alpha_{ \pm}^{m}=\frac{3}{2+[\mu(\omega) \mp g(\omega)]}  \tag{7.13}\\
\beta_{ \pm}^{l}=\frac{1-[\mu(\omega) \mp g(\omega)]}{2+[\mu(\omega) \mp g(\omega)]} R^{3}
\end{array}\right.
$$

The dynamic magnetic fields inside the nanoparticle for the plus and minus waves $h_{ \pm}^{m}$ are related to $\bar{h}_{ \pm}$through the following equation

$$
\begin{equation*}
h_{ \pm}^{m}=\frac{3}{2+[\mu(\omega) \mp g(\omega)]} \bar{h}_{ \pm} \tag{7.14}
\end{equation*}
$$

$\mathrm{Eq}(7.14)$ indicates that the dynamic magnetic field inside nanoparticle is uniform. As shown in the previous section, for the minus wave, the real part of $\mu+g$ can be negative at a certain frequency. When the denominator of $\mathrm{eq}(7.14)$ goes to zero, the magnetic field inside the nanoparticle is significantly strengthened. Mathematically, this condition for achieving the maximum field is written as

$$
\begin{equation*}
2+\operatorname{Re}\left[\mu\left(\omega_{\mathrm{c}}\right)+g\left(\omega_{\mathrm{c}}\right)\right]=0 \tag{7.15}
\end{equation*}
$$

The root of this equation $\omega_{c}$ corresponds to the resonance frequency. It is remarkable that this frequency is different from the natural precession frequency $\omega_{\mathrm{r}}$ given by eq.(7.6). This resonance is caused by the interactions of magnons with the surrounding media when the real part of the effective permeability of the minus-wave changes the sign from positive to negative.


Figure 7.4 Distribution of dimensionless fields $h_{-}^{i} / \bar{h}_{-}, i=l, m$ around and inside a single domain ferromagnetic nanoparticle with magnetization $M=4.3 \times 10^{5} \mathrm{~A} / \mathrm{m}$. The static field $\mu_{0} H_{\mathrm{s}}=0.31 \mathrm{~T}$ (a) $\omega / 2 \pi=9.7 \mathrm{GHz}$ (b) $\omega / 2 \pi=16 \mathrm{GHz}$.

The distribution of dimensionless field ( $\left.h_{-}^{i} / \bar{h}_{-}, i=l, m\right)$ inside and outside the nanoparticle for the minus-wave is shown in Figure 7.4. The distinct behavior of magnetic fields is illustrated with two different frequencies. In calculations, we assumed that the snapshots are taken at a certain time moment $t$ and at this moment the magnetic field $\overline{\boldsymbol{h}}_{-}$is pointing in the $x$-direction. The minus-wave is propagating perpendicular to the plane in z-direction with the field rotating in the anti-clockwise direction within the xy-plane. The magnetic field $h_{-}^{i}(i=l, m)$ is considered as the superposition of the magnetic field generated by the dynamic magnetization $\boldsymbol{m}$ and the average field $\overline{\boldsymbol{h}}_{-}$.

Inside the nanoparticle, the magnetic field generated by the magnetization $\boldsymbol{m}$ is $\boldsymbol{m} / 3$ and is exactly the demagnetization field as shown in Chapter I. The black circle represents the surface of the nanoparticle. All the parameters are the same as the one for Figure 7.3 (static field $\mu_{0} H_{\mathrm{s}}=0.31 \mathrm{~T}$, magnetization $M=4.3 \times 10^{5} \mathrm{~A} / \mathrm{m}$ and $\alpha=0.05$.). Under these conditions, the two resonance frequencies $\omega_{\mathrm{r}}$ and $\omega_{\mathrm{c}}$ are very different: $\omega_{\mathrm{r}} / 2 \pi=10.1 \mathrm{GHz}, \omega_{\mathrm{c}} / 2 \pi=16 \mathrm{GHz}$.

For a 9.7 GHz wave (in the vicinity of the natural precession frequency $\omega_{\mathrm{r}} / 2 \pi$ ), the dynamic permeability of nanoparticle is positive and reaches a maximum (Figure 7.3(a)). In this case, the field inside the nanoparticle is very weak: its amplitude is about $0.1 \bar{h}_{-}$as shown in Figure 7.4(a). This is caused by a subtle interplay between the demagnetization field $-\boldsymbol{m} / 3$ and the average field $\overline{\boldsymbol{h}}_{-}$. The demagnetization field is almost antiparallel to the average field $\overline{\boldsymbol{h}}_{-}$and its magnitude is also very close to $\overline{\boldsymbol{h}}_{-}$(Figure 7.4(a)). Physically, the reduction of the internal magnetic field is due to the large
permeability of the nanoparticle: the demagnetization field generated by the magnetization has a strong shielding effect on the external field $\overline{\boldsymbol{h}}_{-}$.

For a 16 GHz wave (in the vicinity of the resonance frequency $\omega_{c} / 2 \pi$ ), the magnetic field inside the nanoparticle is significantly enhanced. The demagnetization field generated by the induced magnetization $\boldsymbol{m}$ is almost perpendicular to the average field $\overline{\boldsymbol{h}}_{-}$and the magnitude is much greater than $\overline{\boldsymbol{h}}_{-}$hence the main contribution of $\boldsymbol{h}_{-}^{m}$ comes from the demagnetization field generated by magnetization $\boldsymbol{m}$ (Figure 7.4b).


Figure 7.5 Amplitude and phase of internal field $h_{-}^{m}$ and magnetization $m$ as a function of frequency. Both $h_{-}^{m}$ and $m$ are normalized by $\bar{h}_{-}$.

It follows from Figure 7.4 that the orientation and magnitude of the magnetization $\boldsymbol{m}$ strongly depends on the frequency of the microwave. Since microwave is circularly polarized, the orientations of internal field $\boldsymbol{h}_{-}^{m}$ and magnetization $\boldsymbol{m}$ with respect to $\overline{\boldsymbol{h}}_{-}$actually corresponds to the phase shift with respect to $\overline{\boldsymbol{h}}_{\boldsymbol{-}}$.

The amplitude and phase of the magnetic field $\boldsymbol{h}_{-}^{m}$ and the magnetization $\boldsymbol{m}$ of the nanoparticle for the minus-waves from 1 to 25 GHz are shown in Figure 7.5. The phase of magnetization is always negative because it is induced by the magnetic field $\overline{\boldsymbol{h}}_{-}$and
there will always be a phase lag. When the frequency of EM wave is low $\left(\omega \ll \omega_{r}\right)$, the phase of magnetization approaches 0 meaning that the magnetization rotates in phase with the field. In the other limit $\left(\omega \gg \omega_{r}\right)$, the phase approaches $-\pi$ meaning that magnetization $\boldsymbol{m}$ is always antiparallel to the average field $\overline{\boldsymbol{h}}_{\boldsymbol{-}}$.

In both limits, the amplitude of the magnetic moment is very small indicating that the precession shown in Figure 7.1 is very weak. This precession becomes rigorous and significantly changes the amplitudes of the field when the frequency hits the solution of eq.(7.15). In our case $\omega_{\mathrm{c}} / 2 \pi=16 \mathrm{GHz}$. At this point, magnetization $\boldsymbol{m}$ becomes almost perpendicular to the field $\overline{\boldsymbol{h}}_{\mathrm{*}}$, in other words the phase shift is 1.68 . The magnetic field inside the nanoparticle also maximize at the same frequency as magnetization as shown in Figure 7.4(b)

It is interesting to observe that close to the point $\omega_{\mathrm{r}} / 2 \pi(9.7 \mathrm{GHz}$ for this case), the amplitude of magnetic field attains a minimum corresponding to Figure 7.4(a). As discussed above, at this frequency, the demagnetization field is almost antiparallel to the average field $\overline{\boldsymbol{h}}_{-}$and magnetic field $\overline{\boldsymbol{h}}_{-}$is strongly shielded.

### 7.2.4 Two resonance frequencies

When we discussed the behavior of a single domain nanoparticle, the two resonance frequencies $\omega_{\mathrm{r}}$ and $\omega_{\mathrm{c}}$ were introduced. The natural precession frequency of the magnetization in the given material, $\omega_{\mathrm{r}}$ appears to be different from the resonance frequency $\omega_{\mathrm{c}}$ of a single domain nanoparticle embedded in a nonmagnetic matrix. The second resonance is a result of the negativity of the permeability of the nanoparticle and
is due to the interaction of ferromagnetic material with the host. When the inclusions are spherical nanoparticles, the relation between the two frequencies can be found by substituting eq.(7.8) into eq.(7.15):

$$
\begin{equation*}
\omega_{\mathrm{c}}=\omega_{\mathrm{r}}+\gamma \mu_{0} M / 3 \tag{7.16}
\end{equation*}
$$

This relation can be put in terms of the demagnetization field $\boldsymbol{H}_{\mathrm{d}}$. For a spherical nanoparticle $\boldsymbol{H}_{\mathrm{d}}=-\boldsymbol{M} / 3$. Based on eqs.(7.2) and (7.6), the natural precession frequency $\omega_{\mathrm{r}}$ can be written as $\omega_{\mathrm{r}}=\gamma \mu_{0} H_{\mathrm{s}}=\gamma \mu_{0}\left(H_{\mathrm{in}}+H_{\mathrm{a}}-M / 3\right)$. Using eq.(7.16), the resonance frequency $\omega_{\mathrm{c}}$ for an embedded nanoparticle is obtained as $\omega_{\mathrm{c}}=\omega_{\mathrm{r}}+\gamma \mu_{0} M / 3=\gamma \mu_{0}\left(H_{\mathrm{in}}+H_{\mathrm{a}}\right)$ and it is independent of the demagnetization field $H_{\mathrm{d}}$. As illustrated in Figure 7.1, for a composite film, the magnetic field inside the film $\boldsymbol{H}_{\text {in }}$ is related to the external magnetic field $\boldsymbol{H}_{\mathrm{ex}}$ as: $\boldsymbol{H}_{\mathrm{in}}=\boldsymbol{H}_{\mathrm{ex}}-\boldsymbol{\boldsymbol { M }} \boldsymbol{M}$. Therefore, the resonance frequency for an embedded nanoparticle can be tuned by varying the external magnetic field $\boldsymbol{H}_{\mathrm{ex}}$, the volume concentration of nanoparticle $\chi$, or by choosing materials with different magnetization $M$ and effective anisotropic field $H_{\mathrm{a}}$. Table 7.1 lists three different materials and they show resonance in different frequency range. All the materials are with uniaxial magnetocrystalline anisotropy. The external field $\mu_{0} H_{\mathrm{ex}}=0 \mathrm{~T}$, volume concentration $\chi=0$ (for single nanoparticle) and gyromagnetic ratio $\gamma=2 \times 10^{11}(\mathrm{rad} / \mathrm{T} / \mathrm{s})$ are the same for all cases.

Table 7.1 Room temperature properties of different materials.

| Material | $\mathrm{BaO} \cdot 6 \mathrm{Fe}_{2} \mathrm{O}_{3}[29]$ | $\mathrm{Co}[29]$ | $\mathrm{YCo}_{5}[30]$ |
| :---: | :---: | :---: | :---: |
| Magnetization $M\left(\times 10^{5} \mathrm{~A} / \mathrm{m}\right)$ | 3.8 | 14.4 | 8.5 |
| Anisotropic coefficient $K_{1}\left(\times 10^{4} \mathrm{~J} / \mathrm{m}^{3}\right)[29]$ | 33 | 45 | 550 |
| Effective anisotropic field $\mu_{0} H_{\mathrm{a}}=2 K_{1} / M(\mathrm{~T})$ | 1.74 | 0.63 | 12.94 |
| Natural precession frequency $\omega_{\mathrm{r}} / 2 \pi(\mathrm{GHz})$ | 50.2 | 0.7 | 400.6 |
| Resonance frequency $\omega_{\mathrm{c}} / 2 \pi(\mathrm{GHz})$ | 55.3 | 19.9 | 411.9 |

An external magnetic field $\boldsymbol{H}_{\text {ex }}$ parallel to the magnetization $\boldsymbol{M}$ will increase the resonance frequency by $\gamma \mu_{0} H_{\mathrm{ex}} / 2 \pi$. It should also be noted that the effective anisotropic field $H_{\mathrm{a}}$ equals to the coercivity of a single domain nanoparticle (see Chapter 1). Therefore, one can also apply a magnetic field $\boldsymbol{H}_{\text {ex }}$ which is antiparallel to the magnetization $\boldsymbol{M}$ and smaller than the coercivity to decrease the resonance frequency by $\gamma \mu_{0} H_{\mathrm{ex}} / 2 \pi$.

### 7.3 Heating of a single domain nanoparticle

The heat produced by a single domain nanoparticle per unit time and per unit volume is interpreted as[11, 31]:

$$
\begin{gather*}
P=P_{h}+P_{E}  \tag{7.17}\\
P_{h}=\frac{\mu_{0}}{2} \operatorname{Im}\left(\mu^{m}\right) \omega\left|h_{ \pm}^{m}\right|^{2}, P_{E}=\frac{\varepsilon_{0}}{2} \operatorname{Im}\left(\varepsilon^{m}\right) \omega|E|^{2} \tag{7.18}
\end{gather*}
$$

where $\omega$ is the angular frequency of the microwave. $\varepsilon_{0}$ and $\mu_{0}$ are the permittivity and permeability of vacuum, respectively. $\varepsilon^{m}$ and $\mu^{m}$ are the relative permittivity and permeability of the magnetic nanoparticle. $E$ and $h_{ \pm}^{m}$ are the electric and magnetic field of
the microwave inside the nanoparticle. The heat production is attributed to both electric loss $P_{E}$ and magnetic loss $P_{h}$. Both losses have units of W $/ \mathrm{m}^{3}$.

Assume the nanoparticle is suspended in free space, the power of the microwave is $P_{0}=c_{0} \mu_{0} h_{0}^{2} / 2=c_{0} \varepsilon_{0} E_{0}^{2} / 2 . c_{0}$ is the speed of light in vacuum, $h_{0}$ and $E_{0}$ are the magnetic and electric fields of the microwave in the free space. $P_{0}$ has a unit of $\mathrm{W} / \mathrm{m}^{2}$. Assuming the radius of the spherical nanoparticle is $R$, we can normalize $P_{E}$ and $P_{h}$ as follows:

$$
\begin{equation*}
\frac{P_{h} R}{P_{0}}=\frac{\omega}{c_{0}} \operatorname{Im}\left(\mu^{m}\right)\left|\frac{h_{ \pm}^{m}}{h_{0}}\right|^{2}, \frac{P_{E} R}{P_{0}}=\frac{\omega}{c_{0}} \operatorname{Im}\left(\varepsilon^{m}\right)\left|\frac{E}{E_{0}}\right|^{2} \tag{7.19}
\end{equation*}
$$



Figure 7.6 Heat production rate for a single domain cobalt nanoparticle (a) in the vicinity of natural precession frequency $\omega_{\mathrm{r}} / 2 \pi(\mathrm{~b})$ in the vicinity of the resonance frequency $\omega_{\mathrm{c}} / 2 \pi$

We first study the magnetic loss. The relative permeability $\mu^{m}=\mu \pm g$ is interpreted by eq.(7.8). Since the imaginary part of $\mu^{m}$ for the plus-wave is almost zero (Figure 7.3), only minus-wave will induce the magnetic loss. The magnetic field $h_{ \pm}^{m}$ of microwave inside the nanoparticle is determined by eq.(7.14). For a cobalt nanoparticle, we estimate the heat production rate $P_{h} R / P_{0}$ induced by the minus-wave in the vicinity of
the two frequencies $\omega_{\mathrm{r}} / 2 \pi=0.7 \mathrm{GHz}$ and $\omega_{\mathrm{c}} / 2 \pi=19.9 \mathrm{GHz}$ (Table 7.1). Figure 7.6 illustrates that, at the resonance frequency $\omega_{\mathrm{c}} / 2 \pi$, the heat production rate reaches a maximum. At this frequency, the magnetic field $h_{-}^{m}$ inside the nanoparticle is significantly enhanced (Figure 7.4(b)). No peak can be observed in the vicinity of the natural precession frequency $\omega_{\mathrm{r}} / 2 \pi$ because the internal magnetic field $h_{-}^{m}$ is almost zero at this frequency (Figure 7.4(a)).

The electric loss is negligibly small compared to the magnetic loss in the vicinity of the resonance frequency $\omega_{\mathrm{c}} / 2 \pi$. This statement can be justified using the following argument. The electric field $E$ inside the nanoparticle can be found by solving an electrostatic problem. The result takes a similar form as eq.(7.14):

$$
\begin{equation*}
E=\frac{3 \varepsilon^{l}}{2 \varepsilon^{l}+\varepsilon^{m}} E_{0} \tag{7.20}
\end{equation*}
$$

where $\varepsilon^{l}$ is the relative permittivity for the host material and $E_{0}$ is the electric field of the microwave far from the particle. For a cobalt nanoparticle, the electric permittivity $\varepsilon^{m}$ in the GHz range satisfies the relation $\left|\varepsilon^{m}\right| \gg \varepsilon^{l}$. Hence the electric field inside the nanoparticle is diminished $\left(\left|E / E_{0}\right| \ll 1\right)$. As a result, the electric loss is negligibly small.

Using the heat production rate, we can also calculate the heating rate $(\mathrm{K} / \mathrm{s})$ of a single domain nanoparticle. Consider only magnetic loss $P_{h}$, the heat produced by a cobalt nanoparticle per unit time is $P_{h} V$, where $V$ is the volume of the nanoparticle. The heating rate $K_{\mathrm{T}}$ can be calculated as: $K_{\mathrm{T}}=P_{h} V / C_{\mathrm{v}} V=P_{h} / C_{\mathrm{v}}$, where $C_{\mathrm{v}}$ is the heat capacity at constant volume. For cobalt, $C_{\mathrm{v}}=3.75 \times 10^{6} \mathrm{~J} / \mathrm{m}^{3} / \mathrm{K}$. Using eq.(7.18), the heating rate can be written as:

$$
\begin{equation*}
K_{\mathrm{T}}=\frac{P_{h}}{C_{\mathrm{v}}}=\frac{\mu_{0}}{2 C_{\mathrm{v}}} \operatorname{Im}\left(\mu^{m}\right) \omega\left|h_{ \pm}^{m}\right|^{2} \tag{7.21}
\end{equation*}
$$

$h_{ \pm}^{m}$ is related to $h_{0}$ through eq. (7.14) and $h_{0}$ is related to $P_{0}$ as $P_{0}=c_{0} \mu_{0} h_{0}^{2} / 2$. As a result, considering a linear polarized microwave which is composed of equal amount of minuswave and plus-wave, the heating rate can be interpreted in terms of $P_{0}$ as:

$$
\begin{equation*}
K_{\mathrm{T}}=\frac{\omega P_{0}}{2 c_{0} C_{\mathrm{v}}} \operatorname{Im}\left(\mu^{m}\right)\left|\frac{3}{2+\mu^{m}}\right|^{2} \tag{7.22}
\end{equation*}
$$

Take $P_{0}=1 \mathrm{~kW} / \mathrm{m}^{2}$, which is about the power of sunlight. The heating rate of a single domain nanoparticle at the resonance frequency $\omega_{\mathrm{c}} / 2 \pi(19.9 \mathrm{GHz})$ is estimated as $3.2 \mathrm{~K} / \mathrm{s}$, which is extremely high. It is also interesting that, the heating rate of a nanoparticle is independent on the particle size as far as the particle is still single domain. Cobalt nanoparticles are ideal candidates for the applications requiring fast heating of sensitive spots.

### 7.4 Conclusions

In this chapter, we study the property of a composite film containing single domain ferromagnetic nanoparticles.

First, The Landau-Lifshitz-Gilbert equation was employed to derive the constitutive equation of magnetic induction $\boldsymbol{B}$ and calculate the magnetic permeability for individual nanoparticle. Circular polarized waves are introduced to linearize the constitutive equation. The resonance only appears for minus-wave (right-handed) and the resonance frequency of the nanoparticle is found to be equal to the natural precession
frequency of the magnetization vector $\boldsymbol{M}$. This frequency is proportional to the total internal static magnetic field $H_{\mathrm{s}}: \omega_{\mathrm{r}}=\gamma \mu_{0} H_{\mathrm{s}}=\gamma \mu_{0}\left(H_{\mathrm{ex}}-\chi M+H_{\mathrm{a}}+H_{\mathrm{d}}\right)$.

Then, using the quasi-static approximation, we find the magnetic field ( $h$ component of the EM wave) distribution in the vicinity of the nanoparticle. It appears that the magnetic field inside the nanoparticle is significant enhanced at the resonance frequency $\omega_{c}$ which is different from the natural precession frequency $\omega_{\mathrm{r}}$. For a spherical nanoparticle, these two resonance frequencies have a relation: $\omega_{\mathrm{c}}=\omega_{\mathrm{r}}+\gamma \mu_{0} M / 3$. The resonance frequency $\omega_{\mathrm{c}}$ is found to be independent of the demagnetization field $H_{\mathrm{d}}=-M / 3$ i.e. $\omega_{\mathrm{c}}=\gamma \mu_{0}\left(H_{\mathrm{ex}}-\chi M+H_{\mathrm{a}}\right)$.

At last, we study the heating of a single domain nanoparticle. Heat production is attributed to the magnetic loss induced by minus-wave. The resonance only shows up at the frequency $\omega_{\mathrm{c}}$. The heating rate of a single domain cobalt nanoparticle is estimated as high as $3.2 \mathrm{~K} / \mathrm{s}$.

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## CHAPTER VIII

## INTERACTION OF MICROWAVES WITH COMPOSITE FILMS CONTAINING FERROMAGNETIC NANOPARTICLES

In the previous chapter, we studied the ferromagnetic resonance for a single domain nanoparticle and analyzed the heating properties of the particle. In many applications, one has to deal with the composite film containing ferromagnetic nanoparticles. To do that, one has to obtain the effective permittivity and permeability for the composite. In this chapter, we will derive the effective permittivity and permeability of the composite film and discuss the film behavior under the microwave irradiation. Reflection, transmission, absorption, and Faraday effects will be inferred.

### 8.1 Effective permeability and permittivity of nanocomposites

### 8.1.1 Effective permeability

Before derivation of the constitutive equation for the nanocomposite, we note that the magnetic induction in the host non-magnetic material outside the nanoparticles depends on the magnetic field as $\boldsymbol{b}_{ \pm}(\vec{r})=\mu_{0} \boldsymbol{h}_{ \pm}(\vec{r})$. Therefore, we can write the following formula for the difference between the average magnetic induction $\overline{\boldsymbol{b}}_{ \pm}=(1 / V) \int \boldsymbol{b}_{ \pm}(\vec{r}) \mathrm{d} V$ and magnetic field $\overline{\boldsymbol{h}}_{ \pm}=(1 / V) \int \boldsymbol{h}_{ \pm}(\vec{r}) \mathrm{d} V[1]:$

$$
\begin{equation*}
\overline{\boldsymbol{b}}_{ \pm}-\mu_{0} \overline{\boldsymbol{h}}_{ \pm}=\frac{1}{V} \int_{V}\left[\boldsymbol{b}_{ \pm}(\vec{r})-\mu_{0} \boldsymbol{h}_{ \pm}(\vec{r})\right] \mathrm{d} r^{3}=\frac{N}{V} \int_{V_{0}}\left[\boldsymbol{b}_{ \pm}(\vec{r})-\mu_{0} \boldsymbol{h}_{ \pm}(\vec{r})\right] \mathrm{d} r^{3} \tag{8.1}
\end{equation*}
$$

where $V$ is the volume of the sample, $V_{0}$ is the volume of a single nanoparticle, and $N$ is the number of embedded nanoparticles. When the distance between nanoparticles is large enough to neglect their interactions, one can use the solution of magnetostatic problem for a single nanoparticle and plug this solution into the right hand side of Eq. (1.1). As discussed in the chapter VII, magnetic field inside the nanoparticle $\boldsymbol{h}_{ \pm}$is uniform and is related to $\overline{\boldsymbol{h}}_{ \pm}$as:

$$
\begin{equation*}
\boldsymbol{h}_{ \pm}=\frac{3}{2+[\mu(\omega) \mp g(\omega)]} \overline{\boldsymbol{h}}_{ \pm} \tag{8.2}
\end{equation*}
$$

The induced magnetization of the nanoparticle will be:

$$
\begin{equation*}
\boldsymbol{m}_{ \pm}=3 \frac{[\mu(\omega) \mp g(\omega)]-1}{2+[\mu(\omega) \mp g(\omega)]} \overline{\boldsymbol{h}}_{ \pm} . \tag{8.3}
\end{equation*}
$$

Therefore, inside the nanoparticle, the magnetic induction is constant $\boldsymbol{b}_{ \pm}(\vec{r})=\mu_{0}\left[\boldsymbol{h}_{ \pm}(\vec{r})+\boldsymbol{h}_{ \pm}(\vec{r})\right]$. Based on these formulas, the integral in the right hand side of eq.(8.1) can be taken analytically. The result is written through the effective permeability $\mu_{ \pm}^{\text {eff }}$ for the left- and right-handed circularly polarized waves as

$$
\begin{equation*}
\overline{\boldsymbol{b}}_{ \pm}=\mu_{0} \mu_{ \pm}^{\text {eff }} \overline{\boldsymbol{h}}_{ \pm} \quad \mu_{ \pm}^{\text {eff }}=1+3 \chi \frac{(\mu \mp g)-1}{2+(\mu \mp g)}, \tag{8.4}
\end{equation*}
$$

where $\chi=N V_{o} / V$ is the volume fraction of ferromagnetic nanoparticles in the sample. Eq.(8.4) can be also written in a vector form as

$$
\begin{equation*}
\overline{\boldsymbol{b}}=\mu_{0}\left(\mu_{+}^{\mathrm{eff}}+\mu_{-}^{\mathrm{eff}}\right) \overline{\boldsymbol{h}}+i \mu_{0}\left(\mu_{+}^{\mathrm{eff}}-\mu_{-}^{\mathrm{eff}}\right)(\overline{\boldsymbol{h}} \times \hat{z}) . \tag{8.5}
\end{equation*}
$$



Figure 8.1 Effective permeability of composite containing $1 \%$ cobalt nanoparticles. The external magnetic field $\mu_{0} H_{\mathrm{ex}}=0 \mathrm{~T}$. The damping coefficient $\alpha$ is 0.01 .

Figure 8.1 shows the effective permeability of the composites containing $1 \%$ cobalt nanoparticles. The real part of the effective permeability of the plus-wave mostly inherits the magnetic properties of the non-magnetic host material and thus close to one. The imaginary part is almost zero $\left(10^{-5}\right)$, hence the material is almost transparent to such a circular polarization. The real part of the effective permeability for the minus-wave demonstrates a resonance behavior. For this wave, the imaginary part of effective permeability reaches its maximum at the resonance frequency $\omega_{c} / 2 \pi$ corresponding to an absorption peak of the microwave irradiation.

As shown in the previous chapter, the resonance frequency $\omega_{c}$ depends on the field: $\omega_{\mathrm{c}}=\gamma \mu_{0}\left(H_{\mathrm{ex}}-\chi M+H_{\mathrm{a}}\right)$, where $H_{\mathrm{ex}}$ is the external magnetic field, $M$ is the magnetization of the nanoparticle and $H_{\mathrm{a}}$ is the effective field of crystalline anisotropy. It follows that the resonance frequency $\omega_{\mathrm{c}}$ depends linearly on the volume concentration $\chi$.


Figure 8.2 Effective permeability of the composite film containing different concentrations of cobalt nanoparticles ( $\chi=0.5 \%, 1 \%, 3 \%$ ) (a) Real part (b) Imaginary part.

Figure 8.2 illustrates how the magnetic permeability of the composite film varies as the concentration of cobalt nanoparticles changes. As the concentration increases, the resonance frequency $\omega_{c}$ shifts to the lower frequency and the peak values increase as well. The permeability dependence on concentration is not linear, though.

### 8.1.2 Effective permittivity

The effective permittivity can be calculated in a similar way [1]. Using the effective medium theory for composites containing spherical nanoparticles, we obtain[1]:

$$
\begin{equation*}
\varepsilon^{\mathrm{eff}}=\varepsilon^{l}+3 \chi \frac{\varepsilon^{m}-\varepsilon^{l}}{2 \varepsilon^{l}+\varepsilon^{m}} \tag{8.6}
\end{equation*}
$$

where $\varepsilon^{l}$ is the relative permittivity of the host material and $\varepsilon^{m}$ is the relative permittivity of the nanoparticle. The volume concentration $\chi$ is assumed small, $\chi \ll 1$. In calculations, we consider paraffin as the host material $\left(\varepsilon^{l}=2.2\right)$.

If the nanoparticles are made of oxides $\left(\mathrm{Fe}_{2} \mathrm{O}_{3}, \mathrm{Fe}_{3} \mathrm{O}_{4}\right.$, etc. $), \varepsilon^{m}$ is positive and comparable with the $\varepsilon^{l}$ in the microwave frequency range $[2,3]$, therefore the second term
in eq. (1.6) is always less than one, $\left|\left(\varepsilon^{m}-\varepsilon^{l}\right) /\left(2 \varepsilon^{l}+\varepsilon^{m}\right)\right|<1, \chi \ll 1$, hence $\varepsilon^{\text {eff }}$ is approximately equal to $\varepsilon$.

If the nanoparticles are metals or metal alloys such as $\mathrm{Ni}, \mathrm{Co}, \mathrm{YCo}_{5}, \mathrm{FeCo}$, etc., their permittivity $\varepsilon^{m}$ is negative and the relation $\left|\varepsilon^{m}\right| \gg \varepsilon^{l}$ holds true in the microwave frequency range $[2,3]$. Again, the second term in eq. (1.6) can be dropped again, $\varepsilon^{\text {eff }} \cong \varepsilon^{l}$, because the factor $\left(\varepsilon^{m}-\varepsilon^{l}\right) /\left(2 \varepsilon^{l}+\varepsilon^{m}\right) \cong 1$ and the volume fraction of nanoparticles is small.

As a result, in the weakly loaded magnetic composites, the effective permittivity remains non-perturbed and equal to the permittivity of the host material $\varepsilon^{\text {eff }} \cong \varepsilon^{l}$. Moreover, the effective permittivities for the plus- and minus-waves are assumed same.

### 8.2 Reflection, transmission, and absorption by the composite film

### 8.2.1 Reflection and transmission

To study the interaction between the microwave and composite film, we only consider the normal incidence of the microwave. The external magnetic field $\boldsymbol{H}_{\mathrm{ex}}$ is assumed parallel to the wave vector of the incident microwave as shown in Figure 8.3. For a thin composite film containing ferromagnetic nanoparticles, the magnetic field inside the composite film $\boldsymbol{H}_{\text {in }}$ is equal to $\boldsymbol{H}_{\mathrm{in}}=\boldsymbol{H}_{\mathrm{ex}}-\boldsymbol{\chi} \boldsymbol{M}$, where $\boldsymbol{M}$ is the magnetization of the nanoparticle and $\chi$ is the volume fraction of nanoparticles.


Figure 8.3 Schematic of a thin composite film under the microwave radiation. Only normal incidence is considered.

The reflection and transmission coefficients are calculated by matching the tangential components of electric and magnetic fields at the two boundaries $z=0$ and $z=$ $d$ as shown in Figure $8.3[1,4,5]$. At the boundary $z=0$, the two resulting equations are:

$$
\left\{\begin{array}{l}
E_{0}-E_{4}=E_{1}-E_{2} \exp \left(-i k_{1} d\right)  \tag{8.7}\\
\sqrt{\varepsilon_{0} / \mu_{0}} E_{0}+\sqrt{\varepsilon_{0} / \mu_{0}} E_{4}=\sqrt{\varepsilon_{1} / \mu_{1}} E_{1}+\sqrt{\varepsilon_{1} / \mu_{1}} E_{2} \exp \left(-i k_{1} d\right)
\end{array}\right.
$$

At the boundary $z=d$, the two resulting equations are:

$$
\left\{\begin{array}{l}
E_{1} \exp \left(-i k_{1} d\right)-E_{2}=E_{3}  \tag{8.8}\\
\sqrt{\varepsilon_{1} / \mu_{1}} E_{1} \exp \left(-i k_{1} d\right)+\sqrt{\varepsilon_{1} / \mu_{1}} E_{2}=\sqrt{\varepsilon_{0} / \mu_{0}} E_{3}
\end{array}\right.
$$

The relation $h=(\varepsilon / \mu)^{1 / 2} E$ is used to replace the magnetic field with the electric field. In eqs.(8.7) and (8.8), $d$ is the thickness of the nanocomposite film; $\boldsymbol{E}_{0}$ and $\boldsymbol{h}_{0}$ are the amplitudes of electric and magnetic fields for the incident microwave; $\boldsymbol{E}_{3}, \boldsymbol{h}_{3}$ are that of the transmitted wave and $\boldsymbol{E}_{4}, \boldsymbol{h}_{4}$ correspond to the reflected wave. Two waves $\boldsymbol{E}_{1}, \boldsymbol{h}_{1}$ and $\boldsymbol{E}_{2}, \boldsymbol{h}_{2}$ travel inside the thin film in the opposite directions. The wave vector for vacuum, $\boldsymbol{k}_{0}=\omega \sqrt{\varepsilon_{0} \mu_{0}} \hat{z}$ and for the nanocomposites $\boldsymbol{k}_{1}=\omega \sqrt{\varepsilon_{1} \mu_{1}} \hat{z}$ depend on the
permittivity $\varepsilon_{0}$ and permeability $\mu_{0}$ of vacuum and on the effective permittivity $\varepsilon_{1}=\varepsilon_{0} \varepsilon^{\text {eff }}$ and permeability $\mu_{1}=\mu_{0} \mu^{\text {eff }}$ of the nanocomposite. The waves are considered circularly polarized. Solving eqs.(8.7) and (8.8) [1,5] one obtains the transmission $T$ and reflection $R$ coefficients:

$$
\begin{align*}
& \left\{\begin{array}{l}
T=\frac{E_{3}}{E_{0}} \exp \left(-i k_{0} d\right)=-\frac{4 \exp \left(-i k_{1} d\right) Z_{1} Z_{0}}{\left(Z_{1}-Z_{0}\right)^{2} \exp \left(-2 i k_{1} d\right)-\left(Z_{1}+Z_{0}\right)^{2}} \\
R=\frac{E_{4}}{E_{0}}=\frac{\left(Z_{1}^{2}-Z_{0}^{2}\right) \exp \left(-2 i k_{1} d\right)-\left(Z_{1}^{2}-Z_{0}^{2}\right)}{\left(Z_{1}-Z_{0}\right)^{2} \exp \left(-2 i k_{1} d\right)-\left(Z_{1}+Z_{0}\right)^{2}}
\end{array}\right.  \tag{8.9}\\
& Z_{0}=\sqrt{\frac{\mu_{0}}{\varepsilon_{0}}}, Z_{1}=\sqrt{\frac{\mu_{1}}{\varepsilon_{1}}}
\end{align*}
$$

$Z_{0}$ and $Z_{1}$ are the wave impedance in vacuum and nanocomposite, respectively. Using eq.(8.9), one can calculate the ratio of transmitted $\left(|T|^{2}\right)$ and reflected $\left(|R|^{2}\right)$ energy to the incident energy.

As an illustration, we examine the 1 mm thick composite film without any bias DC external magnetic field, $\mu_{0} H_{\mathrm{ex}}=0 \mathrm{~T}$. As the magnetic fillers, we consider cobalt nanoparticles. Different volume fractions of nanoparticles are examined: $\chi=3 \%, 1 \%$ and $0.5 \%$. The damping coefficient $\alpha$ is set to be $\alpha=0.01$. In Figure 8.4, we calculated the energetic coefficients of transmission and reflection for the minus- and plus-waves. It follows that the absorption resonance shows up only for the minus wave.

For the plus-wave, the relation $|R|^{2}+|T|^{2} \cong 1$ holds true implying that the EM energy is almost conserved and just a minute amount of energy dissipates in the nanocomposite film. This results follows from the fact that the nanocomposite has almost zero imaginary part of the permeability (Figure 8.1(b)). The main dissipation comes from the reflection $\left(|R|^{2}\right)$ by the composite film. As shown by eq. (8.9), the reflection coefficient is mainly
determined by the mismatch of the wave impedance between the composite film $\left(Z_{1}\right)$ and air $\left(Z_{0}\right)$ through the term $\left|\left(Z_{1}-Z_{0}\right) /\left(Z_{1}+Z_{0}\right)\right|=\left|1-2 Z_{0} /\left(Z_{1}+Z_{0}\right)\right|$. The smaller this term is, the smaller amount of energy would be taken away with the back bouncing waves.

For the plus-wave, the permittivity is almost constant, $\varepsilon^{\text {eff }}=2.2$, while the effective permeability goes to one, $\mu^{\text {eff } \cong 1 ~(F i g u r e ~} 8.1(\mathrm{~b})$ ). Therefore, for the plus-wave, the wave impedance in nanocomposite $Z_{1}=\left(\mu^{\text {eff }} / \varepsilon^{\text {eff }}\right)^{1 / 2} Z_{0}$ is always smaller than that in vacuum, $Z_{1}$ $<Z_{0}$. Decreasing effective permeability $\mu^{\text {eff }}$ (Figure $8.1(\mathrm{~b})$ ), one increases the term |1$2 Z_{0} /\left(Z_{1}+Z_{0}\right) \mid$. This leads to even greater reflection (Figure $8.4(\mathrm{~d})$ ) and consequently, to a less energy transmission (Figure 8.4(b)).


Figure 8.4 Coefficients of the energy transmission, $|T|^{2}$ and reflection $|R|^{2}$ in composite films containing cobalt nanoparticles with the volume fractions with the volume fraction $\chi=0.03,0.01$ and 0.005 , no external magnetic field, $\mu_{0} H_{\mathrm{ex}}=0 \mathrm{~T}$, damping coefficient $\alpha=0.01$, film thickness $d=1 \mathrm{~mm}$. (a) Transmission coefficient for the minus-wave (b) Transmission coefficient for the
plus-wave (c) Reflection coefficient for the minus-wave (d) Reflection coefficient for the pluswave.

The transmission coefficient of the minus-wave has a characteristic minimum (Figure 8.4(a)). It is attributed to the resonance of the imaginary part of the permeability (Figure 8.1(a)). The critical frequencies at the minimum transmission for the $\chi=3 \%, 1 \%$ and $0.5 \%$ composite films are $\omega_{\mathrm{c}} / 2 \pi=18.2 \mathrm{GHz}, 19.3 \mathrm{GHz}, 19.6 \mathrm{GHz}$, respectively. These frequencies equal to the corresponding peak frequencies of the imaginary part of effective permeability for minus-wave. For a 1 mm thick film containing $\chi=3 \%$ cobalt nanoparticles, less than $10 \%$ energy of the 18.2 GHz minus-wave is transmitted while almost all the energy of the plus-wave is transmitted. This significant circular dichroism makes the composite film a good candidate for the microwave filtering application where the right-handed minus-wave can be almost completely eliminated.

The dispersion of the reflection coefficient of the minus-wave has both minimum and maximum. As discussed above, the reflection is mainly determined by the term $\mid\left(Z_{1^{-}}\right.$ $\left.Z_{0}\right) /\left(Z_{1}+Z_{0}\right)\left|=\left|1-2 Z_{0} /\left(Z_{1}+Z_{0}\right)\right|\right.$. For the minus wave in the vicinity of the resonance frequency $\omega_{\mathrm{c}} / 2 \pi$, the impedance $Z_{1}=\left(\mu^{\text {eff }} / \varepsilon^{\text {eff }}\right)^{1 / 2} Z_{0}$ varies significantly and is expected to experience both minimum and maximum according to Figure 8.1(a). Hence, the term |1$2 Z_{0} /\left(Z_{1}+Z_{0}\right) \mid$ should also reach both maximum (worst match, maximum reflection) and minimum (best match, minimum reflection) while the frequency is varied. The minimum reflections of $3 \%$ and $1 \%$ composites are very close to zero implying that the composite film might also be a good candidate for zero-reflection material.

For the reflection and transmission coefficients, the peak frequency shifts with the nanoparticle concentration. This shift is caused by the linear dependence of the internal field on concentration, $\omega_{\mathrm{c}} / 2 \pi=\gamma \mu_{0}\left(H_{\mathrm{ex}}-\chi M+H^{\mathrm{a}}\right) / 2 \pi$.

### 8.2.2 Absorption by the composite film

The energy gets lost not only because of the waves bouncing back from the film. A cirtain part of the energy dissipates in the form of heat. We introduce a dimensionless absorption coefficient

$$
\begin{equation*}
\eta=1-|T|^{2}-|R|^{2} \tag{8.10}
\end{equation*}
$$

measuring the energy absorbed by the film with respect to the incident energy. The same sample is examined.

Absorption of the minus- and plus-waves is shown in Figure 8.5(a) and (b), respectively. We introduced the ferromagnetic resonance as the phenomenon associated with the maximum absorption of the EM irradiation Therefore, as follows from Figure 8.5(a) and (b), the resonance can only be observed for the minus-wave. The absorption peak is about four orders of magnitude greater than the average absorption of the pluswave! Figure 8.5 (a) also indicates that absorption peak is stronger in the samples with a greater concentration of magnetic nanoparticles.


Figure 8.5 Microwave absorption by composite films containing cobalt nanoparticles with the volume fraction $\chi=0.03,0.01$ and 0.005 , external magnetic field $\mu_{0} H_{\mathrm{ex}}=0 \mathrm{~T}$, damping coefficient $\alpha=0.01$, film thickness $d=1 \mathrm{~mm}$.

The absorbed energy dissipates into heat. This dissipation is conveniently measured with respect to the power density of the incident wave, $P_{0}\left(\mathrm{~W} / \mathrm{m}^{2}\right)$. Assuming that half of the incident wave makes the circular polarized minus-wave, the heat produced per unit area for a composite film containing magnetic nanoparticles will be $P_{\mathrm{h}}=\eta P_{0} / 2$. If the heat capacity of the composite is $C_{\mathrm{v}}$ and the film thickness is $d$, the heat capacity per unit area of the composite film is $C_{\mathrm{v}} d$. The heating rate $K_{\mathrm{T}}$ of the sample will be:

$$
\begin{equation*}
K_{\mathrm{T}}=\frac{\eta P_{0}}{2 C_{\mathrm{v}} d} \tag{8.11}
\end{equation*}
$$

Take an EM wave with the power $P_{0}=1 \mathrm{~kW} / \mathrm{m}^{2}$ and consider it hitting a 1 mm paraffin film containing 3\% cobalt nanoparticles. The heat capacity of paraffin is $C_{\mathrm{v}}=2.8 \times 10^{6} \mathrm{~J} /\left(\mathrm{K} \cdot \mathrm{m}^{3}\right)$ and the $3 \%$ volume fraction does not change this value appreciably. The heating rate at the peak absorption $(18.1 \mathrm{GHz}, \eta=0.61)$ will be $K_{\mathrm{T}}=0.1 \mathrm{~K} / \mathrm{s}$ which is
about of the same order of magnitude as that of the heating rate of water in a conventional microwave oven.

### 8.3 Polarization Change (Faraday, Kerr effects)



Figure 8.6 Schematic of a linear polarized wave becoming an elliptically polarized wave
Figure 8.6 illustrates the polarization change of the EM wave after passing a composite film. Assume the incident wave is linearly polarized and consider it as the superposition of two identical circularly polarized waves rotating in the opposite directions (the plus- and minus-waves). Due to the circular birefringence shown in Figure 8.4, one would expect that the amplitude and phase of the two circularly polarized waves to change after passing the composite film. Therefore, the transmitted and reflected waves are no longer linear polarized waves. They become elliptically polarized instead.

Such a wave is characterized by two parameters: polarization angle $\theta$ and ellipticity $\tan \delta$. The angle $\theta$ is the angle formed by the major axis of the ellipse and the polarization direction of the linear polarized wave and the ellipticity $\tan \delta$ is the ratio of the minor to major axes of the ellipse. If the ellipticity goes to zero, the wave becomes
linearly polarized; when the ellipticity goes to 1 , the wave becomes circularly polarized. The effect of the polarization change of wave after passing the film is called the Faraday effects; in the case of reflected wave, this effect is called the Kerr effects.

The polarization angle and ellipticity can be defined using the transmission and reflection coefficients defined by eq.(8.9). These coefficients are the complex numbers and can be written in the following forms: $T_{ \pm}=\left|T_{ \pm}\right| \exp \left(i \varphi_{ \pm}\right), R_{ \pm}=\left|R_{ \pm}\right| \exp \left(i \psi_{ \pm}\right) .\left|T_{ \pm}\right|,\left|R_{ \pm}\right|$are the modulus and $\varphi_{ \pm}, \psi_{ \pm}$are the corresponding phases for the two circularly polarized waves. The polarization angle and ellipticity of the transmitted wave are calculated as [5]:

$$
\begin{gather*}
\theta=\frac{\varphi_{-}-\varphi_{+}}{2}  \tag{8.12}\\
\tan \delta=\frac{\left|T_{+}\right|-\left|T_{-}\right|}{\left|T_{+}\right|+\left|T_{-}\right|} \tag{8.13}
\end{gather*}
$$

For the reflected wave, the corresponding parameters are obtained by replacing $\varphi_{ \pm}$ with $\psi_{ \pm}$and $\left|T_{ \pm}\right|$with $\left|R_{ \pm}\right|$. The rotation angle $\theta$ is due to the phase difference between the two circularly polarized waves while the ellipticity is caused by the amplitude difference.


Figure 8.7 Polarization angle and ellipticity of the transmitted and reflected waves. Thickness of the layer $d=1 \mathrm{~mm}$, concentration of cobalt nanoparticles is $\chi=1 \%$.

Figure 8.7 illustrates both polarization angle and ellipticity of the transmitted and reflected waves. The composite film is 1 mm thick and contains $1 \%$ cobalt nanoparticles. It follows that the resonance appears at the same frequency $\omega_{\mathrm{c}} / 2 \pi$. When the bias external magnetic field is zero, a polarization changes strongly in the vicinity of the resonance frequency as for both types of waves, the transmitted and reflected waves. The signs of the polarization angle and ellipticity are defined in the following figure:


Figure 8.8 Definition of the signs of polarization angle and ellpiticity.
For the transmitted wave, the ellipticity is always positive indicating that the transmission coefficient for the plus wave is always greater than that for the minus wave, $\left|T_{+}\right|>\left|T_{-}\right|$, see eq.(8.13). This effect is caused by a significant absorption of the minus wave leading to the change of the amplitude of the transmitted wave: it is always smaller than that of the plus-wave (Figure 8.4). Since the absorption is mainly determined by the imaginary part of the permeability, the ellipticity shows a similar frequency dependence as the imaginary part of the permeability of the minus-wave (Figure 8.1(a) and Figure 8.7(a)).

On the other hand, the polarization angle changes its sign in the vicinity of the resonance frequency. As shown by eq.(8.12), the polarization angle is determined by the phases of the two circularly polarized waves. Since the phase is mainly determined by the real part of the permeability, one would expect the polarization angle to follow a similar
frequency dependence as the real part of the permeability of the minus-wave (Figure 8.1(a) and Figure 8.7(a)).

The reflected wave appears to be a "conjugate" case of the transmitted wave. The ellipticity changes its direction near the resonance and the polarization angle remains positive. As discussed in section 8.2.1, the reflection coefficient $R$ is determined by the term $\left(Z_{1}-Z_{0}\right) /\left(Z_{1}+Z_{0}\right)$. Since the amplitudes of the reflected waves are mainly determined by the real part of the permeability, the ellipticity is expected to follow the frequency dependence of the real part of this ratio. On the other hand, the phases of the reflected waves mainly depend on the imaginary part of this ratio. Indeed, if $Z_{1}$ is a real number, then the term $\left(Z_{1}-Z_{0}\right) /\left(Z_{1}+Z_{0}\right)$ will also be a real number. Consequently, there would not be any phase shift $\left(\psi_{+}=\psi_{-}=0\right)$. As a result, the polarization angle follows the behavior of the imaginary part of the ratio $\left(Z_{1}-Z_{0}\right) /\left(Z_{1}+Z_{0}\right)$.

We'll focus on studying the change of the polarization angle of transmitted wave. We consider a 22 GHz microwave propagating through a 1 mm thick composite film. The external magnetic field $\mu_{0} H_{\mathrm{ex}}$ is varied in the range from 0 T to 0.2 T .


Figure 8.9 The dependence of the polarization angle on the external magnetic field, $\mu_{0} H_{\mathrm{ex}}$. The inset shows the polarization angle as a function of concentration at a fixed external magnetic field $\mu_{0} H_{\mathrm{ex}}=0.1 \mathrm{~T}$.

Figure 8.9 illustrates the variation of the polarization angle as a function of external magnetic field containing different concentrations of nanoparticles. Unlike the conventional Faraday effects, for which the polarization angle is proportional to the external magnetic field, the composite film shows a nonlinear effect due to the ferromagnetic resonance. The polarization angle first increases and reaches the maximum. Then it starts to decrease rapidly, changes the sign at some point and reaches a negative minimum. At last, it starts to increase again but remains negative.

Such a variation of the polarization angle can be explained as follows. When the magnetic field is weak, the resonance frequency is less than 22 GHz . The 22 GHz frequency is positioned at the right tail of the dispersion curve for polarization angle shown in Figure 8.7(a). Therefore, the polarization angle is positive. As the magnetic field increases, the resonance frequency gradually increases and the two curves in Figure 8.7(a) gradually shift to the right. Such a variation is similar to the case that the resonance
frequency is fixed but the frequency of EM wave is gradually decreasing in Figure 8.7(a). Hence, the response of a wave at a fixed frequency with increasing magnetic field is similar to the case when the magnetic field is fixed (resonance frequency is fixed) and the frequency of the wave is decreasing. Following this argument, the polarization angle shown in Figure 8.9 can be obtained by reversing the frequency axis of Figure 8.7(a).

There is also an interesting dependence of the polarization angle on the concentration illustrated by the inset in Figure 8.9 where as an illustration we use the external magnetic field $\mu_{0} H_{\mathrm{ex}}=0.1 \mathrm{~T}$. When the concentration is low, the negative polarization angle decreases almost linearly with concentration. When the concentration is sufficiently high, the resonance shifts significantly and the angle starts to increase and at some point even changes the sign.

### 8.4 Conclusions

In this chapter, we studied interactions of a composite film with electro-magnetic waves.

First, the effective magnetic field and effective magnetic induction was introduced. Then, using the results from the previous chapter the effective permeability was derived. The permeability was found to have a strong dependence on the nanoparticle concentration. On the other hand, the effective permittivity was proved to be almost the same as that of the host material.

Next, using the effective permeability and permittivity, the transmission and reflection coefficients of a composite film were derived. A strong circular birefrigence was discovered. Only the minus-waves are subject to the resonances and the composite
film appears almost transparent for the plus-wave. Based on these calculations, the composite films are found to be good candidates for the potential applications as microwave filters, zero reflection materials, and microwave heating materials.

At last, the polarization change of the EM wave was studied. A linear polarized wave became an elliptically polarized after interacting with the nanocomposite film. The resonances were present for polarization angle $\theta$ and ellipticity $\tan \delta$ for both transmitted and reflected waves. The polarization angle of the transmitted wave follows the frequency dependence of the real part of permeability; the ellipticity follows the dependence of the imaginary part of permeability. The reflected wave is a "conjuagate" case of the transmitted wave (polarization angle: imaginary part, ellipticity: real part). The polarization angle of the transmitted wave was also shown to have a strong but nonlinear dependence on the external magnetic field due to the resonance. In the limit of low concentration, the angle has an almost linear dependence on the concentration of nanoparticles. But the concentration induced resonance shift will be the dominant effect when the concentration is sufficiently high.

### 8.5 References

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