

## The Basis of Nanomagnetism

**Summary.** What is the origin of the observed differences in magnetic behavior between a sample with nanometric dimensions and a macroscopic sample of the same material? These differences are shown to arise from broken translation symmetry in nanometric samples, from the higher proportion of atoms on the surface, or interface, from the fact that the sizes of nanoscopic objects are comparable to some fundamental or characteristic lengths of the constituent material, and other effects. The exchange length and the magnetic domain wall width are some of the characteristic lengths that are more relevant to the magnetic properties. The shape of the density of electronic states curve is also dependent on the dimensionality of the samples.

### 1.1 Introduction: The Importance of Nanomagnetism

The objects of study of Nanoscience are the phenomena involving objects of dimensions usually in the range from 1 ( $1\text{ nm} = 10^{-9}\text{ m}$ ) to 100 nm. This is the range of sizes of many molecules and viruses, and is also the characteristic length scale of many physical processes. The lateral dimensions of present-day integrated circuit components, as well as the dimensions of grains in magnetic-recording film media, are contained in this range.

Nanomagnetism is the area of research in physics, which deals with the magnetic properties of objects that have at least one dimension in the nanoscopic range. Nanomagnetism includes in its scope the study of properties and applications of the magnetism of isolated nanoparticles, nanodots, nanowires, thin films and multilayers, and also macroscopic samples that contain nanoscopic particles. Materials that contain particles, films, and other structures in the nanometric scale are often described as nanostructured materials.

Objects with dimensions from 100 to 1,000 nm are usually described as mesoscopic; although our focus in the present work is on magnetic properties of objects of nanoscopic dimension, we will also consider the behavior of objects of mesoscopic size.

Nanomagnetism has many practical applications, from geology to magnetic recording, from ferrofluids [20] used in loudspeakers to small particles used in

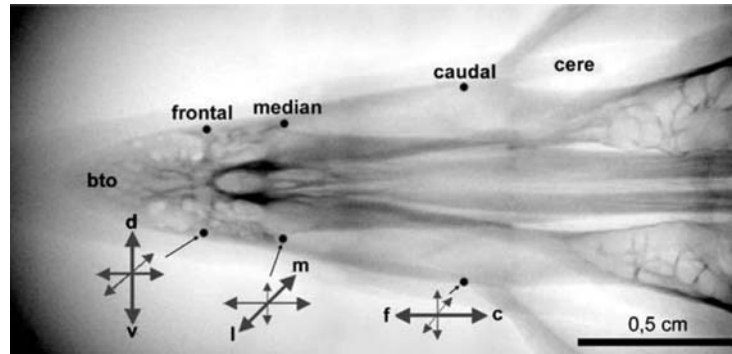
medicine, that can be directed to specific organs and tissues, either for drug delivery [1] or for the application of the technique of magnetic hyperthermia [14].

Magnetic nanoparticles are present in many rocks and soils. The alignment of their magnetic moments under the influence of the geomagnetic field allows the study of the evolution of Earth's magnetism and the determination of their age; this alignment can also inform on past anthropic activities [7].

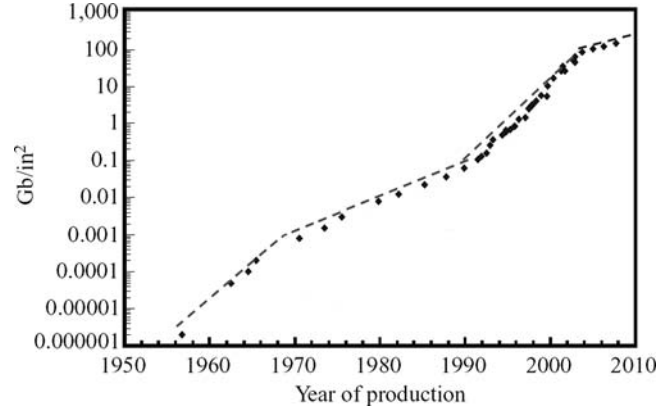
Nanoparticles of magnetic materials, usually of magnetite, also occur in living beings; perhaps the best studied example is that of magnetotactic bacteria, which, through magnetic grains of nanometric dimension, align themselves in the Earth's magnetic field. These grains are synthesized by the bacteria, in a process called biomineralization. Nanomagnets have also been found in insects, birds, and other creatures [26]. Figure 1.1 illustrates this with the cross section of the beak of a pigeon, where the presence of clusters of magnetite nanoparticles with diameters of 2–4 nm was observed [8].

Finally, the most successful application of nanomagnetism has been to magnetic recording, which has taken this technology through a swift evolution in the last 5 decades. This is measured by the evolution of the areal bit density in magnetic hard disks, which has increased by a factor of many tens of millions since the introduction in the market of this technology (Fig. 1.2) (e.g., [25]). The rapid increase in the density of electronic circuits made on individual silicon chips, which has doubled every 18 months, is a tendency known as Moore's Law, a name arising from a 1965 paper by Moore that discussed the subject. Alongside this evolution, the density of magnetic storage in hard disks, measured by the data areal density, has progressed even faster, doubling every 2 months.

To reach higher and higher storage densities, a great effort was necessary in the study of the properties of small magnetic particles, and also of the magnetic thin films that are a constitutive part of hard disk platters and magnetic read heads.



**Fig. 1.1.** X-ray of a homing pigeon beak showing the six regions where there are found clusters of magnetite nanoparticles, of 2–4 nm diameter. Also shown the orientation of the nerve bundles where these clusters are located. Strings of maghemite particles are also present, and both systems participate in the magnetoreception [8] (With kind permission from Springer Science + Business Media [8], Fig. 3a)



**Fig. 1.2.** Evolution of magnetic recording: hard disk areal density in gigabits per square inch as a function of the year in which the products became available in the market [10]. (Reprinted from [8] with permission from IBM Technical Journals)

The application to devices, particularly spintronic devices, has represented another frontier in rapid expansion (e.g., [9]). This application is based on the interaction of the spin degree-of-freedom of an electric current with the magnetic materials, and also uses films and other structures with nanometric dimensions.

## 1.2 The Origin of Nanomagnetic Behavior

The emergence of the new phenomena that are the object of nanomagnetism has its origin in the fact that the magnetism of samples of nanoscopic or mesoscopic sizes presents important differences compared to the magnetism of macroscopic samples. One could describe these differences, in a simplified way, as arising from the fact that the magnetic systems of nanoscopic or mesoscopic scales present: (1) dimensions comparable to characteristic lengths, such as the limiting size of magnetic domains; (2) broken translation symmetry, which results in sites with reduced coordination number, with broken exchange bonds and frustration. Also, nanoscopic or mesoscopic objects exhibit a higher proportion of surface (or interface) atoms.

Another factor that modifies the magnetic properties of the nanoobjects is that they are in general in close contact with other physical systems, for example, with a substrate or a capping layer, in the case of most thin films and multilayers. In the case of nanoparticles, these objects may be immersed in solid matrices, or compacted in a container: in both cases, each particle may feel a strong interaction with its immediate neighborhood.

Also, in general, as systems such as ensembles of nanoparticles are prepared with smaller dimensions, the presence of imperfections and defects becomes more relevant, making the obtention of identical sets of nanoobjects more difficult. Often the properties of the nanoscopic objects have to be derived from samples formed of ensembles of such objects.

The spin wave spectra of samples of nanoscopic dimensions are also modified (e.g., [17]). The dispersion relation for spin waves for wavelengths longer than the lattice spacing is  $\hbar\omega = Dk^2$ , where  $D$  is the stiffness constant, and  $k$  is the magnitude of the spin wavevector. For a spin wave energy comparable to the thermal energy, one has  $k \approx (k_B T/D)^{1/2}$ , where  $k_B$  is the Boltzmann constant. For Fe,  $D(4.2K) \approx 3 \text{ meV nm}^2$  and the corresponding length  $L = 1/k \approx 3 \text{ nm}$  at liquid helium temperature, which implies that spin wave spectra of nanoscopic objects are significantly modified, if compared to those of bulk samples.

The dynamic behavior of magnetic objects of nanometric size also differs from the behavior of macroscopic samples of the same constituents. The main cause for this difference is the enhanced importance of thermal fluctuations under the usual experimental conditions. The phenomenon of superparamagnetism is observed in magnetic nanoparticles if the thermal energy  $k_B T$  is of the same order-of-magnitude of the anisotropy energy of the particles, leading to an effectively zero measured magnetic moment. The superparamagnetism of nanoparticles is discussed in Sect. 3.3 (p. 68).

### 1.2.1 Sample Dimensions and Characteristic Lengths

The simplest example of the effect of the characteristic lengths on the magnetic properties is the case of magnetic particles that have dimensions smaller than the critical magnetic single-domain diameter. These particles therefore have the single domain as their lowest energy configuration.

Some of these characteristic lengths, which include the exchange interaction length, the domain wall width and the spin diffusion length, are given in Table 1.1, together with their typical values. From this table, it is evident that nanoobjects have dimensions in the range of many of these characteristic lengths. The derivation of the expressions for some of these lengths, in terms of the magnetic parameters of the constituent materials, will be discussed in Chap. 2.

**Table 1.1.** Some characteristic lengths in magnetism and their typical magnitudes

Symbol	Length	Typical magnitude (nm)
$d_a$	Interatomic distance (Fe)	$2.5 \times 10^{-1}$
$d_{\text{ex}}$	Range of exchange interaction	$\sim 10^{-1} - \sim 1$
$d_{\text{RKKY}}$	Range of RKKY interaction	$\sim 10^{-1} - \sim 10$
$d_c$	Domain size	$10 - 10^4$
$D_{\text{cr}}^{\text{spm}}$	Superparamagnetic critical diameter	$\sim 1 - \sim 10^2$
$D_{\text{cr}}$	Critical single-domain size	$\sim 10 - \sim 10^3$
$\delta_0$	Domain wall width	$\sim 1 - \sim 10^2$
$l_{\text{ex}}$	Exchange length	$\sim 1 - \sim 10^2$
$l_{\text{sd}}$	Spin diffusion length	$\sim 10 - 10^2$
$\lambda_{\text{mfp}}$	Electron mean free path	$\sim 1 - 10^2$
$\zeta$	Superconducting coherence length	$\sim 1 - 10^3$
$\lambda_F$	Fermi wavelength/metal	$\sim 10^{-1}$
$\lambda_F$	Fermi wavelength/semiconductor	$\sim 10^2$

The critical size for magnetic domains  $D_{\text{cr}}$ , which is the largest size that a ferromagnetic particle may have, beyond which it will be energetically more favorable to divide itself into two or more domains, varies from material to material. This size varies from about 10 nm to some thousands of nanometers (or microns); some values of this dimension for spherical particles for different materials are shown in Table 2.9, on p. 38. This critical diameter is given by the following expression, to be demonstrated in Chap. 2 (p. 49):

$$D_{\text{cr}} = \frac{72\sqrt{AK}}{\mu_0 M_s^2} . \quad (1.1)$$

In this expression,  $A$  is the exchange stiffness constant, or parameter,  $K$  is the uniaxial anisotropy constant (assumed  $>0$ ) and  $M_s$  is the saturation magnetization;  $\mu_0$  is the vacuum magnetic permeability (or magnetic constant), equal to  $4\pi \times 10^{-7} \text{ H m}^{-1}$  in the SI.

The characteristic lengths that are more relevant in defining the magnetic properties of nanoobjects are the exchange length and the domain wall width parameter. The exchange length is given by:

$$l_{\text{ex}} = \sqrt{\frac{2A}{\mu_0 M_s^2}} . \quad (1.2)$$

Table 1.2 illustrates the magnitude of the exchange length  $l_{\text{ex}}$  with some examples from the 3d metals.

The domain wall width parameter  $\Delta$  characterizes the width of the transition region between two magnetic domains, as will be discussed in Chap. 2. It is given, as a function of the exchange stiffness constant  $A$  and the uniaxial anisotropy constant  $K$ , by

$$\Delta = \sqrt{\frac{A}{K}} . \quad (1.3)$$

And the domain wall width  $\delta_0$  is given by

$$\delta_0 = \pi \Delta . \quad (1.4)$$

The domain wall energy is also related to the same parameters  $A$  and  $K$ . In the simple case of a  $180^\circ$  wall of a cubic crystal, the energy per unit area of the wall is

$$\gamma = 4\sqrt{AK} . \quad (1.5)$$

**Table 1.2.** Exchange lengths for 3d metals (From Table 2.8, Chap. 2)

Element	$l_{\text{ex}}$ (nm)
Fe	3.28
Co	4.70
Ni	7.64

In Chap. 2, where the properties of magnetic domains are studied, Table 2.9 (p. 38) presents values of critical domain diameters and domain wall energies for some materials.

### 1.2.2 Broken Translation Symmetry

Every finite crystal has frontiers, where the translational symmetry is lost or broken. In solids of nanometric size a significant proportion of the atoms are on or near these frontiers. The absence of translation symmetry brings about several important consequences to the physical properties of these systems.

Three aspects of the problem of symmetry breaking will be discussed: (1) the relation of the physical properties of the samples to their dimensionality (samples with quasi-zero dimension (0D), unidimensional (1D), bidimensional (2D) or tridimensional (3D)); (2) the change in coordination of the atoms at the interface, and (3) the effect of the increase in the proportion of surface (or interface) atoms in nanoscopic samples.

#### 1.2.2.1 Dimensionality and Density of Electronic States

The electronic band structure of a solid depends on its dimensionality. This can be exemplified in the simplest description of a conducting solid, the free electron model, in which the electrons are treated as a gas (called a Fermi gas) only subject to the infinite potentials at the walls of the container. An electron gas in a limited spatial region will show an availability of electronic states (measured by its density of states  $D(E)$ ) that depends on the dimensionality of this region: if it is in one dimension or two dimensions,  $D(E)$  will differ from the three-dimensional case. The effects of the difference in dimensionality may be shown through the differences in  $D(E)$ , and are summarized in Fig. 1.3.

Let us examine initially a Fermi gas in three dimensions; we wish to obtain the form of the density of states  $D(E)$ . The electrons are supposed to be in a container with three dimensions and infinitely high walls; there are no interactions between the electrons.

Let us consider that the potential  $V(x, y, z)$  inside the box of side  $L$  is  $V_0 = \text{const}$  for  $0 \leq x \leq L$ ,  $0 \leq y \leq L$ , and  $0 \leq z \leq L$ ;  $V = \infty$  otherwise.

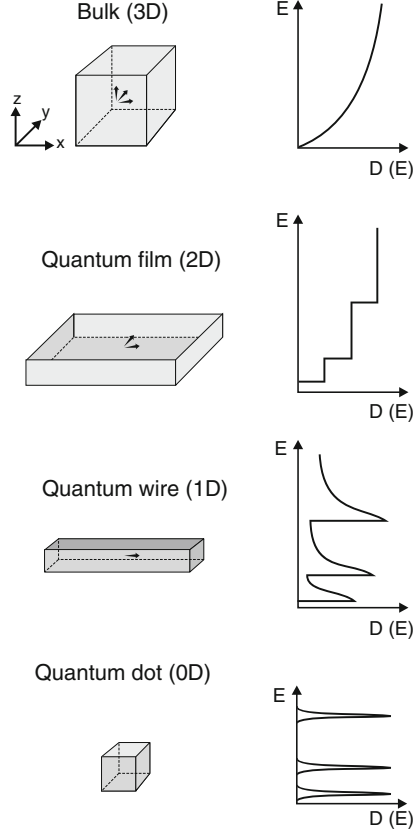
The time-independent Schrödinger equation will be

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r) \psi(r) = E' \psi(r). \quad (1.6)$$

Using  $E = E' - V_0(r)$  one obtains

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) = E \psi(r). \quad (1.7)$$

Since the infinite potential at the walls forbids the presence of the electrons outside them, the boundary conditions for  $\psi(r)$  will be:  $\psi = 0$  for  $x = 0$  and  $x = L$ ,  $y = 0$  and  $y = L$  and  $z = 0$  and  $z = L$ .



**Fig. 1.3.** Density of electronic states  $D(E)$  as a function of energy for electrons, from *bottom to top*, in zero dimension, in one dimension, two dimensions, and three dimensions (Based on [4])

The solution of Schrödinger's equation, using these boundary conditions, will be:

$$\psi(r) = \left(\frac{2}{L}\right)^{3/2} \sin k_x x \sin k_y y \sin k_z z. \quad (1.8)$$

The corresponding energies are obtained by substituting  $\psi(x)$  from (1.8) into (1.7):

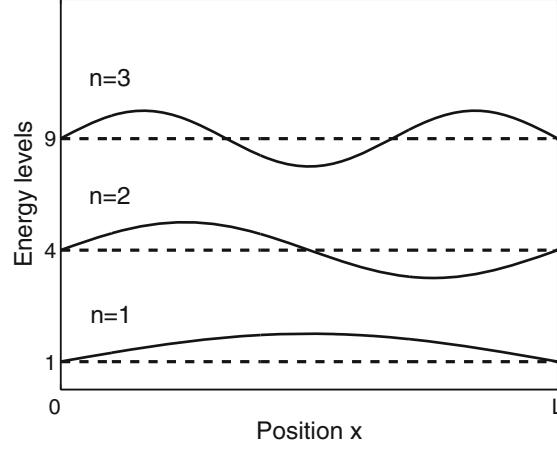
$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2), \quad (1.9)$$

where  $m$  is the electron mass and  $k_i$  are the components of its wavevector.

From the boundary conditions, one obtains

$$k_x = \pm \frac{2\pi}{L} n_x, \quad k_y = \pm \frac{2\pi}{L} n_y, \quad k_z = \pm \frac{2\pi}{L} n_z, \quad (1.10)$$

where  $n_x$ ,  $n_y$ , and  $n_z$  take values 1, 2, 3, ...



**Fig. 1.4.** Graph of  $E/E_0$  (dotted lines) for the lower three energy levels and wavefunctions vs.  $x$  (continuous lines) for a free electron gas confined to a one-dimensional box

The wave functions for a free electron in a one-dimensional box, for the first three values of  $n$ , and the corresponding energies  $E$  are illustrated in Fig. 1.4. This figure shows the form of the first three lowest energy wave functions, as well as the corresponding energies  $E/E_0$ , where  $E_0$  is the energy for the level with  $n = 1$ .

According to the Pauli exclusion principle, two electrons (spin up and spin down) occupy one state defined by  $(n_x, n_y, n_z)$ . But how many states are there to be occupied? To count the number of states, one has to count the number of values of  $k$ .

At  $T = 0$  K, all states are occupied up to  $k_F$ , the Fermi wavevector, in a volume  $V_k = \frac{4}{3}\pi k_F^3$ . Since each triplet  $(k_x, k_y, k_z)$  occupies a volume of  $v = (2\pi/L)^3$  in  $k$ -space, the number of states  $N$  will be

$$2 \cdot \frac{V_k}{v} = 2 \cdot \frac{\frac{4}{3}\pi k_F^3}{(2\pi/L)^3} = \frac{V}{3\pi^2} k_F^3 = N, \quad (1.11)$$

where  $V$  is the volume occupied by the electrons in real space.

From this equation one derives  $k_F$ , and substituting into the expression of the energy (1.9), one obtains the Fermi energy  $E_F$ :

$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}. \quad (1.12)$$

This allows writing  $N$  as a function of  $E_F$ . The derivative of the expression obtained for  $N$  is the density of electron states at the Fermi level  $D(E_F)$ :

$$D(E_F) \equiv \frac{dN}{dE_F} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E_F^{1/2}. \quad (1.13)$$



This result is the density of electron states at the Fermi level for the free electron gas contained in a three-dimensional “box.” The two-dimensional and the one-dimensional densities of states may be derived, using in (1.11) the corresponding expressions for the volume of the box, total volume in  $k$ -space  $V_k$  and volume per point in  $k$ -space in two and one dimensions. In two dimensions,  $V_k = \pi k^2$ , the volume per point is  $(2\pi/L)^2$  and the volume of the box is  $L^2$ .

In one dimension, the total volume in  $k$ -space is  $V_k = 2k$ , the volume per point is  $(2\pi/L)$  and the volume of the box is  $L$ . Consequently, the general expression for the density of states is

$$D(E) = \left( \frac{2m}{\hbar^2} \right) \frac{V_k}{v} \frac{p}{k^2}, \quad (1.14)$$

where  $p = 1, 2, 3$  are the corresponding dimensionalities, as can be easily verified. Substituting, one obtains the densities of states  $D(E)$ , for the different dimensionalities.

In three dimensions:

$$D(E) = V \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}. \quad (1.15)$$

In two dimensions,

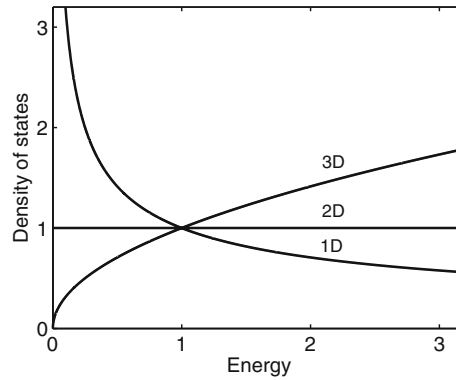
$$D(E) = V \frac{1}{2\pi} \left( \frac{2m}{\hbar^2} \right). \quad (1.16)$$

Note that in this case the density of states  $D(E)$  does not depend on the energy, it is a constant.

And finally, in one dimension,

$$D(E) = V \frac{1}{\pi} \left( \frac{2m}{\hbar^2} \right)^{1/2} E^{-1/2}. \quad (1.17)$$

These expressions for the densities of states of the free electron gas for different dimensions (1, 2, and 3) are represented in the graphs of Fig. 1.5.



**Fig. 1.5.** Normalized densities of electronic states  $D(E)/C_p$  (where  $C_p$  is a constant factor for each dimensionality  $p$ ) as a function of energy, for different dimensionalities

We will now discuss what happens if the object that contains the electrons is a solid of nanometric dimensions. There will be quantum confinement in any case where one or more dimensions of the volume that contains the electron gas are comparable to the Fermi wavelength  $\lambda_F = 2\pi/k_F$  of the electron. In objects with dimensions comparable to this wavelength the wave character of the electrons will be dominant, and their energies will be quantized.

To obtain the densities of states in the confined systems, one has to take into consideration the boundary conditions. The electrons may be confined in the three dimensions, i.e., they may be contained in an object that is nanometric in the three dimensions – this is the case of a quantum dot. If the electrons are confined in two dimensions, i.e., if the third dimension is macroscopic, one has a quantum wire, or a nanowire. If the electrons are confined in one dimension, one has a quantum well, or a quantum film. If the electrons are not confined in any dimension, one has a macroscopic object.

#### 1. Object confined in three dimensions (quantum dot):

The allowed values for the energy of the electrons are given by (1.9). The energies of the different levels depend on  $k_x$ ,  $k_y$ , and  $k_z$ . The condition of infinite potential at the walls implies  $k_x = n_x\pi/L_x$ ,  $k_y = n_y\pi/L_y$  and  $k_z = n_z\pi/L_z$ , where  $L_x$ ,  $L_y$  and  $L_z$  are the dimensions of the box where the electrons are contained.

$$E = \frac{\hbar^2\pi^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right). \quad (1.18)$$

The separation between the energy levels is given by  $dE_k$ . One assumes to simplify  $L_x = L_y = L_z = L$ , and also  $n_x = n_y = n_z = n$ . For a nanoscopic solid with  $L = 1$  nm, the energy levels are separated by  $dE = 3\hbar^2\pi^2/mL^2 \sim 1$  eV. Therefore, the energy spectrum is formed of discrete levels, similar to the atomic levels, with energies given by

$$E_n = \frac{3\hbar^2\pi^2}{2mL^2} n^2. \quad (1.19)$$

The density of states curve  $D(E)$  is formed of a series of delta functions at the energies  $E_n$ .

#### 2. Object confined in two dimensions, and free in one dimension (quantum wire or nanowire):

One may assume that the object is macroscopic in the  $z$  direction, and the dimensions  $L_x = L_y$  are nanoscopic.

From (1.18), taking  $L_z = L$  and  $n_z = n$  one obtains

$$E = \frac{\hbar^2\pi^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n^2}{L^2} \right). \quad (1.20)$$

In this case the separation between the energy levels labelled by  $n_x$  and  $n_y$  remains large, of the order of  $eV$ . The separation of the levels corresponding to  $n$  is much smaller, since  $L$  is a number typically  $10^7 - 10^9$  times larger than the  $x$  and  $y$  dimensions. One may consider these levels as occupying a practically continuous range of values.  $E(k)$  is then given by parabolas displaced by  $\hbar^2\pi^2/2mL^2$ .

The density of states curve  $D(E)$  is formed of a series of peaks at the values of  $E_n$ ; above each peak there exists a region with a continuous dependence with  $E$ .

3. Object confined in one dimension and free in two dimensions (quantum film or quantum well):

If the confinement is limited to the  $x$  axis, the electrons are free to move in the directions of the plane ( $y$  and  $z$  axes) and the energy levels are given (for  $L_y=L_z=L$ ) by

$$E = \frac{\hbar^2\pi^2}{2m} \left( \frac{n_x^2}{L_x^2} + 2\frac{n^2}{L^2} \right). \quad (1.21)$$

In the same way as in the preceding case, the energies of the levels, labelled by  $n_x$ , exhibit a large difference.  $E$  vs.  $k_x$  and  $k_y$  is given by parabolic surfaces displaced of  $\hbar^2\pi^2/2mL^2$ . The density of states curve  $D(E)$  is formed of a series of steps, within a parabolic envelope.

4. Object without confinement, electrons free to move in the three directions (macroscopic object):

Taking the frontiers defined by  $L_x = L_y = L_z = L$  as macroscopic lengths, the energies are given by

$$E = \frac{\hbar^2\pi^2}{2m} \left( 3\frac{n^2}{L^2} \right). \quad (1.22)$$

The energy levels are now distributed over a continuum of states, as shown in Fig. 1.5. The graph of  $E_k$  is represented by a parabolic surface and the density of states curve  $D(E)$  is the familiar parabola shown in Fig. 1.5.

The density of state curves shown in Fig. 1.3 differ from those that appear in Fig. 1.5, since there are obvious steps or discontinuities in Fig. 1.3. These steps arise, for example, in the case of a  $D2$  solid (quantum film, or quantum well), from the electron confinement in the dimension perpendicular to the plane. This confinement induces the appearance of discrete levels in the density of states; the dependence  $D(E) = \text{constant}$  is observed at the energies corresponding to these levels.

A simple visual examination of the density of states curves  $D(E)$  shown in Fig. 1.3 reveals important differences in this function. The appearance of  $D(E)$  for the 0D sample is similar to the same function for atoms:  $D(E)$  has narrow peaks, corresponding to well-defined values of the kinetic energy of the conduction electrons. For this reason, quantum dots are often referred to as “artificial atoms.”

The curve  $D(E)$  for quantum wires (one-dimensional) also has narrow peaks, but in this case there are electronic states that may be occupied for intermediate values of

the energy  $E$ . The curve for a two-dimensional nanosystem shows some well-defined steps, and again there exists a quasi-continuum of states that may be occupied in the whole range of energies. The result of  $D(E)$  for a macroscopic system in the free electron approximation is the well-known parabola, applicable in the simplest description of the metals.

Many physical properties of a solid may be directly related to the electronic density of states  $D(E)$ , such as the Pauli susceptibility, the conduction electron contribution to the specific heat, and so on. The Pauli susceptibility, that measures the response of the free electron gas to an applied magnetic field, is given by

$$\chi_P = \mu_0 \mu_B^2 D(E_F), \quad (1.23)$$

where  $D(E_F)$  is the density of states at the Fermi level.

The importance of the effect of low dimensionality on the properties of the conduction electrons can be estimated from the size of the nanoobject relative to the Fermi wavelength. This wavelength can be computed from the expression relating  $N$  to  $k_F$  (1.11).

$$k_F = \left( \frac{3\pi^2 N}{V} \right)^{1/3}. \quad (1.24)$$

Using the electronic density  $n = N/V$ , the Fermi wavelength becomes

$$\lambda_F = 2\pi \left( \frac{1}{3\pi^2 n} \right)^{1/3}. \quad (1.25)$$

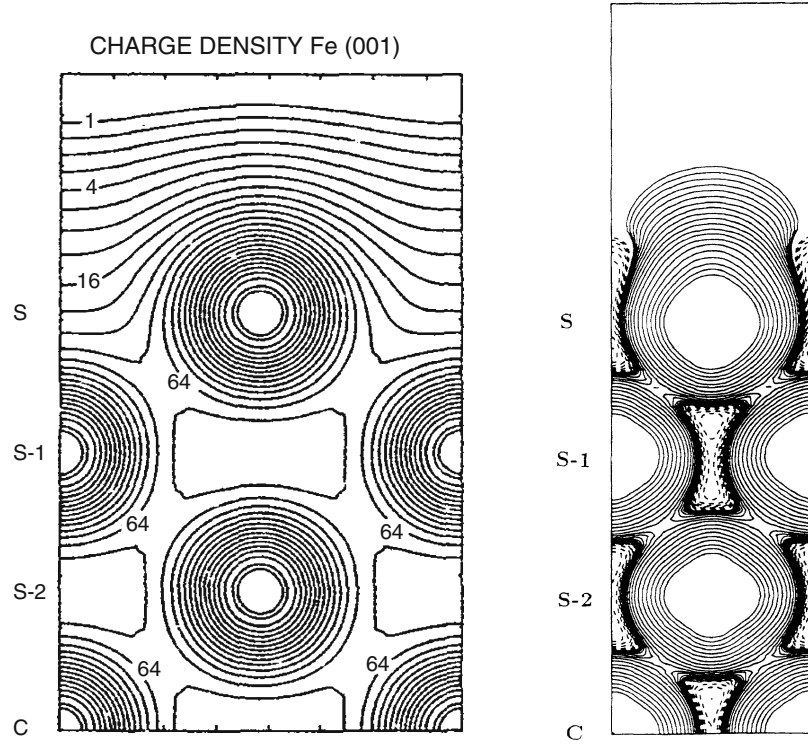
Therefore, the Fermi wavelength is inversely proportional to  $n^{1/3}$ , and consequently this wavelength is much larger in semiconductors ( $\sim 100$  nm) than in the metals ( $\sim 0.1$  nm). For example, in Fe, the Fermi wavelength is  $\lambda_F = 0.37$  nm.

The magnetic moments of the transition element atoms also depend on the dimensionality of the structures where they are found. This dependence is evident in the computed magnetic moments of Ni and Fe for different dimensionalities, given in Table 1.3. The iron magnetic moment, for example, varies from  $2.27 \mu_B$ , for a three-dimensional solid, to  $4.0 \mu_B$  for 0D (free atom).

The charge and spin densities near surfaces and interfaces are modified, as is illustrated in Fig. 1.6, where there are shown the computed charge density in the Fe(001) surface of a thin film [21] and the spin density on a Fe(110) surface [12]. It is apparent that the charge and spin densities of the surface atoms are significantly different from the corresponding densities at the inner rows of atoms.

**Table 1.3.** Computed magnetic moments (in  $\mu_B$ ) and dimensionality for Ni and Fe samples [23]

Element	Zero (0D)	One (1D)	Two (2D)	Three (3D)
Ni	2.0	1.1	0.68	0.56
Fe	4.0	3.3	2.96	2.27

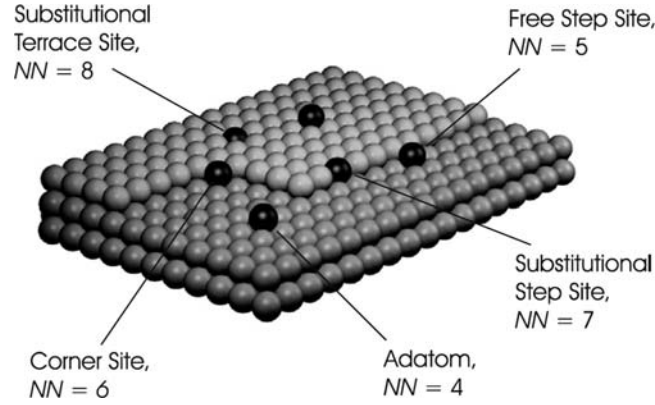


**Fig. 1.6.** *Left:* representation of the computed conduction electron charge density at the surface of a seven-layer Fe(001) film; from each line to the next the density varies by a factor of  $\sqrt{2}$  [21]. (Reprinted figure with permission from [21]. Copyright (1983) by the American Physical Society); *Right:* total spin density for Fe(110) surface. *Solid and dashed lines* indicate positive and negative spin density, respectively [12]. (Reprinted figure with permission from [12]. Copyright (1992) by the American Physical Society)

An additional circumstance that modifies the magnetic properties of nanoscopic systems is the relevance of their immediate neighborhood, or physical systems in close contact. This is the case of magnetic thin films that are deposited on substrates or are covered with protective capping layers. For example, films of Co deposited on Cu(001) have Curie temperatures that vary a few degrees, in an oscillatory way, with the thickness of a Cu capping layer [24].

#### 1.2.2.2 Dimensionality and Reduced Coordination Number

An effect related to the broken translation symmetry at surfaces is that, atoms in these regions have a reduced number of neighbors, as compared to atoms in the bulk of the sample. Let us take as an example of the interface between two regions, one formed of atoms *A* and the other of atoms *B*. The *A* atoms at the interface may have



**Fig. 1.7.** Atomic sites on a thin film showing the different coordination numbers. The number  $NN$  of nearest neighbors of the atoms on the surface (adatom,  $NN = 4$ ), atom near a step ( $NN = 5$ ), atom in the step ( $NN = 7$ ) and finally, a substitutional atom at the surface ( $NN = 8$ ). (Reprinted with permission from [22])

the same number of nearest neighbors as in the macroscopic sample, but there, of course, they will have a different neighborhood, formed of atoms  $A$  and  $B$ .

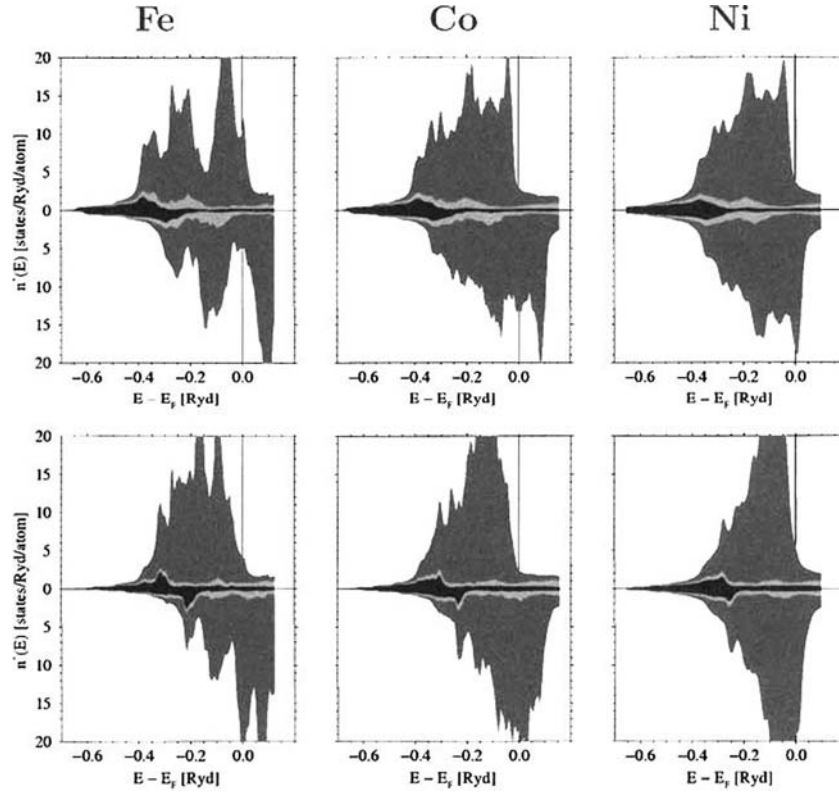
The atoms at the boundary of the sample, e.g., at the interface sample–vacuum are surrounded by a smaller number of neighbors: they may have one neighbor less, two less, and so on. These surface atoms may be at a plane surface, at the corner of a step, or inside a step. An illustration of these different surroundings is given in Fig. 1.7. The figure shows atoms on different locations of the same surface, atoms with 4, 5, 6, 7, and 8 near neighbor atoms.

In general, the electronic structure of the atoms with a smaller coordination number is different from that of the atoms in the bulk. The density of states shows that the reduction in the coordination number results in a narrowing of the electronic bands (e.g., [5]). This effect is illustrated in Fig. 1.8, with densities of states of bulk metals compared to those of atoms on a (100) surface. For Fe, Co, and Ni, the (100) surface atoms exhibit narrower density of states curves, compared to those of bulk samples of the same materials.

The increasing orbital contribution to the magnetic moment with decreasing dimensionality is made evident from measurements made on Co in Pt, as illustrated on Table 1.4; the increase in anisotropy energy is also apparent.

The atoms located on the interfaces also have the point symmetry at their sites reduced, an effect that leads to level splitting and modification of the magnitude of the atomic magnetic moments. In Fe thin films in contact with Cu, Pd, and Ag, for example, the Fe atoms exhibit enhanced magnetic moments (e.g., [24]).

The magnetic properties of atoms in interfaces are also affected by the presence of defects and impurities, such as adsorbates; strain may also change these properties, and modify the lattice parameters.



**Fig. 1.8.** Density of states for Fe, Co, and Ni in bulk metals (*above*) and on a (100) surface (*below*), showing the narrowing of the electronic bands in the latter case. The darkest areas represent the contribution of s electrons, the lightest p, and the intermediate d electrons. (Reprinted with permission from [19])

**Table 1.4.** Magnetic orbital moment and magnetic anisotropy energy of Co in Pt with different dimensionalities [11]

	Bulk	Monolayer	Diatomic wire	Monoatomic wire	Two atoms	Single atom
Orbital moment ( $\mu_B$ /atom)	0.14	0.31	0.37	0.68	0.78	1.13
Anisotropy energy (meV/atom)	0.04	0.14	0.34	2.0	3.4	9.2

Also, materials in the form of small particles may present a crystal structure that is different from that observed in bulk samples. This is the case, for example, of metallic cobalt that changes from hcp (hexagonal close packed) to fcc (face centered cubic) for particle diameters below approximately 30 nm.

**Table 1.5.** Proportion of number of surface atoms in cubic nanoscopic clusters [15]

Number of atoms on each side	Number of surface atoms	Total number of atoms	Ratio of surface atoms to total number
5	98	125	78.5
10	488	1,000	48.8
100	58,800	$1 \times 10^6$	5.9
1,000	$6 \times 10^6$	$1 \times 10^9$	0.6

### 1.2.2.3 Nanoscopic Samples and Proportion of Surface Atoms

The role of surface atoms is widely utilized in catalysis. Catalysts are usually prepared in the form of finely divided powders, or porous matrices, since their activity relies on the contact of the substances that participate in the chemical reaction with atoms at their surface.

In the study of nanoscopic samples the contribution of the surface atoms to the physical properties increases with decreasing sample sizes. This is obvious, since the area of the surface of the samples varies typically as  $\sim r^2$ , while the volume of the samples varies as  $\sim r^3$ . As a consequence, the ratio of surface to volume varies roughly speaking as  $r^{-1}$ , therefore increasing with decreasing sample size. This is illustrated with the ratio of surface atoms to total number of atoms in cubic clusters, in Table 1.5. For example, a cube with 10 atoms of side has about half of the atoms on its surface.

The area per unit mass, or specific surface area can be very large: for typical 2 nm spherical particles this may be in the range of hundreds of square meters per gram.

In some limiting cases, as for example, in a thin film formed of only one or two atomic layers, every atom of the sample is a surface atom.

### 1.2.3 Nanoscopic Samples and Magnetization Reversal

The dynamic behavior of the magnetization of nanomagnets may also be very different from that of macroscopic objects. This arises because, under the usual experimental conditions, thermal fluctuations play in this case a more important role. For example, in nanoscopic magnetic particles it is observed the phenomenon of superparamagnetism: in such particles the magnetization inverts spontaneously, since the thermal energy  $k_B T$  is comparable to their anisotropy energy (see Sect. 3.3, p. 68). A single-domain magnetic particle may spontaneously invert its magnetization, i.e., its direction may change from  $+z$  to  $-z$ , if its temperature  $T$  is above a certain blocking temperature  $T_B$ . This effect has important implications, since if the magnetization of such particle were to be used for information storage, at  $T = T_B$  the information would be lost. Therefore, in magnetic storage, with the reduction in physical size of the recorded bit, its thermal stability becomes more and more an important issue.

This phenomenon will be discussed in Chap. 3, which is devoted to magnetic nanoparticles.



### 1.3 Dimensionality and Critical Behavior

The change in magnetic behavior of the physical systems as a function of dimensionality is also reflected in the critical exponents that appear in the description of the divergences in the neighborhood of their critical temperatures.

Measurements of physical quantities in ferromagnetic samples at temperatures close to the transition temperature  $T_C$  – the Curie temperature – exhibit a power law dependence. From this dependence there may be defined critical exponents, or critical indices. We therefore, have for the specific heat  $C$ , for the saturation magnetization  $M_s$ , for the magnetic susceptibility  $\chi$  and for the magnetic induction  $B$ :

$$\begin{aligned} C &\sim |T - T_C|^{-\alpha} \\ M_s &\sim |T_C - T|^\beta \quad (T < T_C) \\ \chi &\sim |T - T_C|^{-\gamma} \\ B &\sim M^\delta \quad (T = T_C) \end{aligned}$$

The experimentally measured values of the critical exponents for different magnetic systems are  $\alpha \sim 0$ ,  $\beta \sim 0.3$ , and  $\gamma \sim 1 - 2$ .

In the Weiss model (mean field) description of ferromagnetism, the magnetization  $M$  can be written, in the case of magnetic ions with angular momentum  $J = 1/2$ , as

$$M = M_0 B_{1/2}(x) = M_0 \tanh\left(\frac{\mu_B B + \lambda_m M}{k_B T}\right), \quad (1.26)$$

where  $B_{1/2}(x)$  is the Brillouin function, given by (2.6), on p. 25. This equation can be re-written as

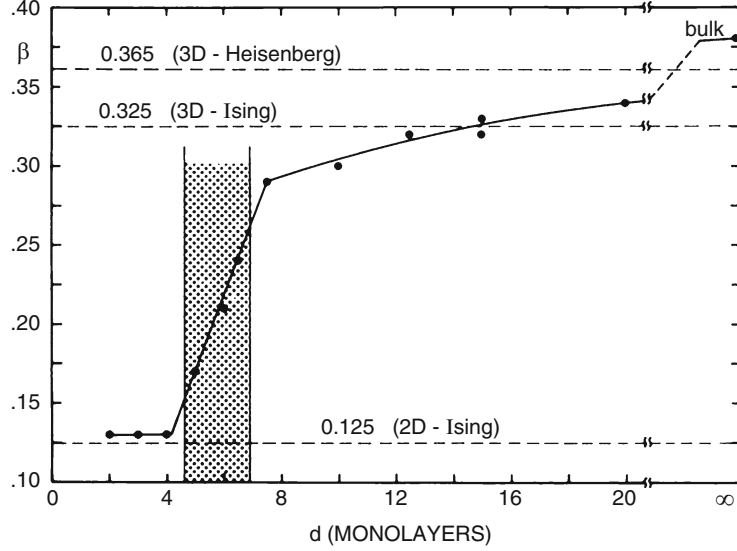
$$\tanh^{-1}\left(\frac{M}{M_0}\right) = \frac{\mu_B B}{k_B T} + \frac{\lambda_m}{k_B T} M, \quad (1.27)$$

where  $\lambda_m$  is the molecular field parameter.

For temperatures close to the critical temperature  $T_C$ , the magnetization will be small and we can expand the Brillouin function. From this expansion, one can determine (e.g., [2]) the critical exponents in the case of the mean field model. The exponents in this case are given at Table 1.6, together with values calculated numerically using a high temperature expansion for dimensionality  $D = 3$ . In general the agreement between the mean field critical exponents and the calculated values increases with increasing dimensionality.

**Table 1.6.** Critical exponents in the mean field model, and values calculated numerically using a high temperature expansion for three dimensions ( $D = 3$ ) [2]

Magnitude	Exponent	Mean field	High $T$ expansion ( $D = 3$ )
Specific heat	$\alpha$	0	$0.110 \pm 0.005$
Magnetization	$\beta$	$\frac{1}{2}$	$0.312 \pm 0.003$
Susceptibility	$\gamma$	1	$1.238 \pm 0.002$
Induction B	$\delta$	3	$5.0 \pm 0.05$



**Fig. 1.9.** Critical exponent  $\beta$  as a function of thickness, measured in number of monolayers, in thin films of Ni(111) on W(110), showing the transition from a bidimensional to a tridimensional behavior [18]. (Reprinted figure with permission from [18]. Copyright (1992) by the American Physical Society)

Magnetization measurements as a function of temperature in mesoscopic and nanoscopic systems have been used to obtain critical exponents, and from these, verify the change in dimensionality as a function of their diameter, length, thickness and so on. For example, in thin films the transition from bidimensional to tridimensional behavior was observed (Fig. 1.9). For the thinnest samples of Ni films, the observed critical exponent is near 0.325, the value predicted for bidimensional systems (in the Ising model); as the thickness increases, the exponent changes, at about six monolayers, to a value close to that expected for tridimensional physical systems (0.365), in the same model [18]. The same effect was observed in Ni on Cu(111) and Ni on Cu(100) [16].

It is not easy to identify experimentally the effects of change in dimensionality on the magnetic properties of low-dimensional samples. For example, the variation of magnetic ordering temperature  $T_C$  of thin films as a function of thickness may be related to the morphology of the films. Clusters may be formed in the process of film growth [24]; percolation of these clusters produces magnetic transitions, and at finite temperatures, smaller islands will exhibit superparamagnetic behavior.

If one atomic magnetic moment changes its direction, it will affect the direction of the moments of the neighbor atoms within a radius  $r$ . The correlation length  $\xi$  in magnetism can be understood in simple terms as associated to this radius. Another critical exponent relevant to the study of magnetic systems is the exponent  $\nu$  that enters the expression of the temperature dependence of the correlation length  $\xi$ :

$$\xi \sim |T - T_C|^{-\nu}. \quad (1.28)$$

This exponent is related to the shift exponent  $\lambda$ , that appears in the Curie temperature shift in geometrically confined samples. In this case the relation between the Curie temperatures  $T_C$  of the low-dimensional system ( $T_C(d)$ ) and  $T_C$  of the material in bulk form ( $T_C(\infty)$ ) is:

$$\frac{(T_C(\infty) - T_C(d))}{T_C(\infty)} = \left(\frac{\xi}{d}\right)^\lambda. \quad (1.29)$$

In the above equation,  $d$  is the thickness of a thin film or the diameter of a particle, and  $\lambda = 1/\nu$  is the displacement, or shift exponent, a number between 1.0 and 2.0. In mean field theory  $\lambda = 1$ , and an estimate in the three-dimensional Heisenberg model obtained  $\lambda = 1.419 \pm 0.006$  [6]. An experimental study of maghemite nanoparticles resulted in a value of  $\lambda = 1.1 \pm 0.2$  [13].

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