Surface Effect Of Ferromagnetic Nanoparticles On Transition Between Single- And Multi-Domain Structure Or Between Single-Domain Structure And Superparamagnetic Phase

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SURFACE EFFECT OF FERROMAGNETIC NANOPARTICLES ON TRANSITION BETWEEN SINGLE- AND MULTI-DOMAIN STRUCTURE OR BETWEEN SINGLE-DOMAIN STRUCTURE AND SUPERPARAMAGNETIC PHASE

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

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Surface effects on critical dimensions of ferromagnetic nanoparticles were studied. Algebraic equations were derived and numerically solved for critical radius $R_{c2}$ of ferromagnetic nanoparticles describing the transition between single- and multi-domain magnetic structure. Results were analyzed to illustrate the effect of surface parameters related to saturation magnetization $\alpha$, exchange interaction $\beta$, and anisotropy $K_S$ on the critical radius of nanoparticles with a core value of anisotropy $K_V$. Available experimental data for MnBi, FePt, and CoPt or for Fe nanoparticles were used as examples of nanoparticles with high and low values of $K_V$, respectively. Our studies clearly show that discrepancies existing between theoretical and experimental values for $R_{c2}$ could be explained readily by modification of magnetic surface parameters.

The equation for lower critical radius $R_{c1}$ from a single domain structure to superparamagnetic phase has been derived to study the effect of the surface parameter $K_S$ on its critical radius. This equation for $R_{c1}$ was solved analytically and numerically for high and low core anisotropy $K_V$ in magnetic nanoparticles. The results were examined for Fe as an example of low $K_V$ magnetic nanoparticles, and for MnBi, FePt, and CoPt as examples of strong $K_V$ nanoparticles. Discrepancies between theoretical results for $R_{c1}$ and available experimental data again can be explained by changes of magnetic properties of nanoparticles near their surface.
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DEDICATION

I lovingly dedicate my dissertation work to my parents, Mr. Ahmed Adawi and Mrs. Halima Ibrahim, and to my spouse, Qasem Adawi, who have given me so much love and support. There are not enough words in the world to express my gratitude to them, but without each of them, I would not be the person I am still and still working on becoming.
I. INTRODUCTION

Nanoscience is one of the most important research fields in modern science. It allows engineers, scientists, and physicians, for example, to work at the cellular and molecular levels with the intent to provide a significant improvement in life span and health of humans. Major role from materials point of view, as far as nanoscience is concerned, has been played by many types of nanoparticles which are referred to the materials having dimensions between 0.1 nm and a few hundred nanometers (nm), and usually containing from several hundred to $10^5$ atoms [1]. Among them, specially, magnetic nanoparticles are those nanoparticles that show a response to ac and dc external applied magnetic field and because of this response, magnetic nanoparticles are widely used in medicine (hyperthermia, drug delivery, and so on). Due to the unique size and physicochemical properties, the use of nanoparticles also offers major advantages in other areas of research such as electronics (transistors) and chemistry (catalysts). As the size of the nanoparticle decreases, the ratio of surface to volume of the nanoparticle increases. The large surface to volume ratio of nanoparticles is the key factor to novel studies of physical, chemical, and mechanical properties compared to those of corresponding bulk materials. Recently, much attention has been paid to different methods of magnetic nanoparticles synthesis due to widespread applications of magnetic nanoparticles in biomedical, biotechnology, engineering, material science, and environmental areas. In this paper, we shed the light on the properties of magnetic nanoparticles, which appear significantly different from the bulk. Some of the magnetic properties can be greater or smaller in nanomaterials than in the bulk materials. For instance, saturation magnetization $M_S$ of the magnetic nanoparticles with its quantized character increases at low temperatures whereas the $M_S$ drop at ambient temperatures [2-6] in comparison to bulk $M_S$. Coercivity $H_C$ of nanograin materials increases [7-9], whereas for free standing
nanograin $H_C$ drops [10]. Curie temperature $T_C$ of nanoparticles drops hundreds of degrees with their dimensions in comparison to the bulk material [11-13]. Tuning these properties will allow scientists to modify dimension of nanoparticles for different application resulting in increase of their effectiveness.

**GOALS OF MY THESIS**

The main goal of my Thesis is to understand how surface layer affects the critical dimensions of magnetic nanoparticles. First, an equation for the critical radius describing transition between single-domain and multi-domain structure of the magnetic nanoparticles is theoretically derived for low and high anisotropy. Secondly, an effect of surface layer on the theoretically derived critical radius of magnetic nanoparticles for the transition between single-domain structure and superparamagnetic phase is studied and thirdly these critical radii are compared and discussed in context of the existing, in the literature, experimental data.

**CHAPTERS SUMMARY**

Chapter I (Introduction) outlines a role of magnetic nanoparticles in nanoscience. The goal of my study is stated and Thesis contents in this chapter are summarized.

Chapter II (Magnetism) reviews the fundamental concepts of magnetism with a focus on different types of magnetic materials and their responses to applied magnetic field.

Chapter III (Magnetic Domains) explains the process of formation of the magnetic domain structures including $180^\circ$ magnetic domain Bloch wall.

Chapter IV (Magnetic Materials) reviews the process of magnetization (hysteresis curve including remnant magnetization $M_r$ and coercivity $H_C$) versus externally applied magnetic field for soft and hard magnetic materials, and discusses the types of energies that contribute to the formation of the domain structure.
Chapter V (Magnetic Properties of Single Domain Magnetic Nanoparticles) demonstrates the properties of single-domain configuration. The critical sizes involving the transition from single-domain of ferromagnetic nanoparticles to multi-domain structure for strong and weak anisotropy will calculate. Additionally, this chapter will deal with thorough discussion of anisotropy energies.

Chapter VI (Superparamagnetism) focuses on superparamagnetic properties of nanoparticles and the equation of the critical radius between single-domain and superparamagnetic phase.

Chapter VII (Surface Effects) emphasizes the surface effect of nanoparticle on its critical size and explains how magnetic properties such as saturation magnetization, anisotropy, Curie temperature and exchange integral change due to the surface effect when the bulk size magnetic material reduces to the nanometer scale.

Chapter VIII (Transition from Single- to Multi-Domain Structure) shows derivation for the critical radius of ferromagnetic nanoparticle with high and low anisotropy describing the transition from single-domain to multi-domain configuration in terms of surface parameters.

Chapter IX (Transition from Single-Domain Structure to Superparamagnetic Phase) shows the method of deriving the equation for the critical nanoparticle’s radius of the transition between single-domain and superparamagnetic phase as a function of the surface parameter Ks.

Chapter X (Results and Discussion) analyses the theoretical results from the solutions of the equations for the critical dimensions of magnetic nanoparticles and comparing them with experimental results taken from the literature.

Chapter XI (Conclusion and Future Goals) concludes my Thesis by summarizing the important results and putting forward some ideas for future research in this area.

Chapter XII and Chapter XIII are (References) and (Appendix), respectively.
II. MAGNETISM

Quantum mechanical description of matter is required to understand magnetism. There are two fundamental sources of magnetism due to electrons only: an intrinsic magnetic moment that electrons provide through an intrinsic angular momentum (spin – a rotation of electron around its own axis) and an orbital magnetic moment coming from orbital angular momentum that is a result of orbital motion of electrons around the nucleus. Both intrinsic and orbital angular momentum contributes to the total magnetic moment (called simply magnetic moment from now on). Generally, magnetic materials respond to an externally applied magnetic field $H$ by interaction with their magnetic moment $m$. The magnetization $M$ is defined as the magnetic moment per unit volume $[14]$.

The relationship between magnetic flux density $B$, magnetization $M$, and magnetic field $H$ is described by Eqs. (1) - (3)

$$B = \mu H = \mu_0 (H + M)$$  \hspace{1cm} (1)

$$M = \chi_m H$$  \hspace{1cm} (2)

$$B = \mu_0 (H + M) = \mu_0 (H + \chi_m H) = \mu_0 (1 + \chi_m) H$$ \hspace{1cm} (SI)  \hspace{1cm} (3)

$$B = H + 4\pi M = H + 4\pi \chi_m H = (1 + 4\pi \chi_m) H$$ \hspace{1cm} (gauss)

where $\chi_m$ is the magnetic susceptibility, $\mu = \mu_r \mu_0$ is the magnetic permeability with $\mu_0 = 4\pi \times 10^{-7}$ N/A as a vacuum magnetic permeability and $\mu_r$ as a relative permeability, $\mu_r = 1 + \chi_m$ [15].

Based on the response of magnetic materials to an applied magnetic field, we can divide magnetic materials into the following main categories: diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic materials. The way that the magnetic moments connect to each other by being parallel, antiparallel, or to create any other angle, provides the way of classifying magnetic materials.
DIAMAGNETIC AND PARAMAGNETIC MATERIALS

The orbital motion of an electron about the nucleus creates a tiny atomic current loop, which produces a magnetic field around it. When an external magnetic field is applied to a diamagnetic material, these current loops will tend to align in such a way as to oppose the applied magnetic field as in Lenz’s law. The induced magnetic field tends to oppose the applied magnetic field that creates it. Diamagnetic materials have negative susceptibility \( \chi_m < 0 \) (Eq. (4))[14]

\[
\chi_m = -\frac{NZe^2r^2}{mc^2}
\]  

where \( N \) is the number of atoms per unit volume, \( Z \) is the number of electrons, \( e \) is the charge of the electron, \( r \) is the orbital radius and \( c \) is the speed of light. The temperature independence is the characteristic of diamagnetic materials. Materials such as Cu, S, N\(_2\), B, and the most organic compounds are diamagnetic [16].

Paramagnetic materials have a small, positive susceptibility. In paramagnetic phase, a weak field-induced magnetization appears due to uncoupled magnetic moments \( m \) aligned partially as in Fig.1a. Materials such as O\(_2\), NO, Cr and Mn are paramagnetic [16]. The susceptibility of paramagnetic materials is inversely dependent on temperature (Curie law) (Eq. (5))

\[
\chi_m = \frac{C}{T}
\]  

where \( C \) is the Curie constant [14, 16].

FERROMAGNETIC, FERRIMAGNETIC, AND ANTIFERROMAGNETIC MATERIALS

The atomic moments couple to each other and align cooperatively in the absence of an applied magnetic field characterize ferromagnetic, antiferromagnetic, and ferrimagnetic materials (see Fig.1) [14, 16].
Ferromagnetic materials have spontaneous magnetization even in zero applied magnetic fields due to the exchange coupling between neighboring magnetic moments leading to align the magnetic moments parallel to each other. Generally, ferromagnetic materials can obtain a large magnetization in a weak magnetic field. Magnetic moments of ferromagnetic material can be easily aligned under influence of the applied magnetic field. In this situation, its susceptibility can be defined as $\chi_m = \frac{dM}{dH}$. The magnetization of ferromagnetic materials at zero magnetic field vanishes above temperature that is called the Curie temperature $T_C$. At a temperature below $T_C$, the magnetic moments are aligned, while above Curie temperature material losing magnetic ordering and behave as paramagnetic phase. In this temperature range for $T > T_C$, susceptibility depends on temperature in the same way as Curie law described before by Eq. (5) with a slight modification expressed by law that is called Curie-Weiss law (see Fig.1b and Eq. (6))

$$\chi_m = \frac{C}{(T - \theta)} \tag{6}$$

where $C$ is a constant and $\theta$ is Weiss constant.

Iron, nickel, cobalt, and some rare earths are the most common examples of ferromagnetic materials. If a ferromagnetic material is subjected to an external magnetic field, it stays magnetized to some extent after eliminating the magnetic field [14, 16]. This magnetization is called remnant magnetization $M_r$. 
Figure 1. Magnetic moment arrangements in (a) paramagnetic, (b) ferromagnetic, (c) ferrimagnetic, (d) antiferromagnetic, and (e) superparamagnetic materials.

Antiferromagnetic materials have different magnetic moments configuration in comparison to ferromagnetic materials as seen in Figs. 1d and 1b, respectively. Magnetic moments align antiparallel to each other. The susceptibility of antiferromagnetic materials follows the Curie-Weiss law (Eq. (6)) with negative Weiss constant $\theta$. The well-known antiferromagnetic materials are MnO, FeO, CoO, and NiO [14,16].

In ferrimagnetic materials, the magnetic moments are aligned antiparallel to each other as in antiferromagnetic ordering. However, the magnitude of the magnetic moment in one direction is different than the magnetic moment in the opposite direction as shown in Fig. 1c. As a result, the net magnetic moment remains in the absence of the applied magnetic field. Ferrimagnetic
susceptibility obeys the Curie-Weiss law with negative Weiss constant $\theta$. The most commonly known ferrimagnetic materials are cubic spinel ferrites [14, 16].

**SATURATION MAGNETIZATION $M_S (T, H)$**

Saturation magnetization $M_S$ in magnetic materials is the magnetization, which arises when all magnetic dipole moments are aligned in the same direction with or without the magnetic field direction. $M_S$ is a function of temperature $T$ and intensity of magnetic field $H$. Fig.2 shows how the saturation magnetization decreases with temperature at $H = 0$ reaching zero value at $T = T_C$.

![Figure 2. Saturation magnetization as a function of temperature for Ni [17].](image)
III. MAGNETIC DOMAINS

It is quite common that ferromagnetic materials do not always display magnetic property, but they often appear to be demagnetized or nonmagnetic. They begin to respond magnetically or expose their magnetism only when an external field is applied, for example, when they are near to permanent magnet. The reason behind this behavior is that actual samples are composed of magnetic domains. The magnetic domain is a region of magnetic material, where the local saturation magnetization is aligned in the same direction. The directions of magnetization within a domain point in a uniform direction, but the magnetization of different domains need not be parallel. The magnetic domain structure is accountable for the magnetic behavior of ferromagnetic material such as iron, nickel, and cobalt. The regions separating magnetic domains are domain walls or Bloch walls, which we will explain later. Pierre Weiss developed domain theory in 1906. He proposed that the existence of magnetic domains in ferromagnetic material. Weiss explained the reason for spontaneous alignment of the atomic moment within ferromagnetic materials and came up with Weiss molecular field that described later as the mutual interaction between neighboring electrons that tend to line up the magnetic moments parallel to one another. The reason of magnetic material spontaneously divides into multi-domains structure rather than existing in single-domain configuration throughout the material is to minimize its energy. Fig.3a shows that the resultant magnetization of a single crystal is zero. In polycrystalline samples, which contain a multi-domain structure, could have zero magnetization by virtue of the random distribution of grain axes as in Fig.3b [17] assuming that grains and domains are the same in size in this particular situation.
Figure 3. Domain arrangement for zero resultant magnetization in (a) single crystal and (b) polycrystalline samples.

The increase in the magnetization of the specimen under the action of an applied magnetic field occurs by two independent processes. First, by increasing in the volume of domains, which are oriented in the field direction, compare to the domain that oriented in other directions. Second, direction of magnetization rotates in the field direction as shown in Fig.4.

Figure 4. Essential process of magnetization [17].

On closer examination, it turns out that in a weak applied magnetic field, the magnetization changes occur due to the domain boundary displacement, that the change of domain size. In a strong magnetic field, the magnetization changes by the rotation the direction of the magnetization [17].
DOMAIN STRUCTURE

Domain structure has its origin in making the energy of a system low by going from a saturated structure with high magnetic energy to a domain configuration with a lower energy. Domain structure is a consequence of the several contributions to the energy exchange, anisotropy, and magnetic of a ferromagnetic body. We can understand the origin of domains by considering the structures shown in Fig.5. Each section shows a cross section of ferromagnetic single crystal. In Fig.5a, we have saturated configuration consisting of a single domain as a consequence of the magnetic poles formed on the surfaces of the crystal. This configuration will have a high value of the magnetic energy \( \left( \frac{1}{8\pi} \right) \int H^2 dV \). The magnetic energy for a square cross section will be of the order of \( M_S^2 = 10^6 \) ergs/cm\(^3\) where \( M_S \) denotes the saturation magnetization. In Fig.5b, the magnetic energy reduces by an one-half as a result of dividing the crystal into two domains magnetized in opposite directions. The subdivision process may carry further as in Fig.5c. N domains it turns out that the magnetic energy reduces to approximately \( 1/N \) of the magnetic energy of the saturated configuration (see Fig.5a) because of the reduced spatial extension of the field. This subdivision may continue until the required energy to establish transition boundary is greater than the reduction in magnetic field energy. The boundary layer indeed has a certain amount of energy associated with it. In Fig.5d, the boundaries of the triangular prism domains near the end faces of the crystal make equal angles 45° with the magnetization in the rectangular domains and with the magnetization in the domains.
Therefore, the component of magnetization normal to the boundary is continuous across the boundary, and no poles are formed anywhere in the crystal. As there are no poles there is no demagnetizing magnetic field associated with it [17].

**180° MAGNETIC DOMAIN WALL**

Magnetic domain wall or Bloch wall is the transition layer in a crystal that separates two adjacent domains that magnetized in a different direction. The entire change in the magnetic moment direction does not occur as a jump, but it takes place in a gradual manner by taking into account as many as 300 atomic planes as in Fig.6. Magnetic domain wall is created in order to reduce the magnetostatic or demagnetized magnetic energy, which arises from the interaction between the magnetization and the magnetic field produced by this magnetization. In 180° domain wall (see Fig.6), the adjacent domains are antiparallel to each other. If the direction of the magnetization changes from 0° to 180°, two energies play the most important role in its creation: the exchange and the anisotropy energy.
**Figure 6.** The Bloch wall.

The energy per unit area $\sigma_w$ of the magnetic domain wall is the sum of contribution from anisotropy and exchange energies (Fig.7) that we will discuss later [15]

$$\sigma_w = \sigma_{\text{ex}} + \sigma_{\text{anis}}$$  \hspace{1cm} (7)

where $\sigma_{\text{ex}}$ is the exchange energy and $\sigma_{\text{anis}}$ is the anisotropy energy.
IV. MAGNETIC MATERIALS

HYSTERESIS LOOP

Hysteresis loop occurs in multi-domain ferromagnetic materials under the influence of external magnetic field $H$. The process of hysteresis loop is depicted in Fig.7. Let us consider ferromagnetic material that is demagnetized initially. If a weak magnetic field $H$ is applied, it produces a motion of domain walls to expand the volume of these domains that have magnetization $M$ closer approximately to the direction of magnetic field $H$.

The magnetic potential energy density $U$ (Eq. (8)) in applied magnetic field $H$ is given as follows

$$U = - M \cdot H$$  \hspace{1cm} (8)

In small value of $H$, the induced resultant magnetization $M$ is produced in response to $H$. At a higher field of $H$, $M$ increases. Usually, the domain wall whose magnetization is in the same direction of the magnetic field increases in its volume during increasing $H$. When the most domain walls motion is completed, still there are magnetic domains remain with a component of resultant magnetization not exactly in the direction of magnetic field $H$. The magnetization of these domains must rotate into the field direction to minimize the potential energy. Because this process involves rotating the magnetization away from the easy axis direction, it cost more energy than the wall motion. The sample reaches the saturation magnetization when the applied field is sufficient so that the two processes are completed, the motion of the domain walls and the rotation of the magnetization to $H$ field. When decreasing the magnitude of applied field, magnetization rotates back to its easy axis direction. When the applied field decreases further, domain walls start to move back to its original size. When the applied field reaches zero value, the magnetization remains in the sample, which is called remanence $M_r$ respectively as showing
in Fig.7. The reverse direction of magnetic field $H$ is needed to turn off resultant magnetization $M$ to zero which is called coercivity $H = H_C$.

The coercivity plays an important role in hard magnet because in soft magnet $H_C << M_S$ [15]. Coercivity is the most sensitive property of ferromagnetic material as far as their structure and impurities are concerned.

![Hysteresis loop of magnetic material showing the variation of $M$ with $H$.](image)

**Figure 7.** Hysteresis loop of magnetic material showing the variation of $M$ with $H$.

The coercivity may reach value of 600 G in loudspeaker permanent magnet (Alnico V). Soft materials have low coercivity while hard materials characterized by much higher value of coercivity. Fig.8 shows a typical magnetization curve or hysteresis loop for different types of nanomaterials: ferromagnetic, superparamagnetic, paramagnetic, and diamagnetic nanoparticles. It demonstrates the characteristic position of magnetization on the curve related to the saturation magnetization $M_S$ and remanence magnetization $M_r$. 

15
Figure 8. Magnetization under the influence of an external magnetic field for different types of materials: ferromagnetic, superparamagnetic, paramagnetic, and diamagnetic nanoparticles [18].

In Fig.8, ferromagnetic nanoparticles show hysteresis while superparamagnetic nanoparticles follow a sigmoidal curve with no hysteresis. The responses of paramagnetic and diamagnetic nanoparticles are linear in dependence of $M$ in terms of $H$.

**SOFT MAGNETIC MATERIALS**

Magnetic materials are also classified as soft and hard magnetic materials according to the ease of magnetizing the materials. Soft magnetic materials are easy to magnetize or demagnetized. The magnetization process occurs in a weak range of magnetic field. Because of that, the movement of the domain walls is easy to happen, so they small hysteresis area. The coercivity of soft materials is less than for hard material, $H_C \leq 10^3$ A/m. The soft materials also are known to have a high value of their susceptibility and permeability. Soft magnetic materials are used in transformers, inductors, motors, and generators [15].

**HARD MAGNETIC MATERIALS**

Conversely to easy magnetic materials, hard magnetic materials retain their magnetization and are difficult to magnetize. In some hard magnetic materials, the coercivity can be as strong
as \(2 \times 10^6\) A/m. They have large hysteresis loop due to large hysteresis loop area. In this case, the materials may have defects that strongly impede wall motion, the materials tend to have high anisotropy and need a strong magnetic field to magnetize. Hard magnets are used generally in applications where they resist a negative applied field that pushes them to the demagnetization status. Hard materials are used in motors and actuators. There are also applications in frictionless bearings, microwave generators, and lenses for charged particle machines [15].

**MAGNETIC ENERGY**

There are several types of magnetic energies that contribute to the domain structure of magnetic materials: exchange, magnetoelastic, magnetostatic, and anisotropy energy.

**Exchange Energy** density \(f_{\text{ex}}\) is defined as (Eq. (9))

\[
f_{\text{ex}} = JS^2 \sum_{i>j} \varphi_{ij}^2
\]

where \(\varphi_{ij}\) is the angle between the directions of \(S_i\) and \(S_j\) spins or magnetic moments, \(J\) is the exchange interaction, \(S\) is spin, and \(\sum\) is the summation sign.

**Magnetoelastic Energy** density is the energy that arises from the interaction between the magnetization and mechanical strain of the lattice. The magnetoelastic energy density \(f_{\text{me}}\) is given by Eq. (10)

\[
f_{\text{me}} = \frac{3}{2} \lambda T \sin^2 \theta
\]

where \(\lambda\) is the isotropic magnetostriction and \(\theta\) is the angle between the tension \(T\) and the magnetization.

**The Magnetostatic Energy** it is known also as a self-energy. It is the energy when the magnetic field due to the magnetization is doing the work on the magnetization itself. The magnetostatic energy density is given by Eq. (11)

\[
f_{\text{mag}} = -\frac{1}{2} M_s \cdot H
\]
ANISOTROPY ENERGY

Anisotropy energy is also known as magnetocrystalline energy of the ferromagnetic material. In ferromagnetic nanoparticles, the magnetization tends to align along certain crystallography axis which known as easy magnetization axis which is the most dynamically favorable direction. When the nanoparticle is magnetized along direction that it is difficult to magnetize, this direction is known as hard direction. It is found experimentally that more energy is required to magnetize the magnetic material to its saturation in hard direction. The energy required for the magnetization to be along the hard direction is called anisotropy energy. The anisotropy energy density $f_k$ can be expressed by the following expression (Eq. (12)),

$$ f_k = K_1 \sin^2 \theta + K_2 \sin^4 \theta $$

(12)

where $K_1$ and $K_2$ are anisotropy constants and $\theta$ is the an angle between the magnetization direction and the easy axis direction. It is found experimentally that at room temperature $K_1 = 4.1 \times 10^6$ erg/cm$^3$ and $K_2 = 1.0 \times 10^6$ erg/cm$^3$ for Co and $K_1 = 4.8 \times 10^5$ erg/cm$^3$ and $K_2 = 1.5 \times 10^5$ erg/cm$^3$ for Fe. For example, in cobalt, which has a hexagonal crystallographic structure, the easy magnetization in room temperature is hexagonal axis, while other directions along the basal plane are the hard directions as depicted in Fig.9 [17].
Figure 9. Magnetization curves for Fe, Ni, and Co, in direction of easy and hard magnetization axes [17].
V. MAGNETIC PROPERTIES OF SINGLE DOMAIN MAGNETIC NANOPARTICLES

The magnetic properties change with size when the size of magnetic sample reduces to the nanometer dimension. The surface energy becomes more significant than the volume energy. Surface energy is, for example, the energy of transition layer (Bloch wall) between domains, while volume energy is the magnetostatic energy. The sample becomes, more likely, one domain when it shrunk to nanosize. Then it acts as a permanent magnet and creates a single-domain structure. Single domain configuration occurs when more energy is required to create a domain wall than the magnetostatic energy of single-domain state. Critical size of nanoparticle is the size where the nanoparticle composed of the only single-domain structure is energetically more favorable than multi-domain configurations. Let us consider a spherical ferromagnetic nanoparticle of radius $R$ as a single crystal. In a single-domain structure, magnetic moments tend to align along the same easy axis direction and, in the same time, they are parallel to each other. The magnetization of the nanoparticle is the saturation magnetization $M_S$. The magnetic energy density of single-domain configuration due to the magnetostatic energy density (see Eq. (11)) is described by Eq. (13) for a spherical magnetic nanoparticle

$$f_{\text{mag}} = \frac{2}{3} \pi M_S^2$$

(13)

CRITICAL RADIUS OF SINGLE-DOMAIN STRUCTURE

We have defined the critical size of nanoparticles as the size of nanoparticle that separates single-domain configuration from multi-domain configuration. We shall consider spherical ferromagnetic nanoparticle of radius $R$. The magnetic energy density of saturated single domain structure given by Eq. (13) leads to the magnetostatic energy for spherical single-domain nanoparticle (Eq. (14))
\[ w_{\text{mag}} = f_{\text{mag}} \cdot V = \left( \frac{8\pi^2}{9} \right) M_S^2 R^3 \]  
(14)

By using Eq. (14), we can find that \( w_{\text{mag}} = 24 \times 10^6 \) ergs for \( R = 1 \) cm and \( w_{\text{mag}} = 2.4 \times 10^{-12} \) ergs for \( R = 10^{-6} \) cm = 10 nm. We see that the energy value we have got from Eq. (14) for magnetic nanoparticle with radius \( R = 1 \) cm is significantly larger than for \( R = 10 \) nm suggesting that a larger nanoparticle has to have a multi-domain configuration to lower its single-domain configuration energy.

LOW ANISOTROPY

Fig. 10 shows three possible magnetic configurations for magnetic structure of spherical nanoparticle with two extreme anisotropy values: low anisotropy (Fig. 10a) and high anisotropy (Fig. 10b and c).

![Figure 10](image-url)

**Figure 10.** The domain arrangements in small spherical nanoparticles for low anisotropy (a) and for high anisotropy in cubic crystal (b), and in uniaxial crystal (c), respectively [17].

There is preferable flux closure configuration represented in Fig. 10a when the anisotropy energy is low. The magnetic energy is largely in the form of exchange energy (see Eq. (9)) related to the interaction between spins. The reason behind that is a low anisotropy of spherical magnetic nanoparticle. In the same time, the Bloch wall energy exceeds energy incorporated in magnetostatic energy (or the exchange energy). This is reasonable assumption only when the thickness of the Bloch wall is greater than the critical radius. Let us consider the spins on a
circular ring of radius \( r \) with the length of a side of the unit cell equal to \( a \). The number of spins \( n \) on the ring is given by the circumference of the ring divided by lattice constant \( a \) (\( n = 2 \pi r / a \)). If \( |\vec{S}_i| = |\vec{S}_j| = |\vec{S}| = S \) then the exchange energy (see Eq. (9)) between two nearest-neighbor spins \( \vec{S}_i \) and \( \vec{S}_j \) is given by Eq. (15) for \( n \) spins

\[
\Delta w_{\text{ex}} = nJ S^2 \phi^2
\]  

where \( \phi \ll 1 \) is the small angle between two nearest-neighbor spins \( i \) and \( j \), \( J \) is the exchange interaction, and \( S \) is the spin.

The angle between two successive spins from Fig. 11 is (Eq. (16))

\[
\phi = \frac{a}{r}
\]  

Figure 11. Arrangement of nearest-neighboring spin vectors [18].

Using Eq. (16) and \( n = \frac{2 \pi r}{a} \) for \( S = 1 \) (e.g., Fe) and plug it into Eq. (15) then the exchange energy of ring can be expressed in the form (Eq. (17))

\[
w_{\text{ring}} = \pi J a / r
\]
Figure 12. Spherical magnetic nanoparticle with a couple of cylinders [18].

Now let consider a sphere of magnetic nanoparticle made up of circular cylinders each unit cell in thickness (Fig. 12). The height of the cylindrical shell $D$ is given by Eq. (18)

$$D = 2\sqrt{R^2 - r^2}$$  \hspace{1cm} (18)

The total number of rings in the shell can be calculated if each ring on a surface of a cylindrical shell is represented by lattice constant $a$, so the number of rings $N$ in the shell can be as follows (Eq. (19))

$$N = \frac{D}{a} = \left(2 \frac{a}{\sqrt{R^2 - r^2}}\right)$$  \hspace{1cm} (19)

The exchange energy between two spins on the surface of cylindrical shell can be obtained by the multiplication of the exchange energy of the ring by the number of rings on the cylindrical shell (Eq. (20))

$$w_{cyl} = N \cdot w_{ring} = 2\pi J \left(\frac{\sqrt{R^2 - r^2}}{r}\right)$$  \hspace{1cm} (20)

The exchange energy of spherical nanoparticle can be expressed by Eq. (21)
The magnetic energy density \( f_{\text{ex}} \) for spherical nanoparticle is the magnetic energy per unit volume (Eq. (22))

\[
f_{\text{ex}} = \left( \frac{3}{2} \right) \left( \frac{1}{aR^2} \right) \left[ \ln \left( \frac{2R}{a} \right) - 1 \right]
\]

We can see from Eq. (22) that the exchange energy density depends on the size of the spherical magnetic nanoparticle. We can also easily compare the values of exchange energy density for different sizes of spherical magnetic nanoparticles. In order to do it we can define for Fe [17] \( S = 1, J = 205 \) \( k_B \) (\( k_B \) is the Boltzmann constant), \( a = 0.286 \) nm and for \( R = 10 \) nm the exchange energy density \( w_{\text{ex}} = 23 \times 10^{-12} \) ergs (\( f_{\text{ex}} = 0.8 \times 10^7 \) ergs/cm\(^3\)) [15, 17]. Thus when the nanoparticles are sufficiently small, the single-domain structure has lower energy than flux-closure configuration. To find then critical radius for magnetic nanoparticle we have to compare Eqs. (14) and (21) [17] (Eq. (23))

\[
\left( \frac{8\pi^2}{9} \right) M_S^2 R^3 = \left( \frac{2\pi J R}{a} \right) \left[ \ln \left( \frac{2R}{a} \right) - 1 \right]
\]

**HIGH ANISOTROPY**

In the previous section, the anisotropy energy associated with the flux-closure configuration was ignored in comparison to the exchange energy. This is sensible if the critical radius is considerably smaller than the thickness of Bloch wall in the material. The exchange and anisotropy energies are equal in Bloch wall. If the change in spin direction is constrained to a distance less than the wall thickness, the exchange energy will be dominant. However, it might be possible for critical radius size to exceed significantly the wall thickness if the anisotropy energy is high sufficiently. We will discuss two different types of crystallographic configurations of magnetic nanoparticles in the following section [17].
CUBIC CRYSTAL

Fig. 10b shows the model of a cubic crystallographic arrangement in magnetic nanoparticle. The size of the ferromagnetic nanoparticle is large enough to create domain walls and the transition takes place between single- and multi-domain structures. The energy needed to create Bloch wall $w_{\text{wall}}$ (see Eq. (24))

$$w_{\text{wall}} = 2\sigma_w \pi R^2$$  \hspace{1cm} (24)

(where $\sigma_w$ denotes the Bloch wall energy per unit area of the wall, $R$ is the radius of the spherical nanoparticle, and factor two denotes the number of the Bloch walls in this case (see Fig. 12 b) contributes to the total energy of magnetic nanoparticles who have high anisotropy energy. The exchange energy is minimized due to the Bloch wall energy.

Let us assume that the wall contains $N$ atomic planes which are separated by lattice constant $a$. $Na$ is the thickness of the Bloch wall. Bloch wall represents the transition layer, which separates two adjacent magnetized domains in opposite directions. This transition does not occur in one step on one atomic plane, but it will change gradually within several atomic layers. The reason behind this gradual change is the exchange energy during gradual change is lower than if it has happened suddenly. The spins contained within the Bloch wall are largely oriented away from the easy axis of the magnetization, so there will be a certain amount of anisotropy energy connected with the wall. The total magnetic energy of the wall per unit surface represents the sum of two energies, exchange and anisotropy energies as we mentioned previously in Eq. (7).

The anisotropy energy $\sigma_{\text{anis}}$ is approximately anisotropy constant $K$ multiply by the thickness of Bloch wall equal to $Na$ (Eq. (25))

$$\sigma_{\text{anis}} \approx KNa$$ \hspace{1cm} (25)

The exchange energy $\sigma_{\text{ex}}$ per unit area of $180^\circ$ Bloch wall based on Eq. (15) leads to Eq. (26)
\[ \sigma_{ex} = \pi^2 S^2 / N a^2 \]  \hspace{1cm} (26)

By substituting Eqs. (25) and (26) into Eq. (7) we have (Eq. (27))

\[ \sigma_w \approx \left( \frac{\pi^2 S^2}{N a^2} \right) + K N a \]  \hspace{1cm} (27)

The minimum \( \sigma_w \) (Eq. (27)) with respect to \( N \) leads to the total wall energy per unit area of Bloch wall (Eq. (28))

\[ \sigma_w = 2\pi [ J K S^2 / a ]^{1/2} = 2\pi [ A K ]^{1/2} \]  \hspace{1cm} (28)

where \( A \) is the exchange energy constant. For body-centered cubic (Fe) as in Fig.10b, we can calculate the critical radius of the magnetic nanoparticle by using the fact that at this critical size the energy of the multi-domain configuration is equal to the energy of single-domain configuration when multi-domain structure makes a transition to the single-domain configuration. By combining Eqs. (14) and (24), we can find that the critical dimension of nanoparticle is (Eqs. (29) and (30))

\[ \left( \frac{8\pi^2}{9} \right) M_S^2 R^3 = 2\sigma_w \pi R^2 \]  \hspace{1cm} (29)

\[ R = \left( \frac{9}{4\pi} \right) \left( \sigma_w / M_S^2 \right) \]  \hspace{1cm} (30)

**UNIAXIAL CRYSTAL**

In the uniaxial crystalographic symmetry, the domain structure is represented by domains in which the magnetizations are directed antiparallel to each other as in Fig.10c. There is only one easy magnetization axis and two different alignments. For nanoparticles with radius \( R \), as mentioned above, the critical size of the radius will be when the energy of single-domain structure is identical to the energy of the two-domain configurations. The total magnetic energy for magnetic nanoparticle with uniaxial symmetry leads to the same value for critical dimension
as in cubic symmetry (Eq. (30)). To estimate critical dimension of magnetic nanoparticle with uniaxial symmetry, we can find for MnBi that $R_{c2} = 5.56 \times 10^{-5}$ cm [17].
VI. SUPERPARAMAGNETISM

Superparamagnetism is the special magnetic phase that occurs in fine ferromagnetic or ferrimagnetic nanoparticles. The sizes of superparamagnetic nanoparticles are around few nanometers to a couple of a tenth of the nanometer, depending on the material. The total magnetic moment of the nanoparticles can be considered as one giant magnetic moment, composed of all the individual magnetic moments of the atoms that constitute the nanoparticles. Magnetization can randomly flip direction under the influence of temperature in sufficiently small nanoparticles with uniaxial anisotropy. This is due to the fact that below certain critical dimensions, the anisotropy barrier energy $\Delta E$ of a magnetic nanoparticle is reduced to the point where this energy can be overcome by thermal energy $k_B T$ ($k_B$ is the Boltzmann constant and $T$ is the absolute temperature). The average time between flips is called the relaxation time $\tau$ as derived by Neel is expressed by Eq. (31)

$$\tau = \tau_0 \exp \left( -\frac{\Delta E}{k_B T} \right)$$

(31)

where $\Delta E = KV \sin^2 \theta$ is the energy barrier which it should be overcome by the thermal energy to flip the magnetization, $K$ is the anisotropy, $V$ is the volume of nanoparticle, $\theta$ is the angle between the magnetization and the easy axis, $\tau_0$ is the length of time characteristic of the probed material, and it is often around $10^{-9}$ s to $10^{-12}$ s, and $T$ is the absolute temperature [19].

The magnetization, in superparamagnetic phase, is zero in the absence of an externally applied magnetic field and increases linearly with the field. Each experimental technique comes with its own measurement time $\tau_m$, which can vary from $10^{-8}$ s to 100 s [20]. Depending on the value of relaxation time $\tau$, there are two scenarios which can occur. First, $\tau_m \ll \tau$ when the average time between flips is much larger than the measurement time, the system appear to be stuck and at
given magnetic field we will have a fixed magnetization in the field direction as in Fig.13a. This situation puts the nanoparticles in a defined state and it is known as a blocking state because the magnetization is blocked in one direction and stops flipping. The second scenario is when $\tau_m \gg \tau$, if the average time between flips can be much smaller than the measurement time, the magnetization appears to fluctuate as long as there is no external field applied. The magnetization appears to be zero. This magnetic arrangement is known as a superparamagnetic state, as depicted in Fig.13b.

![Figure 13. Blocking (a) and superparamagnetic (b) states.](image)

Blocking temperature $T_B$ defined as the transition temperature between the blocking and superparamagnetic states. That means when $\tau_m = \tau$, the blocking temperature based on Eq. (31) is given by the following Eq. (32)

$$T_B = \frac{\Delta E}{k_B \ln\left(\frac{\tau_m}{\tau_0}\right)} \quad (32)$$
We can conclude that the blocking temperature is directly proportional to the size of the nanoparticles. Eq. (32) is not necessarily effective for large nanoparticles, where regions of uniform magnetizations are separated by domain boundary [20]. The superparamagnetic state occurs when $\tau_m > \tau$ or when $T > T_B$, while blocking state occurs when $\tau_m < \tau$ or $T < T_B$.

**ENERGY BARRIER $\Delta E$**

For spherical nanoparticles, Stoner-Wohlfarth described the energy barrier due to uniaxial anisotropy for non-interacting single domain nanoparticles in zero magnetic field by Eq. (33)

$$\Delta E = KV \sin^2 \theta$$

(33)

where $K$ is the magnetocrystalline anisotropy, $V$ is the volume of nanoparticle, and $\theta$ is the angle between the magnetization and the easy axis. In Fig.14, $\theta = 0$ and $\pi$ locate the direction of minimum anisotropy energy and symmetrically separated an energy barrier as high as $KV$. As soon as an external field is applied, one of the minima gets preferred. In superparamagnetic state, to flip the magnetization as shown in Fig.14 ($\theta = \pi/2$) [16], the energy required to do it is the value given in Eq. (34)

$$\Delta E = KV$$

(34)

![Figure 14. Energy barrier for magnetization reversal [16].](image)
We have mentioned before that ferromagnetic and ferrimagnetic materials can behave as a paramagnet in the temperature above its Curie temperature $T_C$. We should say that superparamagnetic state occurs in temperature less than Curie temperature [20]. The magnetic nanoparticles tend to have a single-domain structure if magnetic nanoparticles size is maintained above a critical size during nanoparticles synthesis. At smallest sizes, they exhibit superparamagnetic behavior under standard condition. In order to find critical radius $R_{C1}$ of the spherical magnetic nanoparticle to have transition from single-domain to superparamagnetic regime, we have to replace $V = \frac{4}{3} \pi R^3$ in Eqs. (31) and (34) with replacing $\tau = \tau_m$ and leading to Eq. (35)

$$R = 3 \sqrt[3]{\frac{3}{4\pi} \ln \left( \frac{\tau_m}{\tau_0} \right) \frac{k_B T}{K}}$$  (35)
VII. SURFACE EFFECTS

SURFACE EFFECT ON SATURATION MAGNETIZATION

The value of the saturation magnetization $M_s(H,T)$ as a function of temperature and magnetic field can be reached in a strong applied magnetic field. It has been already mentioned that the number of atoms on the surface of nanoparticles are increasing in comparison to the volume atoms carrying magnetic moments as its size decreases. Berkowitz et al. [21] pointed out that at room temperature, saturation magnetization decreases with decreasing nanoparticle size. It was found also that at $T = 0$ K, the magnetic moments of Co and Ni clusters are higher than their bulk values. However, the magnetic moments decrease between 82 K and 267 K. Saturation magnetization at room temperature of Ni thin films decreases with decreasing film’s thickness [9, 11]. Tang et al. [22] derived an empirical relation for size-dependent saturation magnetization $M_s(R)$ (Eq. (36))

$$M_s(R) = M_{s0}(1 - \frac{\alpha}{R})$$  

(Eq. (36))

where $\alpha$ is an experimentally adjustable parameter and $M_{s0}$ is the saturation magnetization of the bulk material. At low temperature the saturation magnetization of nanoparticle increase inversely with ultrafine particles due to the localized charges that are confined in deep potential well on the surface [10]. However, Nikolaev et al. [23] state that $M_s$ increases when the size decrease due to the exchange bonds loss of the surface atoms, which also causing decrease in Curie temperature. The ratio between Curie temperature for nanoparticle and bulk can be expressed by the following formula (Eq. (37))

$$\frac{T_{C_s(R)}}{T_{C0}} = (1 - \frac{\beta}{R})$$

(Eq. (37))

where $T_{C0}$ is Curie temperature for bulk material and $\beta$ is the fitting parameter, which can be treated as the parameter of the imperfection of the magnetic structure of the ultrafine
Zhong et al. [9, 10] developed a model to examine the size, shape, structure and temperature dependence of nanoparticles by incorporating the bond order–length strength (BOLS) correlation and the Brillouin function. It corresponds directly to decrease of the atoms cohesive energy due to the coordination number imperfection of atoms near the surface edge.

\[ M_S(R, T) = \alpha(J, T) \frac{E_{exc}(R)}{E_{exc0}} = 4 \frac{E_{exc}(R)}{E_{exc0}} - 3 \]  

where \( \alpha(J, T) \) denotes a parameter which depends on the temperature, \( J \) is the mean angular momentum, and \( E_{exc} \) is the exchange energy with the subscript 0 denoting bulk value. At room temperature, \( \alpha(J, T = 300 \text{ K}) \) can be taken as a constant and the size effect on \( J \) become insignificant compared to \( E_{exc} \), where \( E_{exc} \) dominates the magnetic behavior. For ferromagnetic nanoparticle \( \alpha(J, T = 300 \text{ K}) \) is equal to 4 [9, 10, 24]. Both Cure temperature \( T_C \) and \( M_S \) can be determined by \( E_{exc}(T) \) which is the sum of cohesive energy \( E_{coh} \) and the thermal vibration energy \( E_V(T) \) [12, 21]. In terms of the BOLS correlation and Ising model (Eq. (39))

\[ E_{exc}(R, T) = A E_{coh}(R) + E_V(T) \]  

where \( A \) is a coefficient. When \( T = T_C \), thermal vibration energy \( E_V(T) = k_B T \) is a part of \( E_{coh} \) which required for disordering the exchange interaction between spins. The \( E_V(T = 300 \text{ K}) \) should also be proportional to \( E_{coh} \) [24] (Eq. (40))

\[ \frac{E_{coh}(R)}{E_{coh0}} = \frac{E_{exc}(R)}{E_{exc0}} = \frac{T_C(R)}{T_{C0}} \]  

where \( E_{coh}(R) \) function has the following form Eq. (41) [27]

\[ \frac{E_{coh}(R)}{E_{coh0}} = \left[ 1 - \frac{1}{\left( \frac{R}{R_0} \right)^{1-1}} \right] \exp \left[ -\frac{2S_b}{3R_g} \left( \frac{R}{R_0} \right)^{-1} \right] \]  

where \( R_g \) implies the ideal gas constant while \( R_0 \) denotes the critical radius, \( S_b = H_V/T_b \) is the bulk solid–vapor transition entropy of crystals. \( H_V \) and \( T_b \) are the bulk solid-vapor transition
enthalpy and the solid-vapor transition temperature respectively, and the solid and vapor structure is indistinguishable, so \( R_0 = \frac{ch}{4} \) where \( h \) is the atomic or molecular diameter. The constant \( c \) \((0 < c \leq 1)\) denotes the normalized surface area where \( c = 1 \) for low-dimensional material with free surfaces [25] that vary if the low dimensional crystals have an interface in such the atomic potential differs from the surface atoms. By substituting Eq. (41) into Eq. (38) and comparing with Eq. (39) and using \( R_0 = \frac{ch}{4} \), we have Eq. (42)

\[
\frac{M_s(R)}{M_{s0}} = \left(1 - \frac{\alpha}{R}\right) = 4 \left[1 - \frac{1}{\frac{4Rg}{ch} - 1}\right] \exp \left[-\frac{2Sb}{3Rg \left(\frac{4R}{ch}\right)}\right] - 3
\]

(42)

For fitting parameter \( \alpha \) in terms of the known parameters \( c, h, S_b, \) and \( R_g \) and using Taylor expansion and keeping its linear term only (Eq. 43))

\[
\alpha = -4R \left\{1 - \left[\frac{1}{\frac{4Rg}{ch} - 1}\right]\right\} \exp \left[-\frac{2Sb}{3Rg \left(\frac{4R}{ch}\right)}\right] + 4R \approx \frac{4R}{ch} \left(2 + \frac{4Sb}{3Rg}\right)
\]

(43)

By using Eq. (41) and substituting it into Eq. (40) and comparing it with Eq. (37), and using \( R_0 = \frac{ch}{4} \) we have Eqs. (44) and (45)

\[
\frac{T_C(R)}{T_{C0}} = 1 - \frac{\beta}{R} = \left[1 - \frac{1}{\frac{4Rg}{ch} - 1}\right] \exp \left[-\frac{2Sb}{3Rg \left(\frac{4R}{ch}\right)}\right]
\]

(44)

\[
\beta = R - R \left[1 - \frac{1}{\frac{4Rg}{ch} - 1}\right] \exp \left[-\frac{2Sb}{3Rg \left(\frac{4R}{ch}\right)}\right] = \alpha/4
\]

(45)

**SURFACE EFFECT ON ANISOTROPY**

The surface effect in small magnetic nanoparticles is the main source of anisotropy because when nanoparticle size decreases, the surface magnetic contribution will eventually become more significant than for bulk of the nanoparticle. The anisotropy energy \( E_{\text{ans}} \) of ferromagnetic nanoparticles can be written as Eq. (46)
\[ E_{\text{ans}} = K \sin^2 \theta \]  

(46)

where \( \theta \) is the angle between the magnetization and the surface symmetry axis and \( K \) is considered as the uniaxial anisotropy constant, which can be described as the sum of the two terms Eq. (47)

\[ K = K_{\text{eff}} = K_V + \frac{3}{R} K_S \]  

(47)

where \( K_S \) is the surface anisotropy contribution, \( K_V \) is the volume anisotropy, and \( R \) is spherical nanoparticle’s radius [26, 27].

**SURFACE EFFECT ON EXCHANGE INTEGRAL CONSTANT**

The relation that connects the exchange integral constant \( J(R) \) with the radius \( R \) and the exchange integral of bulk material \( J_0 \) is described by Eq. (48)

\[ J(R) = J_0 \left( 1 - \frac{\beta}{R} \right) \]  

(48)

where \( \beta \) is the fitting parameter. Also, the exchange integral for the bulk martial \( J_0 \) can be related to bulk Curie temperature \( T_{C0} \) by the following Eq. (49) [28]

\[ T_{C0} = \frac{2S(S+1)}{3k_B} J_0 \]  

(49)
**VIII. TRANSITION FROM SINGLE– TO MULTI–DOMAIN STRUCTURE**

In ferromagnetic nanoparticles, there are two critical size effects, one is the single-domain limit, and other is the superparamagnetic limit. Fig.15 displays the transition between these regimes. Fig.15a shows how coercivity $H_C$ depends on the particle dimension. It appears that the coercivity $H_C$ has a maximum at the critical dimension of nanoparticle $R_{C2}$ at the transition between the single- and multi-domain structure and $H_C = 0$ in superparamagnetic phase which takes place below second critical dimension of nanoparticle $R_{C1}$. Fig.15b shows the critical dimensions of some nanoparticles for several magnetic materials with high or low anisotropy.

![Graph showing transition from single-domain to multi-domain and superparamagnetic regimes](image)

**Figure 15.** Single-, multi-domain, and superparamagnetic states [29].

**TRANSITION FROM SINGLE– TO MULTI–DOMAIN STRUCTURE IN HIGH ANISOTROPY NANOPARTICLES**

In this section, we are going to study the influence of the surface effect on the critical dimension where transition from single- to multi-domain structures for ferromagnetic nanoparticles with high anisotropy takes place. Let us start with Eq. (28) and Eqs. (36), (47), and (48). Taking into account the surface effects that modify anisotropy constant, exchange integral, and saturation magnetization according to Eqs. (36), (47), and (48), respectively, we rewrite Eq. (30) for critical diameter $R_{C2}$ (high anisotropy case) as follows (Eq. (50))
\[ R = R_{C20} \left( \frac{1 - \frac{\beta}{R}}{1 - \frac{\alpha}{R}} \right)^{\frac{1}{2}} \left( 1 + \frac{3}{R} \frac{K_s}{K_V} \right)^{\frac{1}{2}} \left( 1 + \frac{3}{R} \frac{K_s}{K_V} \right)^{\frac{1}{2}} \]  

(50)

where \( R_{C20} \) (see Eq. (51)) is the critical radius for magnetic nanoparticle with no surface effect

\[ R_{C20}^2 = 81J_0K_VS^2/4aM_{S0}^4 = 81AK_V/4M_{S0}^4 \]  

(51)

where \( J_0, K_V, \) and \( M_{S0} \) are exchange integral, anisotropy constant, and saturation magnetization for nanoparticle without contribution from surface effect, respectively, \( S \) is the spin, \( a \) is the lattice constant, \( K_s \) is the surface anisotropy, \( A \) is the exchange energy constant, and \( \alpha, \beta \) are constants. For example, \( R_{C20} = 556 \text{ nm} \) MnBi magnetic nanoparticle with a high anisotropy constant \( K_V = 10^7 \text{ ergs/cm}^3 = 10^6 \text{ J/m}^3 \), \( A = 1.98 \times 10^{-11} \text{ J/m} \), and \( M_{S0} = 4.78 \times 10^4 \text{ A/m} \) based on Eq. (51). The solution of Eq. (50) gives a critical radius \( R_{C2} \) for transition between single- and multi-domain structures for high anisotropy nanoparticles.

**TRANSITION FROM SINGLE- TO MULTI-DOMAIN STRUCTURE IN LOW ANISOTROPY NANOPARTICLES**

The critical radius of low anisotropy nanoparticles has been discussed in Ch. V. Eq. (23) shows the critical radius between single- and multi-domain configurations for low anisotropy nanoparticles. Due to renormalization of saturation magnetization and exchange integral constant, the critical radius \( R_{C2} \) is a solution of Eq. (52) which includes a surface effect

\[ \left( \frac{8\pi^2}{9} \right) M_{S0}^2 \left( 1 - \frac{\alpha}{R} \right)^2 = J_0 \left( 1 - \frac{\beta}{R} \right) \left( \frac{2\pi}{a} \right) \left[ \ln \left( \frac{2R}{a} \right) - 1 \right] \]  

(52)
Figure 16. The dependence of the critical size of iron nanoparticles $R_{C2}$ as a function of $\alpha$ for $\beta = 0, 0.2, \text{ and } 0.4$ [18].

Fig.16 shows numerical solution of Eq. (52) for the critical radius $R_{C2}$ of iron between single- and multi-domain magnetic nanoparticle structures in terms of $\alpha$. It indicates that with a decrease of saturation magnetization in a vicinity of the nanoparticle’s surface ($\alpha$ increases), a value of critical dimension of nanoparticle increases. Fig.17 shows numerical solution of Eq. (52) for the critical radius $R_{C2}$ of iron between single- and multi-domain magnetic nanoparticle structures in terms of $\beta$. It indicates that with a decrease of exchange integral in a vicinity of the nanoparticle’s surface ($\beta$ increases), a value of critical dimension of nanoparticle slightly decreases. As we have discussed already that decreasing the size of magnetic nanoparticles leads to decrease in the interaction between atoms on the surface and a suppression of Curie temperature for magnetic nanoparticles.
Figure 17. The dependence of the critical size of iron nanoparticles $R_{C2}$ as a function of $\beta$ for $\alpha = 0, 2, \text{ and } 4$ [18].
IX. TRANSITION FROM SINGLE-DOMAIN STRUCTURE TO SUPERPARAMAGNETIC PHASE IN HIGH AND LOW ANISOTROPY MAGNETIC NANOPARTICLES

To study how surface effects affect a critical dimension between single-domain and superparamagnetic configurations, we should start with Eq. (35) and replace K by $K_{\text{eff}}$ (see Eq. (47)). After simple manipulation, we have Eqs. (53) and (54) for $R_{C1}$ that can be solved in analytical manner

$$\left(\frac{R}{R_{C10}}\right)^3 \left(1 + \frac{3K_S}{RK_v}\right) = 1 \quad (53)$$

$$R_{C10} = \sqrt[3]{\frac{3}{4\pi \ln \left(\frac{\tau_m}{\tau_0}\right) \frac{k_BT}{K_v}}} \quad (54)$$

where $R_{C10}$ is the critical radius for nanoparticle with no surface effect, $K_v$ is the bulk anisotropy constant, $\tau_0 = 10^{-9}$ s, $\tau_m = 100$ s, $k_B$ is Boltzmann constant, and T is an absolute temperature.

To see how surface effect (surface anisotropy $K_S$) influences the critical radius $R_{C1}$ let us rearrange Eq. (53) to the following form (Eq. (55))

$$R^3 + 3R^2 \frac{K_S}{K_v} - R_{C10}^3 = 0 \quad (55)$$

Eq. (55) we can solve analytically in order to understand how the surface effect affects the critical radius between single-domain structure and superparamagnetic phase. The analytical solution for R of a cubic equation (Eq. (55)) has the following form (Eqs. (56) and (57))

$$R_{C1} = \left\{ q + \left( q^2 - p^6 \right)^{\frac{1}{3}} \right\}^{\frac{1}{3}} + \left\{ q - \left( q^2 - p^6 \right)^{\frac{1}{3}} \right\}^{\frac{1}{3}} + p \quad (56)$$

$$p = -\frac{K_S}{K_v}, \quad q = \left( -\frac{K_S}{K_v} \right)^3 + \frac{R_{C10}^2}{2} \quad (57)$$

There is a condition imposed on interrelationship between material constants to guarantee a real value for the critical size of magnetic nanoparticle to have transition between a single-domain structure and superparamagnetic phase (Eq. (58))
\[ \frac{R_{C10}}{\sqrt[4]{3}} K_V > K_S \quad (58) \]

For the high anisotropy magnetic nanoparticle MnBi, the radius of spherical magnetic nanoparticle \( R_{C10} = 2.93 \text{ nm} \) without surface effect.
X. RESULTS AND DISCUSSION

SURFACE EFFECT ON THE CRITICAL DIMENSION $R_{C2}$ OF HIGH ANISOTROPY FERROMAGNETIC NANOPARTICLES

Surface effect on the critical size $R_{C2}$ (see Eq. (50)) of ferromagnetic nanoparticles with high anisotropy $K_V$ is discussed. Effect of surface on the saturation magnetization (Eq. (36)), the exchange interaction (Eq. (48)), and surface anisotropy (Eq. (47)) is quantified by material constants $\alpha$, $\beta$, and $K_S$, respectively. Ferromagnetic nanoparticles of MnBi with high anisotropy $K_V$ were chosen to see how $R_{C2}$ changes with $\beta$ at $K_S = 0$ for $\alpha = 0$ nm, 10 nm, 100 nm (Fig.18).

![Image of graph showing $R_{C2}$ vs. $\beta$ for MnBi nanoparticles with different $\alpha$ values and $K_S = 0$.](image)

**Figure 18.** The effect of $\beta$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of MnBi nanoparticles when $\alpha = 0$ nm, 10 nm, 100 nm, and $K_S = 0$.

From Fig. 18, the critical radius $R_{C2}$ for MnBi nanoparticles with a high volume anisotropy, $K_V = 10^6$ J/m$^3$, decreases with increasing value of $\beta$ which is related to decreasing strength of the exchange interaction constant between magnetic moments close to the surface of the nanoparticles. As we previously discussed, the interaction between magnetic moments (spins)
close to the surface decreases and so Curie temperature. Magnetic moments (spins) at the surface of spherical nanoparticles have fewer nearest neighbors than inside of it.

In addition, ferromagnetic nanoparticles of MnBi with high anisotropy $K_V$ were chosen to see how $R_{C2}$ changes with $\alpha$ at $K_S = 0$ for $\beta = 0$ nm, 10 nm, 100 nm (Fig.19).

![R$_{C2}$ vs. $\alpha$ of MnBi nanoparticles for $K_S = 0$](image)

**Figure 19.** The effect of $\alpha$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of MnBi nanoparticles when $\beta = 0$ nm, 10 nm, 100 nm, and $K_S = 0$.

From Fig.19, the critical radius $R_{C2}$ for MnBi nanoparticles with a high volume anisotropy, $K_V = 10^6$ J/m$^3$, increases with increasing value of $\alpha$ which is related to decrease of the saturation magnetization close to the surface of the nanoparticles. As we previously discussed, the interaction between magnetic moments (spins) close to the surface decreases and so saturation magnetization. The surface parameter $\alpha$ is connected with the saturation magnetization (see Eq. (36)) leading to the lower value than it is in the bulk.

Finally, ferromagnetic nanoparticles of MnBi with high anisotropy $K_V = 10^6$ J/m$^3$ were chosen to see how $R_{C2}$ changes with $K_S$ at $\alpha = 0$ and $\beta = 0$ (Fig.20), and at $\beta = 10$ nm, $\alpha = 0$ nm, 10 nm, 100 nm (Fig.21), and at $\alpha = 10$ nm, $\beta = 0$ nm, 10 nm, 100 nm (Fig.21).
Figure 20. The effect of $K_S$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of MnBi nanoparticles when $\alpha = \beta = 0$.

Figure 21. The surface effect of $K_S$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of MnBi nanoparticles when $\beta = 10$ nm and $\alpha = 0$ nm, 10 nm, and 100 nm.
Figure 22. The surface effect of $K_S$ in the critical radius $R_{C2}$ between single- and multi-domain configurations of MnBi nanoparticles when $\alpha = 10 \text{ nm}$ and $\beta = 0 \text{ nm, 10 nm, and 100 nm}$. 

In Figs.20-22, we can see how the surface anisotropy $K_S$ affects the nanoparticle’s radius $R_{C2}$ when the single-domain structure transfers to its multi-domain structure. We can conclude from Figs.20-22 that when the surface anisotropy increases then the critical radius $R_{C2}$ increases. Let us compare our theoretical values of MnBi critical radius $R_{C2}$ with experimental data available in the literature. We have from Tab. 1 that experimental values of diameter for ferromagnetic nanoparticles (MnBi) are $R_{C2} = 500 \text{ nm, 250 nm, and 165 nm}$ [30, 31]. The average value of the critical radius of MnBi nanoparticle is $R_{C2} = 305 \text{ nm}$. This experimental critical radius value is less than the theoretical value equal to $R_{C20} = 556 \text{ nm}$. The possible explanation of existing discrepancy lies in the surface effect. Namely, a parameter $\beta$ which is connected with the exchange integral (see Eq. (48)), plays a role in decreasing the experimental critical radius for MnBi nanoparticles as far as its comparison with the theoretical value is concerned. 

Let us calculate the value of $\beta$ for $R_{C2} = 305 \text{ nm}$, and set $\alpha$ and $K_S = 0$. Under these conditions, replacing $R_{C20} = 556 \text{ nm}$ and $R = 305 \text{ nm}$ in Eq. (50), $\beta$ constant algebraically calculated or
chosen from a plot represented in Fig. 18 results in the value of $\beta = 213$ nm. Let us calculate the exchange integral $J(R)$ for MnBi at $R = R_{C2} = 305$ nm by using Eq. (48). Eq. (59) describes relationship between exchange integral $J(R_{C2})$ modified by a presence of surface effect with respect to the value of $J_0$ [32, 33] for the bulk material of MnBi with $T_C = 670$ K [17], lattice constant $a = 4.28 \times 10^{-10}$ m [34], $A = 1.98 \times 10^{-11}$ J/m, $K_v = 10^6$ J/m$^3$, and $M_{s0} = 4.78 \times 10^4$ A/m has the following form

$$J(R_{C2}) = \frac{92}{305} J_0 \text{ for MnBi} \quad (59)$$

From Eq. (59), we can conclude that the exchange integral with surface effect is weaker than for bulk for MnBi.

Ferromagnetic nanoparticles of FePt with high anisotropy $K_v = 6.6 \times 10^6$ J/m$^3$, $A = 6.312 \times 10^{-9}$ J/m, and $M_{s0} = 1.14 \times 10^6$ A/m [35] were chosen, as a second example, to see how $R_{C2}$ changes with $\beta$ at $K_S = 0$ for $\alpha = 0$ (Fig. 23), with $\alpha$ at $K_S = 0$ for $\beta = 0$ (Fig. 24), and with $K_S$ at $\alpha = 0$ for $\beta = 0$ (Fig. 25) based on the numerical solution of Eq. (50). This solution includes a surface effect on the critical radius $R_{C2}$. A value of $R_{C20} = 44.8$ nm used in this calculation, was based on Eq. (51) which allows to estimate this value from existing material constants for FePt magnetic nanoparticles.
**Figure 23.** The effect of $\beta$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of FePt nanoparticles when $\alpha = 0$ and $K_S = 0$.

**Figure 24.** The effect of $\alpha$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of FePt nanoparticles when $\beta = 0$ and $K_S = 0$. 
Figure 25. The effect of $K_S$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of FePt nanoparticles when $\alpha = 0$ and $\beta = 0$.

From Figs. 23, 24, and 25, we can see the effects of $\alpha$, $\beta$, and $K_S$ on the critical size $R_{C2}$ between single-domain and multi-domain configurations, which are showing the same effect on $R_{C2}$ as discussed before for MnBi nanoparticles. From Tab. I, the experimental result of the average critical size of FePt nanoparticle is 27.5 nm [36] which also less than the theoretical value we calculated.

Let us calculate the value of $\beta$ for $R_{C2} = 27.5$ nm, and set $\alpha = 0$ and $K_S = 0$. Under these conditions, replacing $R_{C20} = 44.8$ nm and $R = 27.5$ nm in Eq. (50), $\beta$ constant algebraically calculated or chosen from a plot represented in Fig.23 results in the value of $\beta = 17.1$ nm. Let us calculate the exchange integral $J(R)$ for FePt at $R = R_{C2} = 27.5$ nm by using Eq. (48). Eq. (60) describes relationship between exchange integral $J (R_{C2})$ modified by presence of surface effect with respect to the value of $J_0$ [35] for the bulk material of FePt with $T_C = 750$ K [33, 35], lattice
constant $a = 3.8 \times 10^{-10}$ m, $K_V = 6.60 \times 10^6$ J/m$^3$, $A = 6.312 \times 10^{-9}$ J/m, and $M_{S0} = 1.14 \times 10^6$ A/m [35, 37, 38] has the following form

$$J(R_{C2}) = (10.4/27.5) J_0 \text{ for FePt} \quad (60)$$

From Eq. (60), we can conclude that the exchange integral with surface effect is weaker than for bulk for FePt.

Ferromagnetic nanoparticles of CoPt with high anisotropy $K_V = 4.9 \times 10^6$ J/m$^3$ [35] were chosen, as a third example, to see how $R_{C2}$ changes with $\beta$ at $K_S = 0$ for $\alpha = 0$ (Fig. 26), with $\alpha$ at $K_S = 0$ for $\beta = 0$ (Fig. 27), and with $K_S$ at $\alpha = 0$ for $\beta = 0$ (Fig. 28) based on the numerical solution of Eq. (50). This solution includes a surface effect on the critical radius $R_{C2}$. A value of $R_{C20} = 78.3$ nm used in this calculation, was based on Eq. (51) which allows to estimate this value from existing material constants for CoPt magnetic nanoparticles, namely, $M_{S0} = 8 \times 10^5$ A/m and $A = 6.28 \times 10^{-9}$ J/m [35, 37].

![Diagram](image)

**Figure 26.** The effect of $\beta$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of CoPt nanoparticles when $\alpha = 0$ and $K_S = 0$. 

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Figure 27. The effect of $\alpha$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of CoPt nanoparticles when $\beta = 0$ and $K_S = 0$.

Figure 28. The effect of $K_S$ on the critical radius $R_{C2}$ between single- and multi-domain configurations of CoPt nanoparticles when $\alpha = 0$ and $\beta = 0$.

For CoPt magnetic nanoparticle, we can predict the experimental result of the critical size of the transition between single-domain and multi-domain structures to be less than $R_{C20} = 78.3$ nm.
SURFACE EFFECT ON THE CRITICAL DIMENSION $R_{C2}$ OF LOW ANISOTROPY FERROMAGNETIC NANOPARTICLES

For low anisotropy ferromagnetic nanoparticle such as Fe, we can study the surface effect on the critical dimension of $R_{C2}$. From Figs. 16 and 17, the critical dimension between single- and multi-domain structure with no surface effect is $R_{C20} = 8.5$ nm. The experimental value of $R_{C2} = 9.1$ nm for Fe (Tab. I) is slightly higher than the theoretical value of $R_{C20}$. The only plausible explanation for increase in the critical radius $R_{C2}$ between single-domain and multi-domain regions for low anisotropy is due to the surface effect related to modification of surface magnetization $M_S$ described by parameter $\alpha$ (see Eq. (36)). From Fig.16, we can estimate a value of $\alpha = 0.5$ nm for $R_{C2} = 9.1$ nm. It leads to a modified value of saturation magnetization (Eq. (61))

$$M_S(R_{C2}) = \frac{8.6}{9.1} M_{S0} \text{ for Fe}$$

(61)

where $M_{S0} = 1.71 \times 10^6$ A/m.

We can conclude that the saturation magnetization due to the surface effect in magnetic nanoparticle is lower than the saturation magnetization for the bulk sample.

Table I. Experimental results of critical dimensions $R_{C2}$ (critical radius of transition between single- and multi-domain structure) for different magnetic nanoparticles.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$R_{C2}$(nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnBi</td>
<td>500</td>
<td>[31]</td>
</tr>
<tr>
<td>MnBi</td>
<td>165,250</td>
<td>[30]</td>
</tr>
<tr>
<td>FePt</td>
<td>27.5</td>
<td>[36]</td>
</tr>
<tr>
<td>CoPt</td>
<td>&gt;78.5</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>9</td>
<td>[18,28]</td>
</tr>
<tr>
<td>Fe</td>
<td>9.15</td>
<td>[39]</td>
</tr>
<tr>
<td>Fe</td>
<td>9.925</td>
<td>[40]</td>
</tr>
<tr>
<td>Co</td>
<td>8.5</td>
<td>[39]</td>
</tr>
</tbody>
</table>
SURFACE EFFECT ON THE CRITICAL DIMENSION $R_{C1}$ (SUPERPARAMAGNETIC LIMIT) HIGH ANISOTROPY FERROMAGNETIC NANOPARTICLES

The single-domain magnetic nanoparticles MnBi after further reduction in diameter approach a superparamagnetic limit at $R = R_{C10}$. By using anisotropy constant $K_V = 10^6$ J/m$^3$ for MnBi and Eq. (54), we can predict theoretically that the superparamagnetic limit diameter of MnBi nanoparticles $R_{C10} = 2.93$ nm at the room temperature. A numerical solution of Eq. (55) or Eq. (56) shows how the surface anisotropy $K_S$ affects a critical diameter $R_{C1}$ describing transition between single-domain and superparamagnetic phase. The constants values for MnBi magnetic nanoparticles were chosen as follows: $K_V = 10^6$ J/m$^3$, $\tau_m = 100$ s, $\tau_0 = 10^9$ s, and $T = 300$ K. The result of numerical calculations $R_{C1}$ as a function of $K_S$ is represented by a plot in Fig.29.

Figure 29. The effect of surface anisotropy $K_S$ on the critical radius $R_{C1}$ between single-domain structure and superparamagnetic phase of MnBi magnetic nanoparticles.
The experimental result of the critical size $R_{C1}$ between single-domain structure and superparamagnetic phase can be predicted to be smaller than the theoretical size $R_{C10} = 2.93$ nm due to the surface effect.

FePt magnetic nanoparticles with high anisotropy $K_V = 6.6 \times 10^6$ J/m$^3$ at $T = 300$ K with $\tau_0 = 10^{-9}$ s and $\tau_m = 100$ s leads to the critical radius of superparamagnetic phase transition $R_{C10} = 1.56$ nm (see Eq. (54)) without presence of the surface effect $K_S$. We can see from it that theoretical calculation results in the critical dimension where transition between single-domain and superparamagnetic phase takes place for FePt at $R_{C10} = 1.56$ nm. Comparing it with experimental results for $R_{C1}$ (FePt) as listed in Tab. II, we see that the experimental value in average is slightly lower and equal to $R_{C1} = 1.465$ nm [41, 42, 43]. The discrepancy suggests an importance of surface effects governed by the surface anisotropy constant $K_S$ to explain existing differences between experimental and theoretical values.

From Fig. 30, we see that when the surface anisotropy constant $K_S$ increases, the critical radius $R_{C1}$ of superparamagnetic dimension of magnetic nanoparticles decreases. This is exactly what experimental results for magnetic nanoparticles of FePt shows.

In order to calculate the value of the surface anisotropy $K_S$ for FePt nanoparticles, we replace in Eq. (55), $R_{C1} = 1.465$ nm, $R_{C10} = 1.56$ nm, $K_V = 6.6 \times 10^6$ J/m$^3$ to get Eq. (62)

$$R_{C1}^3 + 3R_{C1}^2 \frac{K_S}{K_V} - R_{C10}^3 = 0$$

(62)

with the value for $K_S$ and $K_{eff}$ (Eq. (63))

$$K_S = 6.3 \times 10^{-4} \, J/m^2 \quad , \quad K_{eff} = K_V + \frac{3}{R_{C1}} K_S = 7.89 \times 10^6 \, J/m^3 \quad \text{for FePt}$$

(63)

Effective anisotropy $K_{eff}$ with surface anisotropy $K_S$ is stronger than $K_V$ for the bulk sample.
Figure 30. The effect of surface anisotropy $K_S$ on the critical radius $R_{C1}$ between single-domain structure and superparamagnetic phase of FePt magnetic nanoparticles.

CoPt magnetic nanoparticles with high anisotropy $K_V = 4.9 \times 10^6$ J/m$^3$ [35, 44] at $T = 300$ K with $\tau_0 = 10^{-9}$ s and $\tau_m = 100$ s leads to the critical radius of superparamagnetic phase transition $R_{C10} = 1.72$ nm (see Eq. (54)) without presence of the surface effect $K_S$. We can see from it that theoretical calculation results in the critical dimension where transition between single-domain and superparamagnetic phase takes place for CoPt at $R_{C10} = 1.72$ nm. Comparing it with experimental results for $R_{C1}$ (CoPt) as listed in Tab. II, we see that the experimental value in average is slightly lower and equal to $R_{C1} = 1.45$ nm [45, 46]. The discrepancy suggests an importance of surface effects governed by the surface anisotropy constant $K_S$ to explain existing differences between experimental and theoretical values.

From Fig.31, we see that when the surface anisotropy constant $K_S$ increases, the critical radius $R_{C1}$ of superparamagnetic dimension of magnetic nanoparticles decreases. This is exactly what experimental results for magnetic nanoparticles of CoPt show.
In order to calculate the value of the surface anisotropy $K_S$ for CoPt nanoparticles, we replace in Eq. (55), $R_{C1} = 1.45$ nm, $R_{C10} = 1.72$ nm, $K_V = 4.9 \times 10^6$ J/m$^3$ to get Eq. (64)

$$K_S = 1.6 \times 10^{-3} \text{ J/m}^2, \quad K_{\text{eff}} = K_V + \frac{3}{R_{C1}}K_S = 8.2 \times 10^6 \text{ J/m}^3 \quad \text{for CoPt}$$

Also, $K_{\text{eff}}$ for CoPt magnetic nanoparticles with the surface effect is stronger than $K_V$ for the bulk sample.

**SURFACE EFFECT ON THE CRITICAL DIMENSION $R_{C1}$ (SUPERPARAMAGNETIC LIMIT) OF LOW ANISOTROPY FERROMAGNETIC NANOPARTICLES**

Let us choose Fe, as an example, for low anisotropy magnetic nanoparticles with $K_V = 4.8 \times 10^4$ J/m$^3$ [15]. We have calculated $R_{C10}$ theoretically for Fe by using Eq. (54) resulting in value of $R_{C10} = 8.1$ nm. If we compare this result with experimental data in the Tab. II we can tell that the size of the superparamagnetic limit of iron experimentally is equal to $R_{C1} = 4.75$ nm, which is less than theoretical value of 8.1 nm which can be due to surface anisotropy $K_S$ (see Fig. 32).
Figure 32. The effect of surface anisotropy $K_S$ on the critical radius $R_{C1}$ between single-domain structure and superparamagnetic phase of Fe magnetic nanoparticles.

In order to calculate the value of the surface anisotropy $K_S$ for Fe nanoparticles, we replace in Eq. (55), $R = R_{C1} = 4.75$ nm, $R_{C10} = 8.10$ nm, $K_V = 4.8 \times 10^4$ J/m$^3$ to get Eq. (65)

$$K_S = 2.9 \times 10^{-4} \text{ J/m}^2, \quad K_{eff} = 2.3 \times 10^5 \text{ J/m}^3 \quad \text{for Fe}$$

(65)

$K_{eff}$ for Fe magnetic nanoparticles with the surface effect is stronger than $K_V$ for the bulk sample.

Table II. Critical dimensions $R_{C1}$ (critical radius of nanoparticles describing transition from single-domain structure to superparamagnetic phase) for different magnetic materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$R_{C1}$ (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePt</td>
<td>1.5</td>
<td>[41]</td>
</tr>
<tr>
<td>FePt</td>
<td>1.4</td>
<td>[42]</td>
</tr>
<tr>
<td>FePt</td>
<td>1.5</td>
<td>[43]</td>
</tr>
<tr>
<td>CoPt</td>
<td>1.5</td>
<td>[45]</td>
</tr>
<tr>
<td>CoPt</td>
<td>1.4</td>
<td>[46]</td>
</tr>
<tr>
<td>Fe</td>
<td>4</td>
<td>[40]</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>[28]</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>[18]</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>[39]</td>
</tr>
</tbody>
</table>
XI. CONCLUSION AND FUTURE GOALS

There are two types of critical dimensions in magnetic nanoparticles: one $R_{C2}$ is the critical dimension between single- and multi-domain structures while the other $R_{C1}$ is the critical dimension between single-domain configuration and superparamagnetic phase. In this paper, we have derived two equations (see, Eqs. (23) and (30)) for critical dimensions $R_{C2}$ in the case of weak and strong bulk anisotropy $K_V$, respectively. Eq. (35) describes a value of critical dimension of $R_{C1}$ applicable simultaneously to weak and strong bulk anisotropy. However, the surface atoms in magnetic nanoparticles experience different environments than those in the center of the nanoparticles causing a modification of magnetic properties at the surface as far as exchange interaction $J$, saturation magnetization $M_s$, and anisotropy $K_V$ are concerned. Atomic vacancies, changes in the atomic coordination, dangling bonds or lattice disorder at the surface of magnetic nanoparticles as possible surface defects can result in an extra surface magnetization due to the presence of the surface uncompensated magnetic moments. In addition, a presence of non-uniform strains in the surface layers could result in a stress-induced surface anisotropy. In summary, the finite size effect of magnetic nanoparticles could include apart from randomly oriented uncompensated surface moments, the presence of canted or spin-glass behavior of the surface moments, a magnetically dead layer at the surface or it can lead to the enhancement of the magnetic anisotropy which results from surface anisotropy.

Surface effects on critical dimensions $R_{C1}$ and $R_{C2}$ are main goals of my Thesis. Because of many aspects of involvement of surface on these transitions, as we mentioned above, my empirical approach includes a general renormalization of three fundamentals magnetic constants in the surface area of magnetic nanoparticles. We have postulated the surface effects on the saturation magnetization $M_s$ by introducing a parameter $\alpha$ (Eq. (36)), on the exchange integral $J$
a parameter \( \beta \) (Eqs. (37) and (48)), and on the anisotropy constant \( K_V \) a parameter \( K_S \) (Eq. (47)).

As results of these modifications, new equations for critical dimensions were derived. First, a critical dimension \( R_{C2} \), which includes surface effects, for transition from single- to multi-domain structure was defined as a solution of Eqs. (50) and (52) for weak and strong bulk anisotropy, respectively. A critical dimension \( R_{C1} \) from single domain to superparamagnetic phase modified by surface effect is a solution of Eq. (56). Numerical results for upper critical dimension of \( R_{C2} \) as a function of surface effects described by parameters \( \beta \) (J), \( \alpha \) (\( M_S \)), and \( K_S \) (\( K_V \)), for example, in the case of MnBi magnetic nanoparticles with a strong bulk anisotropy \( K_V \) are depicted in Figs.18-20, respectively (see Tab. III). Another two cases of FePt and CoPt magnetic nanoparticles with the strong bulk anisotropy were studied and changes of \( R_{C2} \) due to surface modifications are presented in Figs.23-28 and Tab. III. Fe magnetic nanoparticles with a low bulk anisotropy (Tab. III) were chosen to demonstrate how surface effects \( R_{C2} \) critical dimension by changing \( \alpha \) (Fig.16) and \( \beta \) (Fig.17). In general, it is clearly shown in Figs.16-28 that an upper critical dimension \( R_{C2} \) for transition from single- to multi-domain structures decreases due to surface modification of exchange interaction described by parameter \( \beta \) and increases as result of surface modification of spontaneous magnetization and surface anisotropy.

**Table III.** Summary of theoretical \( R_{C20} \) (without surface effect) and experimental value of \( R_{C2} \) modified by its surface and their physical parameters at room temperature.

<table>
<thead>
<tr>
<th>Magnetic Nanoparticles</th>
<th>( K_V ) (10^4 J/m^3)</th>
<th>( M_{S0} ) (10^4 A/m)</th>
<th>( R_{C20} ) (nm)</th>
<th>( R_{C2} ) (nm)</th>
<th>( \alpha ) (nm)</th>
<th>( \beta ) (nm)</th>
<th>( J(R_{C2})/J_0 )</th>
<th>( M_S(R_{C2})/M_{S0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnBi</td>
<td>1.0</td>
<td>4.78</td>
<td>556</td>
<td>305</td>
<td>-</td>
<td>213</td>
<td>0.302</td>
<td>-</td>
</tr>
<tr>
<td>CoPt</td>
<td>4.9</td>
<td>80</td>
<td>78.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FePt</td>
<td>6.6</td>
<td>114</td>
<td>44.8</td>
<td>27.5</td>
<td>-</td>
<td>17.1</td>
<td>0.378</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.048</td>
<td>171</td>
<td>8.5</td>
<td>9.1</td>
<td>0.5</td>
<td>-</td>
<td>0.945</td>
<td>-</td>
</tr>
</tbody>
</table>

described by parameters \( \alpha \) and \( K_S \), respectively.
Table IV. Summary of theoretical $R_{C10}$ (without surface effect) and experimental value of $R_{C1}$ modified by its surface and their physical parameters at room temperature.

<table>
<thead>
<tr>
<th>Magnetic Nanoparticles</th>
<th>$K_V$ $(10^6 \text{J/m}^3)$</th>
<th>$M_{S0}$ $(10^4 \text{A/m})$</th>
<th>$R_{C10}$ (nm)</th>
<th>$R_{C1}$ (nm)</th>
<th>$K_S$ $(10^3 \text{J/m}^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnBi</td>
<td>1.0</td>
<td>4.78</td>
<td>2.93</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoPt</td>
<td>4.9</td>
<td>80</td>
<td>1.72</td>
<td>1.45</td>
<td>1.60</td>
</tr>
<tr>
<td>FePt</td>
<td>6.6</td>
<td>114</td>
<td>1.56</td>
<td>1.465</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe</td>
<td>0.048</td>
<td>171</td>
<td>8.10</td>
<td>4.75</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Numerical result for lower critical dimension of $R_{C1}$ as a function of surface effect described only by parameter $K_S$ ($K_V$), for example, in the case of MnBi magnetic nanoparticles with a strong bulk anisotropy $K_V$ is depicted in Fig.29 (see Tab. IV). Another two cases of FePt and CoPt magnetic nanoparticles with the strong bulk anisotropies were studied and changes of $R_{C1}$ due to surface modifications are presented in Figs.30-31 and Tab. IV. Fe magnetic nanoparticles with a low bulk anisotropy (Tab. IV) were chosen to demonstrate how surface effects $R_{C1}$ critical dimension by changing $K_S$ (Fig.32). In general, it is clearly shown in Figs.29-32 that a lower critical dimension $R_{C1}$ for transition from single domain structure to superparamagnetic phase decreases due to surface modification of anisotropy described by parameter $K_S$. This numerical dependence of $R_{C1}$ versus $K_S$ can be confirmed analytically from existing exact solution $R_{C1}$ expressed by Eq. (56). By assuming a small perturbation from $K_S$ to the critical dimension $R_{C1}$, it is very easy to show that (Eq. (66))

$$R_{C1} = R_{C10}[1 - K_S/(K_V R_{C10}) - (2/3)[K_S/(K_V R_{C10})]^3]$$

(66)

The surface effect on the critical dimensions $R_{C1}$ and $R_{C2}$ of magnetic nanoparticles at different temperatures will be studied theoretically and results of these calculations will be compared with existing experimental data. In addition to experimental data use in our current calculations (Tabs. I and II), Appendix contains extra Tabs. V and VI with a summary of available theoretical and experimental values of $R_{C1}$ and $R_{C2}$ based on thorough literature search.
XII. REFERENCES


XIII. APPENDIX

Table V. The critical dimensions $R_{C1}$ (critical radius of nanoparticles describing transition from single-domain structure to superparamagnetic phase) for different magnetic materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$R_{C1}$(nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCo</td>
<td>8</td>
<td>[29]</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>16.5</td>
<td>[29]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>21</td>
<td>[47]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>8.25</td>
<td>[48]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>10.5</td>
<td>[29]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$(oleic acid coating)</td>
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<td>[48]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
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<td>[49]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>12.5-15</td>
<td>[50]</td>
</tr>
<tr>
<td>Fe</td>
<td>10</td>
<td>[17]</td>
</tr>
<tr>
<td>Fe</td>
<td>16</td>
<td>[29]</td>
</tr>
<tr>
<td>Fe</td>
<td>13</td>
<td>[41]</td>
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<td>[51]</td>
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<td>Fe</td>
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<td>[52]</td>
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<td>Fe (bcc)</td>
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<td>FePt</td>
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<td>[29]</td>
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<td>[53]</td>
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<td>[56]</td>
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<td>CoPt3</td>
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<td>15</td>
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<td>Ni (fcc)</td>
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<td>Co</td>
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Table VI. The critical dimensions $R_{C2}$ (critical radius of nanoparticles describing transition from single- to multi-domain structure) for different magnetic materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$R_{C2}$ (nm)</th>
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<td>FePt</td>
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