1 Magnetism

1.1 Introduction

Over the past several decades, amorphous and more recently nanocrystalline materials have been investigated for applications in magnetic devices requiring magnetically soft materials such as transformers, inductive devices, etc. Most recently, research interest in nanocrystalline soft magnetic alloys has dramatically increased. This is due, in part, to the properties common to both amorphous and crystalline materials and the ability of these alloys to compete with their amorphous and crystalline counterparts. The benefits found in the nanocrystalline alloys stem from their chemical and structural variations on a nanoscale which are important for developing optimal magnetic properties.

In the following sections, we will first revisit the magnetic properties of matter and then pass on to discuss about the magnetic nanomaterials.

1.1.1 Concept

The magnetic field parameters at a given point in space are defined to be the magnetic field strength $H$, the magnetic flux density or magnetic induction $B$ and the magnetization of the material $M$. Inside a magnetic material:

$$ B = \mu_0 (H + M) \quad (1.1) $$

$\mu_0 = 4\pi \times 10^{-7} \text{ H/m}$ is the permeability of free space. $(H = \text{Henry, Vs/A})$

We can also define the magnetic field parameters by this way:

$$ B = \mu_0 H (1 + \chi) = \mu H \quad (1.2) $$

Where $\mu = \mu_0 (1 + \chi)$ is the permeability of the material and $\chi = M/H$ is the magnetic susceptibility of the material.

Finally, we need to define the magnetic moment, $\mu_m$, through the following equation:

$$ M = \mu_m / V \quad (1.3) $$
It needs to be noted that in magnetic theory several unit systems are commonly in use. Historically, workers in magnetic materials have used the cgs (centimetre, gram, second) or Gaussian system. More recently attempts have been made to change over the SI system. As you can see on the next figure, two SI systems are used; we will focus on the Sommerfield convention.

**Table 1-1 : Magnetic units.** A is ampere, cm is centimeter, m is meter, emu is electromagnetic unit, B is magnetic induction, H is magnetic field strength, M is magnetization of a substance per unit volume.


<table>
<thead>
<tr>
<th>Quantity</th>
<th>cgs (emu)</th>
<th>SI (Sommerfeld)</th>
<th>SI (Kennelly)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>gauss</td>
<td>tesla</td>
<td>tesla</td>
</tr>
<tr>
<td>H</td>
<td>oersted</td>
<td>A m⁻¹</td>
<td>A m⁻¹</td>
</tr>
<tr>
<td>M</td>
<td>emu cm⁻³</td>
<td>A m⁻¹</td>
<td>–</td>
</tr>
<tr>
<td>I</td>
<td>–</td>
<td>–</td>
<td>tesla</td>
</tr>
<tr>
<td>Field equation</td>
<td>B = H + 4πM</td>
<td>B = μ₀(H + M)</td>
<td>B = μ₀H + I</td>
</tr>
<tr>
<td>Energy</td>
<td>E = −μ · H</td>
<td>E = −μ₀μ · H</td>
<td>E = −μ · H</td>
</tr>
</tbody>
</table>

### 1.1.2 Phenomena

#### 1.1.2.1 Atomic origins

Magnetic fields are a result of moving charges. From an atomic view of matter, there are two electronic motions:

- the orbital motion of the electron (revolution of electron around the core)
- and the spin motion of the electron (revolve around its own axis).

These two electron motions are the source of macroscopic magnetic phenomena in materials.

#### 1.1.2.2 Classification of magnetic phenomena

We use the word magnetism very loosely when implying the mutual magnetic attraction of pieces of iron. There are, however, several classes of magnetic materials that differ in kind and degree in their mutual interaction. We shall distinguish in the following between:

- **Ferromagnetism:** Imagine the external field strength is increased (in a ferromagnetic solid), then the magnetization rises at first slowly and then more rapidly. Finally, \( M \) levels off and reaches a constant value, called the saturation magnetization \( M_s \). When \( H \) is reduced to zero, the magnetization retains a positive value, called the remanent magnetization or remanence \( M_r \). It is this retained
magnetization which is utilized in permanent magnets. The remanent magnetization can be removed by reversing the magnetic field strength to a value $H_c$, called the coercive field.

- **Paramagnetism**: Without an external magnetic field, orbiting electrons magnetic moments are randomly oriented and thus they mutually cancel one another. As a result, the net magnetization is zero. However, when an external field is applied the individual magnetic vectors tend to turn into the field direction, which is counteracted by thermal agitation alignment (see the Curie law).

- **Diamagnetism**: may be explained by postulating that the external magnetic field induces a change in the magnitude of inner-atomic currents, that is, the external field accelerates or decelerates the orbiting electrons, in order that their magnetic moment is in the opposite direction from the external magnetic field.

- **Antiferromagnetism**: Antiferromagnetic materials exhibit, just as ferromagnetics a spontaneous alignment of moments below a critical temperature. However, the responsible neighbouring atoms in antiferromagnetics are aligned in an antiparallel fashion. Antiferromagnetic materials are paramagnetic above the Neel temperature $T_N$.

- **Ferrimagnetism**: Ferrimagnets are similar to antiferromagnets in that two sublattices exist that couple through a superexchange mechanism to create an antiparallel alignment. However the magnetic moments on the ions of the sublattices are not equal and hence they do not cancel; rather, a finite difference remains to leave a net magnetization. This spontaneous magnetization is defeated by the thermal energy above the Curie temperature, and then the system is paramagnetic having a nonlinear $1/x$ versus $T$ relationship.

![Figure 3.7 B-H curves](image_url)  
Figure 3.7 B-H curves. (a) Non magnets, (b) soft magnets, (c) hard magnets
1.2 Magnetic Properties of small atomic clusters

1.2.1 Introduction

One of the areas of cluster research currently being pursued is the investigation of the magnetic properties of small atomic clusters. Since large numbers of atoms of the clusters are on the surface, one expects the clusters of these elements to exhibit larger magnetic moments. Being small particles, it is possible to measure the magnetic moment directly by measuring the interaction with a magnetic field in terms of their deflection from the original trajectories.

1.2.2 Size dependence

The magnetic moment of transition metals decreases in general with the increase of number of atoms (size) in the clusters. However, the moment of different transition metal clusters are found to depend differently on the number of atom per clusters (N).

---

**Figure 1-1:** Magnetic moment per atom in units of Bohr magnetron for iron, cobalt, nickel and rodium clusters as a function of cluster size (number of atom). The enclosed data points show the sizes of the
respective clusters at which they attain bulk moments. Only the maximum error in the data for each clusters are shown. Iron, cobalt and nickel data are from W. A. de Heer et al. and Billas. The rodinium data is from Cox et. al

Among the ferromagnetic 3d transition metals, Nickel clusters attain the bulk moment at N=150, whereas Cobalt and Iron clusters reach at the corresponding bulk limit at N=450 and N=550 respectively (Figure 1-1). In icosahedral configuration these numbers correspond to 3, 4 and 5 shells respectively. The results show that in the lower size limit the clusters have high spin majority configuration and the behaviour is more like an atom, but with the increase of size an overlap of the 3d-band with the Fermi level occurs, which reduces the moment towards that of the bulk with slow oscillations. In analogy with the layer-by-layer magnetic moments in the studies of surface magnetism, the clusters are assumed to be composed of spherical layers of atoms forming shells and the value of moment of an atom in a particular shell is considered to be independent of the size of cluster. The magnetic moment values of the different shells are optimized to fit with the total moment per atom maintaining the overall trend of observed decrease with size. It is generally observed that the per atom moment for the surface atoms in the 1st layer are close to that of an atom and deep layers correspond the bulk. The intermediate layers show an overall decreasing trend. For both nickel and cobalt, there are oscillations in the values at least up to the 5th shell. For nickel, the second layer is found to have a negative coupling with the surface atoms and the 3rd-4th layers in iron are magnetically dead. The model gives more or less close agreement with the experimental results for cobalt and nickel. But in a more realistic model one has to account for both the geometric shell closing as well as the electronic structure. However this model provides a good first order picture to understand the magnetic behaviour of 3d transition metal clusters.

Though the 4d transition metals are non-magnetic, the small clusters of rhodium are found to be magnetic following the calculations. Within the size range N=10-20, the moment varies between 0.8 to 0.1μB per atom but the clusters become non-magnetic within N=100. Due to reduced size, the individual moments on the atoms in clusters are aligned. First principal calculations show that the ground state of Rh₆ is non-ferromagnetic, while Rh₉, Rh₁₃ and Rh₁₉ clusters have non-zero
magnetic moments. $\text{Rh}_{43}$ is found to be non-magnetic as the bulk. Ruthenium, palladium, Chromium, Vanadium and Aluminium clusters are found to be non-magnetic.

1.2.3 Thermal behaviour

Since ferromagnetic state requires the moments to remain mutually aligned even at relatively high temperatures, it is important to study the thermal behaviour of the magnetic clusters. Temperature dependent studies show that up to 300K the moment remains constant for nickel clusters and then it decreases at higher temperatures resembling closely the bulk behaviour. This indicates that the interactions affecting the mutual alignment of moments with temperature are in the same order of magnitude as in the bulk. $\text{Ni}_{550-600}$ is almost bulk-like. Cobalt clusters also follow the same trend but the moment increases slightly, between 300K to 500K, which might be due to a structural phase transition corresponding to the hcp-fcc phase transition in bulk at 670K, where the moment increases by 1.5%. Clusters of different size ranges of iron behave differently; $\text{Fe}_{50-60}$ shows a gradual reduction of moments from 3$\mu_B$ at 120K to 1.53$\mu_B$ at 800K. Up to 400K, $\text{Fe}_{120-140}$ remains with a constant moment of 3$\mu_B$ and then decreases to finally level off at 700K to 0.7$\mu_B$. The size range $N=82-92$ behaves like $\text{Fe}_{120-140}$ below 400K and like $\text{Fe}_{50-60}$ above 400K. The moment for the higher size ranges decreases steadily with the increase of temperature but $\text{Fe}_{250-290}$ levels off at 700K whereas $\text{Fe}_{500-600}$ levels off between 500-600K to 0.4$\mu_B$. Comparing with the thermal behaviour of bulk iron, the level-off temperature can be termed as the critical temperature ($T_C$) for clusters of a particular size and it decreases with the increase of size of the clusters. But, since the bulk Curie temperature is 1043K, one realizes clearly that this trend must reverse at higher sizes to reach the bulk. It is also interesting to note that for $\text{Fe}_{120-140}$ the moment decreases more rapidly within 600-700K. The specific heat measurement for both $\text{Fe}_{120-140}$ and $\text{Fe}_{250-290}$ also show a peak at 650K. This might be because iron clusters undergo a structural phase transition in this temperature range similar to the bulk iron which undergoes bcc-fcc-bcc phase transition, but only beyond the Curie temperature.
1.2.4 Rare earth clusters

The magnetic interaction in rare earth solids are RKKY type which is mediated by the conduction electrons. RKKY stands for Ruderman-Kittel-Kasuya-Yosida and refers to a coupling mechanism of nuclear magnetic moments or localized inner d or f shell electron spins in a metal by means of an interaction through the conduction electrons. Since in clusters, structure and filling up of the conduction band differs from that in the bulk, rare-earth clusters are expected to exhibit an altogether different magnetism compared to the bulk. Magnetic properties of gadolinium, terbium and dysprosium clusters show a very size-specific behaviour. Gd$_{22}$ behaves super-paramagnetically (1.3.4) but Gd$_{23}$ shows a behaviour like a rigid magnetic rotor as if the moment is locked to the cluster lattice. Gd$_{17}$ shows super-paramagnetism near room temperature but at low temperatures it shows locked-moment behaviour. It indicates that there are at least two groups of clusters sharing the same number of atoms which might correspond to two different isomers, either magnetic or structural. But it is not clear whether the two isomers co-exist in the beam or there occurs a phase transition of any kind. The behaviour of other clusters from N=11-30, is like Gd$_{22}$ or Gd$_{23}$ or Gd$_{17}$. Similar is the case for Tb and Dy clusters. Tb$_{17}$, Tb$_{22}$, Tb$_{27}$, Dy$_{22}$ and Dy$_{27}$ show super-paramagnetic behaviour but Tb$_{23}$ and Tb$_{26}$ show locked-moment behaviour. In fact Tb$_{26}$ is temperature dependent like Gd$_{17}$.

1.3 Small particle magnetism

1.3.1 Classifications of magnetic nanomaterial

The correlation between nanostructure and magnetic properties suggests a classification of nanostructure morphologies. The following classification is designed to emphasize the physical mechanisms responsible for the magnetic behaviour. Figure 1-2 schematically represents the classification. At one extreme are systems of isolated particles with nanoscale diameters, which are denoted by type A. These non-interacting systems derive their unique magnetic properties strictly from the reduced size from the components, with no contribution from interparticle interactions. At the other extreme are bulk materials with nanoscale structure denoted by type D, in
which a significant fraction (up to 50%) of the sample volume is composed of grain boundaries and interfaces. In contrast to type A systems, magnetic properties here are dominated by interactions. The length of the interactions can span many grains and is critically dependent on the character of interface. Due to this dominance of interaction and grain boundaries, the magnetic behaviour of type D nanostructures cannot be predicted simply by applying theories of polycrystalline materials with reduced length scale. In type B particles, the presence of a shell can help prevent particle interactions, but often at the cost of interaction between the core and the shell. In many cases the shells are formed via oxidation and may themselves be magnetic. In type C materials, the magnetic interactions are determined by the volume fraction of the magnetic particles and the character of the matrix they are embedded in.

**Figure 1-2**: Schematic representation of the different types of magnetic nanostructures. **Type-A** materials include the ideal ultrafine particle system, with interparticle spacing large enough to approximate the particles as noninteracting. **Ferrofluids**, in which magnetic particles are surrounded by a surfactant preventing interactions, are a subgroup of Type-A materials. **Type-B** materials are ultrafine particles with a core-shell morphology. **Type-C** nanocomposites are composed of small magnetic particles embedded in a chemically dissimilar matrix. The matrix may or may not be magnetoactive. **Type-D** materials consist of small crystallites dispersed in a noncrystalline matrix. The nanostructure may be two-phase, in which nanocrystallites are distinct phases from the matrix, or the ideal case in which both the crystallites and the matrix are made of the same material.
1.3.1.1 Ferrofluid

A ferrofluid is a synthetic liquid that holds small magnetic particles in a colloidal suspension, with particles held aloft their thermal energy. The particles are sufficiently small that the ferrofluid retains its liquid characteristics even in the pressure of a magnetic field, and substantial magnetic forces can be induced which results in fluid motion.

A ferrofluid has three primary components. The carrier is the liquid element in which the magnetic particles are suspended. Most ferrofluids are either water based or oil based. The suspended materials are small ferromagnetic particles such as iron oxide, on the order of 10 – 20 nm in diameter. The small size is necessary to maintain stability of the colloidal suspension, as particles significantly larger than this could agglomerate. A surfactant coats the ferrofluid particles to help maintain the consistency of the colloidal suspension.

The magnetic properties of the ferrofluid are strongly dependent on particle concentration and on the properties of the applied magnetic field. With an applied field, the particles align in the direction of the field, magnetizing the fluid. The tendency for the particles to agglomerate due to magnetic interaction between particles is opposed by the thermal energy of the particles and by the coating with surfactants. Although, particles vary in shape and size distribution, insight into fluid dynamics can be gained by considering a simple spherical model of the suspended particles.

![Figure 1-3: Representative model of a typical ferrofluid.](image-url)
The particles are free to move in the carrier fluid under the influence of an applied magnetic field, but on average the particles maintain a spacing \( S \) to nearest neighbours. In a low density fluid, the spacing \( S \) is much larger than the mean particle radius \( 2R \), and magnetic dipole – dipole interactions are minimal. Applications for ferrofluids exploit the ability to position and shape the fluid magnetically. Some applications are:

- rotary shaft seals
- magnetic liquid seals, to form a seal between region of different pressures
- cooling and resonance damping for loudspeaker coils
- printing with magnetic inks
- inertial damping, by adjusting the mixture of the ferrofluid, the fluid viscosity may be change to critically damp resonances accelerometers,
- level and attribute sensors
- electromagnetically triggered drug delivery

### 1.3.2 Anisotropy

In many situations the susceptibility of a material will depend on the direction in which it is measured. Such a situation is called magnetic anisotropy. When magnetic anisotropy exists, the total magnetization of a ferromagnet \( M \) will prefer to lie along a special direction called the easy axis. The energy associated with this alignment is called the anisotropy energy and in its lowest form is given by

\[
E_a = K \sin^2 \theta
\]  

(1.4)

Where \( \theta \) is the angle between \( M \) and the easy axis. \( K \) is the anisotropy constant.

Most materials contain some type of anisotropy affecting the behaviour of the magnetization. The most common forms of anisotropy are:

- Crystal anisotropy
- Shape anisotropy
- Stress anisotropy
- Externally induced anisotropy
- Exchange anisotropy.
The two most common anisotropies in nanostructure materials are crystalline and shape anisotropy.

1.3.2.1 Magnetocrystalline anisotropy

Only magnetocrystalline anisotropy, or simply crystal anisotropy, is intrinsic to the material; all other anisotropies are induced. In crystal anisotropy, the ease of obtaining saturation magnetization is different for different crystallographic directions. An example is a single crystal of iron for which Ms is most easily obtained in the [100] direction, then less easy for the [110] direction, and most difficult for the [111] directions. These directions and magnetization curves for iron are given in Figure 1-4. The [100] direction is called the easy direction, or easy axis, and because the other two directions have an overall smaller susceptibility, the easy axis is the direction of spontaneous magnetization when below Tc (Curie Temperature). Both iron and nickel are cubic and have three different axes, whereas cobalt is hexagonal with a single easy axis perpendicular to the hexagonal symmetry. Figure 1-4 also gives magnetization curves for cobalt and nickel.

![Figure 1-4](image-url) Magnetization curves for single crystals of iron, cobalt and nickel along different directions. [K. J Klabunde, Nanoscale Materials in Chemistry, Wiley-Interscience, 2001]

We would now imagine a situation in which the system has spontaneous magnetization along the easy axis but a field is applied in another direction. Redirection of the magnetization to be aligned with the applied field requires energy (through the change in $\vec{M} \cdot \vec{H}$), hence the crystal anisotropy must imply a crystal anisotropy energy given by equation $E_a = K \sin^2 \theta$ (1. 4) for a uniaxial material. This energy is an intrinsic property of the material and is parametrized, to lowest order, by the anisotropy constant $K=K_1$ which has units of energy per volume of material. Roughly speaking $K_1$ is the energy necessary to redirect the magnetization.
For a uniaxial material with only $K_1$, the magnetic field necessary to rotate the magnetization 90° away from the easy axis is

$$H = \frac{2K_1}{M_s} \quad \text{(1. 5)}$$

The physical origin of the magnetocrystalline anisotropy is the coupling of the electron spins, which carry the magnetic moment, to the electronic orbit, which in turn is coupled to the lattice. Recall it was the strong coupling of the orbit to the lattice via the crystal field that quenched the orbital angular momentum.

A polycrystalline sample with no preferred grain orientation has no net crystal anisotropy due to averaging over all orientations.

### 1.3.2.2 Shape anisotropy

It is easier to induce a magnetization along a long direction of a nonspherical piece of material than along a short direction. This is so because the demagnetizing field is less in the long direction, because the induced poles at the surface are farther apart. Thus, a smaller applied field will negate the internal, demagnetizing field. For a prolate spheroid with major axis $c$ greater than the other two and equal axes of length $a$, the shape anisotropy constant is

$$K_s = \frac{1}{2} \left( N_a - N_c \right) M^2 \quad \text{(1. 6)}$$

Where $N_a$ and $N_c$ are demagnetization factors.

For spheres, $N_a = N_c$ because $a = c$.

It can be shown that $2N_a + N_c = 4\pi$; then the limit $c >> a$, that is, a long rod, $K_s = 2\pi M^2$.

Thus a long rod of iron with $M_s = 1714$ A m$^{-1}$ would have a shape anisotropy constant of $K_s = 1.85 \times 10^7$ erg cm$^{-3}$. This is significantly greater than the crystal anisotropy so we see that shape anisotropy can be very important for nonspherical particles.

### 1.3.2.3 Other anisotropy

Stress anisotropy result from internal or external stresses that occur due to rapid cooling, application of external pressure etc. Anisotropy may also be induced by annealing in a magnetic field, plastic deformation, or by ion beam irradiation.

Exchange anisotropy occurs when a ferromagnet is in close proximity to an antiferromagnet or ferromagnet. Magnetic coupling at the interface of the two
materials can create a preferential direction in the ferromagnetic phase, which takes the form of a unidirectional anisotropy. This type of anisotropy is most commonly observed in type – B particles, when an antiferromagnetic or ferromagnetic oxide forms around a ferromagnetic core.

1.3.3 Single Domain Particles

The magnetism of small ferromagnetic particles is dominated by two key features. The first one is the size limit below which the specimen can no longer gain a favourable energy configuration by breaking up into domains, hence it remains with one domain. The second one is the thermal energy that can decouple the magnetization from the particle itself to give rise to the phenomenon of superparamagnetism.

1.3.3.1 The role of the particle volume

The most obvious finite-size effect in magnetic fine-particle systems consists in the fact that each entity (magnetic particle) has a very small volume compared to the typical sizes of the magnetic domains in the corresponding bulk materials. In a sense, the volume of a particle is so small (commonly, a few tens or hundreds of nm3) that it can be considered as a zero-dimension magnetic system, which strongly affects its magnetic behaviour. In real systems, the size of the particles is usually not uniform and distributed following a function \( f(V) \) which is satisfactorily described by a logarithmic-linear distribution of the form

\[
 f(V) = \frac{1}{\sqrt{2\pi \sigma V}} \exp\left[-\frac{\ln^2(V/V_0)}{2\sigma^2}\right]
\]  

(1.7)

Where \( V_0 \) is the most probable particle volume and \( \sigma \) is the standard deviation of \( \ln(V) \).

One fundamental question related to the finite and small volume of the particles is how such volume determines the internal domain structure. In magnetic bulk materials, it is well known that there exists a multidomain structure constituted by regions of uniform magnetization separated by Domain Walls (DWs). The size and shape of these domains depends on the interplay between the exchange, magnetostatic and anisotropy energies of the system. As the volume of the magnetic
system decreases, the size of the domains and the width of the walls are reduced, modifying, at the same time, their inner structure. Below a certain critical volume, the energy cost to produce a DW is greater than the corresponding reduction in the magnetostatic energy. Consequently, the system no longer divides in smaller domains, instead maintaining the magnetic structure of a single domain. This critical value depends on the saturation magnetization of the particle, anisotropy energy and exchange interactions between individual spins. For example, for spherical particles the critical diameter is within 10–800 nm. Typical values for Fe and Co metallic particles are 15 and 35 nm, respectively, while for SmCo₅ it is as large as 750 nm.

In many fine-particle systems, f(V) is narrow and centred at very small V₀ below the critical value, so that all the particles constituting the system can be considered as a single domain.

This is the situation that we are going to assume in what follows. In thermal equilibrium, the resulting magnetization of a particle points in a direction tending to minimize its total anisotropy energy, which for a single-domain particle can be considered as proportional to its volume, at least, in first approximation (Figure 1-6). The total anisotropy of the particle can often be assumed to have uniaxial character, being determined by a single constant K. Therefore, the anisotropy energy can be expressed as

$$E(\theta) = kV \sin^2 \theta$$  \hspace{1cm} (1.8)

where \(\theta\) is the angle between anisotropy axis and magnetization, and \(KV\) is the anisotropy energy barrier (1.3.2) separating both easy directions for magnetization, which in zero magnetic field correspond to \(\theta = 0\) and \(\theta = \pi\). Taking into account the spread of volumes \(f(V)\) given by equation

$$8 f(V) = \frac{1}{\sqrt{2\pi} \sigma V} \exp \left[ -\frac{\ln^2(V/V_0)}{2\sigma^2} \right]$$  \hspace{1cm} (1.7), it is a matter of fact that the magnetization of the particles will behave as if it were driven by an energy barrier distribution \(f(E^0_{\theta})\), where \(E^0_{\theta} = kV\).

Under the application of a magnetic field \(H\) forming an angle \(\psi\) with the anisotropy axis, the energy of a particle is modified as

$$E(\theta) = -KV \sin^2 \theta + HM_S (\cos \theta \cos \psi + \sin \theta \sin \psi \cos \varphi)$$  \hspace{1cm} (1.9)
Where $M_s$ is the spontaneous magnetization of the particle, and the axis system is defined in Figure 1-5. (Spontaneous magnetization is the term used to describe the appearance of an ordered spin state (magnetization) at zero applied magnetic field in a ferromagnetic or ferrimagnetic material below a critical point called the Curie temperature or $T_C$.)

Figure 1-5: Definition of the axis system for a fine particle. The uniaxial-anisotropy axis is along the $z$-axis. [X. Batle, A. Labarta, Finite-size effects in fine particles: magnetic and transport properties, Journal of Physics, 2002, ppR15-R42].

Under zero field, the equilibrium direction for the magnetization vector $M$ coincides with the anisotropy axis, while when a magnetic field is applied, it rotates away from the anisotropy axis towards the field direction, forming an angle $\psi - \theta$ with $H$, and the stability problem can be reduced to a two-dimensional one ($\phi = 0$). In this case, and if $H$ is lower than a certain critical value known as switching field at zero temperature, $H_{SW}^0$, $E(\theta)$ has two minima at different heights which are separated by an energy barrier. When the field is applied opposite to the magnetization, the unstable minimum is separated from the stable one by an energy barrier $E_B$, which can be approximated by the following expression:

$$E_B (H) = E_B^0 \left(1 - \frac{H}{H_{SW}^0}\right)^\kappa$$  \hspace{1cm} (1.10)

Where $\kappa$ is a phenomenological exponent that depends on $\psi$. Consequently, $H_{SW}^0$ is the minimum value of the field at zero $T$, at which $E_B$ vanishes, and the
magnetization inverts its orientation. When H is applied along the anisotropy axis and in the opposite direction to magnetization, equation

\[ E_b(H) = E_b^0 \left( 1 - \frac{H}{H_{SW}^0} \right)^\kappa \]  

(1.10) is exact with \( \kappa = 2 \). In this case, M irreversibly rotates at zero T when \( H = H_{SW}^0 = H_a = 2K/M_s \), where \( H_a \) is the anisotropy field. If H is applied at an arbitrary angle \( \psi \), there is not a simple analytical expression. However, equation (1.10) works quite well with \( \kappa \approx 1.5 \), provided that the applied field forms an angle of a few degrees with the anisotropy axis. On the other hand, Pffeifer gave the following phenomenological approximation for any angle \( \psi \)

\[ E_b(H) = E_b^0 \left( 1 - \frac{H}{H_{SW}^0} \right)^\kappa \]

\[ \kappa = 0.86 + \frac{1.14H_{SW}^0}{H_a} \]  

(1.11)

A method frequently used to characterize the nature and strength of the particle anisotropy consists in the determination of \( H_{SW}^0 \) as a function of \( \psi \). The resulting curve turns to be the so-called Stoner Wohlfarth (SW) astroid. In fact, the SW astroid represents the set of fields (applied opposite to the particle magnetization) at which irreversible jumps occur. For uniaxial anisotropy, \( H_{SW}^0 \) can be evaluated from equation

\[ E(\theta) = -KV \sin^2 \theta + HM_s(\cos \theta \cos \psi + \sin \theta \sin \psi \cos \phi) \]

(1.9) with the conditions \( dE/d\theta = d^2E/d\theta^2 = 0 \), since irreversible jumps occur when the energy barrier vanishes and the maximum in \( E(\theta) \) is substituted by an inflection point. The obtained expression is

\[ H_{SW}^0 = \frac{H_a}{(\sin^{2/3} \psi + \cos^{2/3} \psi)^{3/2}} \]  

(1.12)

Many groups have attempted to study the reversal process in single particles but the experimental precision did not yield quantitative information.
As the particles size continues to decrease (towards some critical particle diameter, $D_c$) below the single domain value, the spins get increasing affected by thermal fluctuations and the system becomes superparamagnetic. Particles with sufficient shape anisotropy can remain single domain to much larger dimensions than their spherical counterparts.

1.3.3.2 Single-Domain Characteristics:

In a granular magnetic solid with a low volume fraction, one has a collection of single domain particles each with a magnetic axis along which all the moments are aligned. In the absence of a magnetic field, parallel and anti parallel orientations along the magnetic axis are energetically equivalent but separated by an energy barrier of $KV$, where $K$ is the total anisotropy per volume, and $V$ is the particle volume. Since the orientation of each single domain remains fixed, under an external field, only the magnetic axes rotate. Thus the measured magnetization $M$ of a granular magnetic field solid with a collection of single domain particles is the global magnetization

$$M = \frac{\langle M \cdot \mathbf{H} \rangle}{H} = M_s \langle \cos \theta \rangle$$

(1.13)

Where $\theta$ is the angle between the magnetic axis of a particle. $M_s$, is the saturation magnetization, $\mathbf{H}$ is the external field, and the average $\langle \cos \theta \rangle$ is taken over many ferromagnetic particles. The hysterisis loop of a granular solid is thus a signature of
the rotation of the magnetic area of the single-domain particles. This should be contrasted with the hysteresis loop of a bulk ferromagnet, in which the sizes and the direction of the domains are altered drastically under an external field.

\[ H \]

\[ M \]

\[ M_S \]

\[ T_B \]

\[ T \]

\[ \chi \]

\[ \chi \]

\[ M_R = M_S/2 \]

\[ (a) \]

\[ (b) \]

\[ (c) \]

\[ (d) \]

\[ Figure 1-7 : (a) Hysterisis loop at 5K; (b) temperature dependence of saturation magnetization \( (M_S) \) and remnant magnetization \( (M_R=M_S/2) \); (c) temperature dependence of field cooled (FC) and zero-field cooled (ZFC) susceptibility. At the blocking temperature \( (T_B) \), \( M_R \) and \( H_C \) vanish, whereas the ZFC susceptibility shows a cusp like feature.

An example of a hysteresis loop of a granular magnetic solid at low temperature is shown in Figure 1-7a. In the initial unmagnetized state with \( M = 0 \) at \( H = 0 \), the magnetic axes of the particles are randomly oriented, each along its own magnetic axis, which is determined by the total magnetic anisotropy of the particles. The directions of the giant moments are random and static at low temperatures. A saturation magnetization \( (M = M_S) \) is realized under a large field when all the magnetic axes are aligned. In the remnant state when \( H \) is reduced to \( H = 0 \), one observes the remnant magnetization \( (M_R) \), whose values at low temperature is \( M_R = M_S/2 \). This is because the magnetic axes are oriented only in one hemisphere due to the uniaxial anisotropy of the single-domain particle.
It should be noted that the initial $M=0$ state and the initial magnetization curve if in Figure 1-7a does not reappear, whereas the field cycle part does. The simple way to recover the initial $M=0$ state is to heat the sample above the blocking temperature and cool the sample in zero field back to low temperatures.

Because of the single domain nature of the magnetic entities, the coercivity ($H_C$) of the ultra fine particles is much higher than that in bulk material.

### 1.3.4 Superparamagnetism

#### 1.3.4.1 The SPM regime

Below the Curie temperature of a ferromagnet or ferrimagnet, all the spins are coupled together and so cooperate to yield a large moment. This moment is bound rigidly to the particle by one or more of the variety of anisotropies that we have discussed (1.3.2). With decreasing particle size, the energy Barrier $E_B$ decreases until the thermal energy $kT$ can disrupt the bonding of the total moment to the particle.

Then this moment is free to move and respond to an applied field independent of the particle. This moment is the particle magnetic moment and is equal to

$$\mu_p = M_S V$$  \hspace{2cm} (1.14)

It can be quite large, thousands of Bohr magnetons. An applied field would tend to align this giant (super) moment, but $kT$ would fight the alignment just as it does in a paramagnet. Thus, this phenomenon is called superparamagnetism.

It is good to notice that if the anisotropy is very weak (zero), one would expect that the total moment $\mu_p$ could point in any direction, hence the Langevin law would apply.

The phenomenon of superparamagnetism is, in fact, timescale-dependent due to the stochastic nature of the thermal energy. The anisotropy energy $E_B$ represents an energy barrier to the total spin reorientation; hence the probability for jumping this barrier is given by Arrhenius law:

$$\tau = \tau_0 \exp\left(\frac{E_B}{kT}\right)$$  \hspace{2cm} (1.15)
Where $\tau_0$ is the attempt time by supposing that the particle spins are rigidly coupled and reverse as a whole. This pre-factor depends on a large variety of parameters: temperature, gyromagnetic ratio, saturation magnetization, energy barrier, direction of the applied field and damping constant. $\tau_0$ is assumed to be constant and equation $\tau = \tau_0 \exp\left(\frac{E_B}{kT}\right)$ (1.15), together with this assumption, is known as the Neel–Brown model. If the characteristic time window of an experiment is much shorter than $\tau$ at a fixed temperature, the particle moment remains blocked during the observation period (blocked regime), while, in the opposite situation, the rapid fluctuations of the particle moment mimics the atomic paramagnetism (SPM regime). In the intermediate regime, the probability that the magnetization has not switched after an observation time $t$ is given by

$$P(t) = \exp\left(-\frac{t}{\tau}\right)$$ (1.16)

A method used to verify the Neel–Brown model in real systems is the scaling of the switching field distributions measured at different $T$ and rates of field ramping. Thermal activation leads to a switching field distribution from the Stoner Wohlfahrt model, the mean switching field being given by

$$H_{SW} = H_{SW}^0 \left[1 - \left(\frac{k_B T}{E_B}\ln\left(\frac{cT}{\nu \varepsilon^{\kappa-1}}\right)\right)^{1/\kappa}\right]$$ (1.17)

Where $c = k_B H_{SW}^0 / (\tau_0 \alpha E_B)$, $\varepsilon = (1 - H / H_{SW}^0)$ and $\nu$ is the field sweeping rate. From the equation above, it is evident that $H_{SW}$ measured at different $T$ and $\nu$ can be collapsed in a single master curve when they are plotted as a function of the scaling variable $\left(\frac{T \ln(cT / \nu \varepsilon^{\kappa-1})}{1/\kappa}\right)$. In fact, the collapse is obtained by choosing the appropriate values of $\kappa$ and $c$ (obtaining $\kappa = 1.5$, as expected for measurements with the field slightly deviated from the anisotropy axis, see paragraph 1.3.3.1). This scaling procedure has been successfully applied to analyse data obtained above about 0.5K from single-particle experiments carried out with different kind of nanoparticles.

At very low temperatures, (below about 0.5 K) strong deviations from the Neel–Brown model have been reported in this kind of scaling when it was applied to single-particle
experiments. The deviations consisted in a saturation of $H_{sw}$ and $\sigma$ (width of the switching field distribution), and a dependence of $H_{sw}$ on $\nu$ faster than the prediction of the Neel–Brown model. All these anomalies have been attributed to the prevalence of a nonthermal process by which the particle magnetization escapes from the metastable state through the energy barrier by macroscopic quantum tunnelling (MQT). The theoretical models propose that there is a crossover temperature $T_B$, below which quantum tunnelling dominates the reversal process, whereas above $T_B$, the escape rate from the metastable state is given by thermal activation, and the Neel–Brown model is accomplished. Consequently, $T_B$ is the temperature at which the thermal and quantum rates coincide.

1.3.4.2 Magnetism relaxation

If the total magnetization of a fine-particle system is measured with an observation time window which for some particle sizes is comparable to their reversal time, $\tau$, the magnetization will evolve during the experiment, a phenomenon known as magnetic relaxation. The study of this non-equilibrium phenomenon is a common method to experimentally characterize the energy spectrum of the system, since it is the macroscopic signature of the distribution of energy barriers separating local minima which correspond to different orientations of the particle moments. Magnetic relaxation experiments are carried out by measuring the time-dependence of the magnetization after the system has been driven out of thermal equilibrium by the application or removal of a magnetic field. For instance, starting from the equilibrium state at a given field and temperature, and then removing the field, the time evolution of the magnetization for noninteracting particles can be written as follows

\[
M(t) = M_0 \int_{E_0}^{E_0 + dE} dE f(E) \exp \left( \frac{-t}{\tau(E)} \right)
\]

Where $f(E)dE$ is the fraction of particles having energy barriers in between $E$ and $E + dE$, and $M_0$ is the initial magnetization. In equation (1.18) and for the sake of simplicity, the particle moment has been assumed to be volume independent, although, in fact, it is proportional to it. This assumption does not significantly affect the results, providing that for a logarithmic-linear
distribution, \( f(E) \) and \( E_f(E) \) (which is equivalent to \( V_f(V) \)) are similarly shaped functions. Let us introduce the function \( p(t, T, E) \), which is defined by

\[
p(t, T, E) = \exp\left[ -\left( \frac{t}{\tau_0} \right) \exp\left( -\frac{E}{kT} \right) \right]
\]  

(1.19)

Taking into account that \( p(t, T, E) \) for a given \( t \) varies abruptly from 0 to 1, as the energy barrier \( E \) increases, we can approximate \( p(t, T, E) \) by a step function whose discontinuity \( E_c(t, T) \) moves towards higher energies as time elapses. Consequently, the integral is cut off at the lower limit by the value of \( E_c(t, T) \) and can be written as

\[
M(t) \simeq M_0 \int_{E_c}^{\infty} dE f(E) \]  

(1.20)

Where \( E_c(t, T) = kBT \ln\left(\frac{t}{\tau_0}\right) \) is the only time-dependent parameter and signals the position of the inflection point of \( p(t, T, E) \). In fact, the narrow energy range spanned by the step at \( E_c(t, T) \) can be understood as the experimental window of the measurements. The experimental window can be swept over \( f(E) \) by varying the temperature or the observation time. From equation (1.20), it can be deduced that \( M(t) \) obtained after integration is a function of the parameter \( E_c(t, T) \), which acts as a scaling variable. The existence of this scaling variable implies that measuring the magnetization as a function of the temperature at a given time is equivalent to measuring the magnetization as a function of \( \ln\left(\frac{t}{\tau_0}\right) \) at a given temperature. This time–temperature correspondence is characteristic of activated processes governed by Arrhenius law. The validity of the scaling hypothesis is only determined by the validity of the cut-off approximation. Therefore, the scaling will be accomplished as long as the width of \( p(t, T, E) \), which is approximately given by \( k_BT \), is small when compared to the width of the energy barrier distribution. Although this condition seems to be very restrictive, it is the usual situation found in experimental observations of the magnetic relaxation in fine-particle systems.

As an example of this scaling method, Figure 1-8 shows the scaling of the relaxation curves obtained at different temperatures for a sample consisting of Fe\(_{0.78}\)C\(_{0.22}\) particles with a mean diameter of 3.6 nm, dispersed in stable dilution with a hydrocarbon oil. In this sample, the dipolar interaction among particles was estimated.
to be very small. Figure 1-8 shows all the relaxation curves corresponding to different temperatures collapsed into a single master curve when plotted as a function of the scaling variable $T \ln(t/\tau_0)$, being $\tau_0 = (3.5 \pm 5) \times 10^{-11}$ s, which is an expected value for ferromagnetic fine particles.

![Figure 1-8](image)

**Figure 1-8**: The resulting scaling for a sample composed of FeC nanoparticles dispersed in a hydrocarbon oil is shown. Open and full circles correspond alternatively to adjoining temperatures, which are indicated above the corresponding interval (K units). The solid line is the theoretical curve calculated by fitting the scaling curve to equation $M(t) \equiv M_0 \int_{E_0}^{\infty} dE f(E)$ \[1.20\] with a logarithmic-linear distribution of energies. The values of the fitted parameters are: $\sigma = 0.44 \pm 0.05$ and $E_0 = 287 \pm 50$K (position of the maximum of the energy barrier distribution). [X. Batle, A. Labarta, Finite-size effects in fine particles: magnetic and transport properties, Journal of Physics, 2002, ppR15-R42].

One of the most interesting aspects of these results is that, in fact, measuring the relaxation at a given temperature is completely equivalent to measuring it at different temperature but shifting the observation time window according to the law $T \ln(t/\tau_0)$. In this sense, the method enables us to obtain the relaxation curve at a given temperature, in a time range that is not experimentally accessible, by simply dividing the $T \ln(t/\tau_0)$ axis by this temperature. For instance, in the case shown in Figure 1-8, we can obtain the relaxation curve at the lowest measured temperature of
1.8K at times as large as $10^{119}$ s, which is obviously an experimentally inaccessible time. The validity of the $T \ln(t/\tau_0)$ scaling method to analyse the relaxation behaviour has been proved in many systems of non or slightly interacting fine particles. Moreover, from the $T \ln(t/\tau_0)$ scaling of relaxation data, insight can be gained into the microscopic details of the energy barrier distribution producing the relaxation. If $f(E)$ is nearly constant in the range of energy barriers which can be overcome during the observation time, then equation

$$M(t) \approx M_0 \int_{E_c}^{\infty} dE f(E)$$

(1.20) can be approximated by

$$M(t) \approx M_0 \left(1 - k_B T f(E_c) \ln \left(\frac{t}{\tau_0}\right)\right)$$

(1.21)

Where $E_c$ is the mean energy barrier within the experimental window. From equation

$$M(t) \approx M_0 \left(1 - k_B T f(E_c) \ln \left(\frac{t}{\tau_0}\right)\right)$$

(1.21) we can define the viscosity parameter as

$$S = -\frac{1}{M_0} \frac{\partial M}{\partial (\ln(t))} = f(E_c) k_B T$$

(1.22)

Therefore, as $E_c$ is varied, the magnetic viscosity maps the energy barrier distribution at low enough temperatures for which the width of $p(t, T, E)$ (equation

$$p(t, T, E) = \exp \left[-\left(\frac{t}{\tau_0}\right) \exp \left(-\frac{E}{kT}\right)\right]$$

(1.19) function around the inflection point is small compared to the width of the energy distribution and the scaling hypothesis is fulfilled. As an example of the applicability of the method, in Figure 1-9, we show $S/T$ derived from the data of Figure 1-8 as a function of $T \ln(t/\tau_0)$. In Figure 1-9, the differential of the thermoremanence relative to the saturation magnetization with respect to the temperature is also shown, the agreement between both sets of data being very good.
Figure 1-9: Numerical derivative of the data of Figure 1-8 with respect to the scaling variable (open circles) and the logarithmic-linear distribution (dashed line) obtained by fitting the data of Figure 1-8 to the equation \( \bar{M}(t) \approx M_0 \int_{E_c}^{\infty} dE f(E) \) (1.20). The differential of the thermoremanence relative to the saturation magnetization versus the temperature is also shown in full circles for comparison. [X. Batle, A. Labarta, Finite-size effects in fine particles: magnetic and transport properties, Journal of Physics, 2002, ppR15-R42].

If \( f(E) \) is almost constant over a certain range of energies, then \( S \) will be linear in \( T \) over the corresponding temperature range; consequently, relaxation as a function of time will follow a time logarithmic decay at fixed \( T \). This behaviour is only accomplished in a narrow region around the maximum of a bell-shaped energy barrier distribution (see for instance, the region around the inflection point of the master curve shown in Figure 1-8).

1.3.4.3 Effects of the interparticle interaction

We have reviewed different aspects of the magnetic relaxation of fine-particle systems with random orientations, volume distribution and negligible magnetic interactions. In this situation, the system is in an SPM regime, for which the time evolution of the total magnetization is simply governed by the thermal activation over the individual energy barriers of each particle. When interparticle interactions (for instance, dipolar interactions) are non-negligible the behaviour of the system is substantially more complicated and the problem becomes non-trivial, even if the spins of the particle are assumed to be coupled to yield a super-spin moment.

The main types of magnetic interactions that can be found in fine-particle assemblies are:

- dipole–dipole interactions, which always exit
• exchange interactions through the surface of the particles which are in close contact
• in granular solids, RKKY interactions through a metallic matrix when particles are also metallic, and super exchange interactions when the matrix is insulating.

Bearing in mind the anisotropic character of dipolar interactions, which may favour ferromagnetic or antiferromagnetic alignments of the moments depending on geometry, fine-particle systems have all the ingredients necessary to give rise to a spin-glass state, namely, random distribution of easy axes and frustration of the magnetic interactions. The complex interplay between both sources of magnetic disorder determines the state of the assembly and its dynamical properties.

Magnetic interactions modify the energy barrier coming from the anisotropy contributions of each particle and, in the limit of strong interactions, their effects become dominant and individual energy barriers can no longer be considered, only the total energy of the assembly being a relevant magnitude. In this limit, relaxation is governed by the evolution of the system through an energy landscape with a complex hierarchy of local minima similar to that of spin-glasses. It is worth noticing that in contrast with the static energy barrier distribution arising only from the anisotropy contribution, the reversal of one particle moment may change the energy barriers of the assembly, even in the weak interaction limit. Therefore, the energy barrier distribution may evolve as the magnetization relaxes.

Three models have been developed to introduce particle interaction:

- **Shtrikmann and Wohlfarth**

For a weak interaction limit, the relaxation time is

\[ \tau = \tau_0 \exp \left( \frac{E_B}{k_B (T_B - T_0)} \right) \]  

(1.23)

Where \( T_B \) is the blocking temperature and \( T_0 \) is an effective temperature which accounts for the interaction effects.

- **Dormann et al**

This model correctly reproduces the variation of the blocking temperature \( T_B \), as a function of the observation time window of the experiment, \( \tau_m \), at least in a range of time covering eight decades. The increase of \( T_B \) with the strength of the dipolar
interactions (e.g. increasing particle concentration or decreasing particle distances) has been predicted by this model and also experimentally confirmed.

- Morup and Tronc

For the weak interaction limit, the opposite dependence of $T_B$ with the strength of the interactions is predicted. Morup suggested that two magnetic regimes, governed by opposite dependencies of $T_B$, occur in interacting fine particles. At high temperatures and/or for weak interactions, $T_B$ signals the onset of a blocked state and $T_B$ decreases as the interactions increase. In contrast, at high temperatures and/or for strong interactions, a transition occurs from an SPM state to a collective state which shows most of the features of typical glassy behaviour. In this case, $T_B$ is associated with a freezing process and it increases with the interactions.

Non-equilibrium dynamics, showing ageing effects in the relaxation of the residual magnetization, have been observed in interacting fine-particle assemblies, but some important differences with spin-glasses have been established. In the last few years, several works demonstrated that for concentrated frozen ferrofluids and assemblies of nanoparticles dispersed in a polymer, the relaxation depends on the waiting time, $t_w$, spent at constant temperature before the magnetic field is changed (Figure 1-10).
**Figure 1-10**: The relaxation rate $S$ versus $\log_{10}(t)$ at different wait times for the concentrated sample (a) and for the most diluted sample (b). The measurements were performed on a ferrofluid consisting of closely spherical particles of maghemite with a mean diameter of 7 nm. [X. Batle, A. Labarta, Finite-size effects in fine particles: magnetic and transport properties, Journal of Physics, 2002, ppR15-R42].

This phenomenon is absent in the most diluted samples, confirming that it is due to dipole–dipole interactions (Figure 1-10). Ageing effects on the magnetic relaxation are the fingerprint of the existence of many minima in the phase space. However, a complex hierarchy of energy minima is not an exclusive feature of spin-glasses and ageing has also been found in other cluster-glass systems not having a true phase transition. In fact, the non-equilibrium dynamics of interacting fine particles largely mimics the corresponding of spin-glasses, including ‘memory experiments’ in which ageing is studied at different heating or cooling rates and/or cycling the temperature. The main differences between the dynamics of canonical spin-glasses and that of fine particles are:

- the dependence of the magnetic relaxation on $t_w$ is weaker than in spin-glasses
- in the collective state, the relaxation times are widely distributed and strongly dependent on temperature
- large particles are blocked in all time scales acting as a temporary random field and not taking part in the collective state of the system.

Another feature that differentiates the low-temperature collective state from the spin-glass one is its extreme sensitivity to the application of an external magnetic field. In particular, it has been shown that the collective state of strong interacting particles can be erased by a field-cooling process with an applied magnetic field of moderate strength which yields an asperomagnetic state. It has also been demonstrated that the dynamics of these systems are strongly affected by the initial magnetic moment configuration, in such a way that the collective state determines the dynamic behaviour only in low-cooling-field experiments, while at high cooling fields the dynamics are mostly dominated by the intrinsic energy barriers of the individual particles.
1.3.4.4 Surface effects

Surface effects result from the lack of translational symmetry at the boundaries of the particle because of the lower coordination number there and the existence of broken magnetic exchange bonds which lead to surface spin disorder and frustration. Surface effects dominates the magnetic properties of the smallest particles since decreasing the particle size increases the ratio of surface spins to the total number of spins. For example, for fcc Co with a lattice constant of 0.355 nm, particles having about 200 atoms will have diameters around 1.6 nm and 60% of the total spins will be at the surface. This represents more than half of the spins. Consequently, the ideal model of a superspin formed by all the spins of the particle pointing in the anisotropy direction and coherently reversing due to thermal activation is no longer valid, since misalignment of the surface spin yields strong deviations from the bulk behaviour. This is true, even for particles with strong exchange interactions such as many ferrimagnetic oxides with magnetically competing sublattices, since broken bonds destabilize magnetic order giving rise to frustration which is enhanced with the strength of the interactions. As a consequence of the combination of both finite-size and surface effects, the profile of the magnetization is not uniform across the particle and the magnetization of the surface layer is smaller than that corresponding to the central spins.

Many experimental results for metallic and oxide particles indicate that the anisotropy of fine particles increases as the volume is reduced because of the contribution of what is known as surface anisotropy. For instance, the anisotropy per unit volume increases by more than one order of magnitude for 1.8 nm fcc Co particles being $3 \times 10^7$ erg cm$^{-3}$ compared with the bulk value of $2.7 \times 10^6$ erg cm$^{-3}$. Even an anisotropy value one order of magnitude larger than the preceding case has been reported for Co particles embedded in a Cu matrix. In fact, surface anisotropy has a crystal-field nature and it comes from the symmetry breaking at the boundaries of the particle. The structural relaxation yielding the contraction of surface layers and the existence of some degree of atomic disorder and vacancies induce local crystal fields with predominant axial character normal to the surface, which may produce easy-axis or easy-plane anisotropies. This can be justified by noting that the axis of the local crystal field, $\hat{n}$, may be evaluated from the dipole moment of the nearest-neighbour atomic positions with respect to the position of a given surface atom as follows:
\[ \hat{n}_i \propto \sum_{j} n_{ij} (P_j - P_i) \]  

(1.24)

Where \( P_i \) is the position of the \( i \)th atom and the sum extends to the nearest neighbours of this atom. Since at the surface some of the neighbours are missing, \( \hat{n} \) is non-zero and directed approximately normal to the surface. The effect of these local fields is obtained by adding a term of the form \( KS_{\xi}^2 \), where \( S_{\xi} \) is the component of the spin along a vector normal to the surface and, \( K < 0 \) corresponds to the easy-axis case and \( K > 0 \) to the easyplane one. When \( |K| \) is comparable to the ferromagnetic exchange energies, spin configurations like those shown in Figure 1-11 are obtained. These result from the competition of surface anisotropy and ferromagnetic alignment. Another kind of surface anisotropy was suggested that treated acicular particles of \( \gamma \)-Fe2O3 as infinite cylinders possessing uniaxial anisotropy parallel to the surface of the cylinder. In general, the surface anisotropy makes the surface layer magnetically harder than the core of the particle.

\[ \begin{align*}
\text{(radial)} & \quad \text{(tangential)}
\end{align*} \]

Figure 1-11: Surface spin arrangement of a ferromagnetic particle with a surface anisotropy of the form \( KS_{\xi}^2 \). Both cases corresponding to \( K < 0 \) (radial) and \( K > 0 \) (tangential) are displayed. [X. Batle, A. Labarta, Finite-size effects in fine particles: magnetic and transport properties, Journal of Physics, 2002, ppR15-R42].

The second contribution due to the existence of boundaries is a consequence of strains related to lattice deformations occurring at the surface, which through magnetostriction effects induce an additional surface anisotropy. Strain anisotropy has been observed in thin films because of stresses induced at the interface between
substrate and film due to non-matching lattice constants. Depending on the structural deformations and the nature of the thin films, strain anisotropy could yield perpendicular anisotropy to the film plane, as has been observed in as-prepared thin films of heterogeneous Co(Fe)–Ag(Cu) alloys. However, for the majority of the nanoparticle systems, the strain energy is weak, it being difficult to give a general formulation, and, in particular, for free particles it is negligible.

An effective anisotropy energy per unit volume, $K_{\text{eff}}$, could be obtained by adding the core (i.e. bulk anisotropy) and surface contributions. For a spherical particle the following phenomenological expression has been used to account for $K_{\text{eff}}$:

$$K_{\text{eff}} = K_b + \frac{6}{d} K_s$$

(1.25)

Where $K_b$ is the bulk anisotropy energy per unit volume, $K_s$ is the surface density of anisotropy energy and $d$ is the diameter of the particle. It is worth noticing that for a spherical particle and based on symmetry arguments, surface anisotropy (normal to the surface) would average to zero. However, this is not true for a nanometric particle with a few atomic layers. For instance, applying equation $K_{\text{eff}} = K_b + \frac{6}{d} K_s$ (1.25) for a 2 nm particle of fcc Co with $K_b = 2.7 \times 10^6$ erg cm$^{-3}$ and $K_s \approx 1$ erg cm$^{-2}$, the surface contribution to the total anisotropy, $K_{\text{eff}}$, is about $3 \times 10^7$ erg cm$^{-3}$, which is one order of magnitude larger than the bulk contribution, and $K_{\text{eff}} = 3.3 \times 10^7$ erg cm$^{-3}$.

This example is representative of the major role of surface contribution to the total anisotropy in fine-particle systems, for which the anisotropy energy is governed by surface anisotropy.

### 1.4 Magnetoelectronics spins

Spintronics is a multidisciplinary field whose central theme is the active manipulation of spin degrees of freedom in solid-state systems. The goal of spintronics is to understand the interaction between the particle spin and its solid-state environments and to make useful devices using the acquired knowledge.

In this chapter, we will focus on magnetoelectronics materials. Typically they cover paramagnetic and ferromagnetic metals and insulators which utilize magnetoresistive...
effects, realized, e.g., as magnetic read heads in computer hard drives, nonvolatile magnetic random access.

1.4.1 Spin-polarized transport and magnetoresistive effects

Some Scientists sought an explanation for an unusual behaviour of resistance in ferromagnetic metals. They realized that at sufficiently low temperatures, where magnon scattering becomes vanishingly small, electrons of majority and minority spin, with magnetic moment parallel and antiparallel to the magnetization of a ferromagnet, respectively, do not mix in the scattering processes. The conductivity can then be expressed as the sum of two independent and unequal parts for two different spin projections, the current in ferromagnets is spin polarized.

1.4.1.1 Tunneling magnetoresistance (TMR)

Tunneling measurements play a key role in work on spin-polarized transport. It is important to study N/F/N junctions, where N was a nonmagnetic metal and F was an Eu-based ferromagnetic semiconductor. These investigations showed that when unpolarized current is passed across a ferromagnetic semiconductor, the current becomes spin-polarized.

Ferromagnet / insulator / superconductor (F/I/S) and Ferromagnet / insulator / Ferromagnet (F/I/F) junctions were studied these last years. F/I/S have proved that the tunneling current remains spin polarized even outside of the ferromagnetic region and was used as a detector of spin polarization of conduction electrons. By analysing the tunnelling conductance from F/I/S to the F/I/F junctions, Jullière (1975) formulated a model for a change of conductance between the parallel (↑↑) and antiparallel (↑↓) magnetization in the two ferromagnetic regions F1 and F2, as depicted in Figure 1-12.
Figure 1-12: Schematic illustration of electron tunneling in F/I/F tunnel junctions: (a) Parallel and (b) antiparallel orientation of magnetizations with the corresponding spin-resolved density of the d states in ferromagnetic metals that have exchange spin splitting $\Delta_{\text{ex}}$. Arrows in the two ferromagnetic regions are determined by the majority-spin subband. Dashed lines depict spin-conserved tunneling. [I. Zutic, J. Fabian, S. Das Sarma, Spintronics: Fundamentals and applications, Reviews of modern physics, volume 76, 2004, pp 323-410]

The corresponding tunneling magnetoresistance (TMR) in an F/I/F magnetic tunnel junction (MTJ) is defined as

$$TMR = \frac{\Delta R}{R_{\uparrow\uparrow}} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\downarrow}} = \frac{G_{\uparrow\downarrow} - G_{\uparrow\uparrow}}{G_{\uparrow\downarrow}}$$  \hspace{1cm} (1.26)

Where conductance $G$ and resistance $R=1/G$ are labeled by the relative orientations of the magnetizations in F1 and F2 (it is possible to change the relative orientations, between $\uparrow\uparrow$ and $\uparrow\downarrow$, even at small applied magnetic fields $\sim 10$ G). TMR is a particular manifestation of a magnetoresistance that yields a change of electrical resistance in the presence of an external magnetic field. Due to spin-orbit interaction, electrical resistivity changes with the relative direction of the charge current (for example, parallel or perpendicular) with respect to the direction of magnetization. Assuming constant tunneling matrix elements and that electrons tunnel without spin flip, equation

$$TMR = \frac{\Delta R}{R_{\uparrow\uparrow}} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\downarrow}} = \frac{G_{\uparrow\downarrow} - G_{\uparrow\uparrow}}{G_{\uparrow\downarrow}}$$  \hspace{1cm} (1.26)$$

yields
\[
TMR = \frac{2P_1P_2}{1 - P_1P_2}
\]  \hspace{1cm} (1. 27)

Where the polarization $P_i$ is expressed in terms of the spin-resolved density of states for majority and minority spin in $F_i$.

### 1.4.1.2 Applications

While many existing spintronic applications are based on the GMR effects, the discovery of large room-temperature TMR has renewed interest in the study of magnetic tunnel junctions, which are now the basis for the several magnetic random-access memory prototypes. Future generations of magnetic read heads are expected to use MTJ’s instead of CIP giant magnetoresonance. To improve the switching performance of related devices it is important to reduce the junction resistance, which determines the RC time constant of the MTJ cell. Consequently, semiconductors, which would provide a lower tunneling barrier than the usually employed oxides, are being investigated both as the nonferromagnetic region in MTJ’s and as the basis for an all-semiconductor junction that would demonstrate large TMR at low temperatures.

### 1.5 Giant Magnetoresistance (GMR)

#### 1.5.1.1 Origin of the GMR effect

For a macroscopic electrical conductor the resistance $R$ is given by $R=P/A$, which is independent of shape, cross section and above all the scattering process involved therein. Especially, electron-electron and electron-proton scattering process bring the out-of-equilibrium distribution of accelerated electrons back to the equilibrium distribution thereby contribution to resistance. This usual picture loses its validity when the dimension of the material becomes of the order of relevant collision-mean-free path ($\lambda$). Now for an elastic scattering process the conductivity due to spin up and spin down electron is given by

\[
\sigma = \sigma_1 + \sigma_2 \hspace{1cm} (1. 28)
\]

For an elastic scattering process\(^{iv}\)

For the occurrence of the GMR effect it is crucial that the angles between the magnetization directions of the ferromagnetic layer can be modified by the application
of an applied magnetic field, the electron scattering probability at the interfaces or within the bulk of the layers is spin-dependent, and in the case of parallel magnetizations, the layer averaged electron mean-free path for (at least) one spin direction is larger than the thickness of the non-magnetic spacer layer.

Now, each layer in a GMR-structure acts as a spin selective valve. In case of parallel-alignment-layer the contribution towards conductance due to spin up electron is highly leading to higher value of total conductance. However, for antiparallel alignments the magnetic layers results in appreciable scattering for electrons in both spin direction and hence a lower total conductance. If the F layers are much thinner than $\lambda^{\uparrow}$ the spin up conductance in the parallel magnetization state is limited by strong spin-dependent scattering in the buffer layer and in the AF layer. The contrast with spindown conductance can then be enhanced by increasing the F-layer thickness. It is to be noted that only a part of F-layer which is of the order of $\lambda^{\uparrow}/2$ from the interface responds to the above situation.
Figure 1-13: Dependence of the MR ratio on the free magnetic layer thickness, measured at 293 K (a) and at 5K (b), for (X/Cu/X/Fe50Mn50) spin valves, grown on 3nm Ta buffer layer on Si(100) substracts, with X=Co (squares), X=Ni66Fe16Co18 (traingles) and (X= Ni80Fe20) (+), measured at 5K. Layer thickness: $t_{Cu} = 3$nm (but 2.5 for F=(X= Ni80Fe20); $t_{F}(\text{pinned layer})=5$nm (but 6nm for F= Ni66Fe16Co18).

Requirements for F/N combinations with a high GMR ratio are:
the F and N materials possess, for one spin direction, very similar electronic structures, whereas for the other spin direction the electronic structures are very dissimilar,

the electron transmission probability (transmission without diffusive scattering) through the F/N interfaces is large for the type of electrons for which the electronic structure in the F and N layers are very similar,

and the crystal structures of the F and N materials match very well.

1.5.1.2 Thermal stability

A number of factors control the use and processing of exchange-biased spin-valve layered structures at elevated temperatures:

- Exchanging biasing field decreases with increasing temperature. For some exchange biasing materials this effect determines the temperature range within which sensors can be applied.

- The induced magnetocrystalline anisotropy of the free layer may be affected by heating the material.

- As multilayers are thermodynamically metastable system the enhanced diffusion rates during annealing will inversibly degrade the layered structure. Diffusion may also affect the effective coupling between the layers. There are three contributions in interlayer coupling:
  
  - Coupling via ferromagnetic bridges between the ferromagnetic layers.
  
  - The mangetostatic Neel-type coupling.
  
  - Interlayer exchange coupling.

1.5.1.3 Factors determining the switching field interval

1.5.1.3.1 Induced magnetic anisotropy

This is believed to be due to the result of a very small degree of divertional pair order of atom a in the otherwise random solid solution. The anisotropy field depends upon the composition, the layer thickness, and the material between which the layers are sandwiched. In case of a GMR spin valve the anisotropy effect is relevant for the thickness below 15 nm. The effect is most likely due to a region with a decreased degree of pair order situated in the ferromagnetic layer close to the interface with the buffer layer.
The result shows that addition of Co to permalloy is unfavourable as far as switching field interval is concerned. But one of the advantages is that the range of linear operation of GMR sensor elements is improved. Annealing the sample can affect the anisotropy field. It is often necessary to anneal the sample after decomposition in a magnetic field that is directly perpendicular to field direction during growth, in order to rotate the exchange direction over an angle of 90°. This leads to cross anisotropy configuration. Therefore it is suggestive to anneal with the field parallel to the induced anisotropy before annealing briefly with perpendicular field. On the other hand strain results in an additional magnetocrystalline anisotropy due to magnetostriction. So for sensor element coefficient of magnetostriction should be small. Ni$_{66}$Co$_{18}$Fe$_{16}$ alloy is a good candidate for application in GMR sensor elements.

### 1.5.1.3.2 Superimposed AMR effect

If the current direction is parallel to the easy axis of the free F layer, the magnetoresistance is given by

$$\Delta R(H) = \frac{\Delta R(GMR)(1-\cos \theta)}{2} + \Delta R(AMR) \sin^2 \theta$$  \hspace{1cm} (1.29)

The AMR-term represents the resistance change due to the change of angle ($\theta$) between the magnetization of the free layer and the current direction. The presence of AMR effect increases the sensitivity $\frac{\partial R}{R} / \partial H$ if an operating point between $H=0$ to $H=+H_a$ is chosen. Experiment shows that due to AMR effects the sensitivity of the spin valve is almost 50% higher than expected from GMR effect. It is suggestive for practical purpose to operate a material around the field $H=0$, where the element is magnetically most stable.

### 1.5.1.3.3 Coupling between the magnetic layer

If we make N layer very thin the free F layer is found to be magnetically coupled. This coupling leads to an offset of the field around which the free layer switches to a field $H= -H_{\text{couple}}$. The coupling field is due to

- Ferromagnetic coupling via pinhole.
- Ferromagnetic Neel-type coupling.
• An oscillatory indirect exchange coupling.

All three contributions are influenced by the microstructure of the material and hence control of the coupling field requires very good control of the deposition condition. This issue is very relevant for sensor application. Most of the cases the coupling field is equal or greater than the anisotropy field. Fortunately, in a sensor element the resulting shift of the switching field is balanced by:

• Application of a bias magnetic field from a current through an integrated bias conductor.

• The magnetostatic coupling between the pinned and the free layer which arises as a result of the stray magnetic field origination from the magnetization of a pinned layer, which is directly along the long axis of the stripe.

Interlayer coupling influences the switching field interval due to the following two effects:

• The magnetization of the pinned layer is not quite fixed upon the rotation of the free layer. This increases the switching field interval. This effect increases upon an increases of the ratio between the coupling field and the exchange biasing field.

• Lateral fluctuations in the coupling field increase the switching field interval.

1.5.1.3.4 Exchange biasing

The interaction energy $E$ between the pinned $F$ layer and the antiferromagnetic layer is given by,

$$E = -K_{cb}\cos \theta$$ (1.30)

Where $\theta$ is the angle between the biasing direction and the magnetization of the pinned $F$ layer. The exchange biasing field varies inversely with the thickness of the pinned layer.

To obtain exchange biasing the AF layer thickness should generally exceed critical valve.

In conclusion, we must say that exchange-biased spin valve layered structures show a combination of properties that are attractive for the application in low field sensors, such as read head in hard disk and tape recording. For a yoke-type GMR
head an output gain of a factor 10 has been obtained compared with a barbar-pole biased AMR head. The following factors contribute to operational gain:

- Larger MR ratio.
- Larger sheet resistance.
- Larger flux efficiency of the head, due to the small thickness of the magnetic layer.

Future developments are expected to focus on exchange-biased spin valve materials with a high thermal stability, on the improvement of the effective softness, of the free magnetic layer while remaining a high GMR ratio, and on relation between micromagnetic aspects such as domain wall nucleation and propagation and sensor noise.

References:

W. D Callister, Science et genie des matériaux, Dunod, 2003

\[\text{References:}\]