ELECTRIC, OPTICAL & MAGNETIC PROPERTIES OF NANOSTRUCTURES

THOMAS GARM PEDERSEN
LARS DIEKHÖNER
AALBORG UNIVERSITY
2009
Table of Contents

Introduction .............................................................................................................................. 3
1. Time-dependent Perturbation Theory .............................................................................. 7
   1.1 Linear Response Theory ............................................................................................... 7
2. Bulk Response of Metals ................................................................................................... 13
   2.1 Spin Magnetization ..................................................................................................... 14
   2.2 Electric Current ............................................................................................................ 17
3. Electric Currents in Nanostructures ............................................................................... 21
   3.1 Electron Reflection and Transmission ...................................................................... 24
   3.2 Simplification: Decoupled Channels ........................................................................ 26
4. Electric Properties of Semiconductors ............................................................................ 31
   4.1 Doping ........................................................................................................................... 35
5. PN Junction and Tunneling Diodes ................................................................................ 40
   5.1 Analysis of the PN Junction ....................................................................................... 41
   5.2 Tunneling Current ....................................................................................................... 45
6. Metal-Semiconductor Junctions ...................................................................................... 51
   6.1 Three-dimensional Non-degenerate Devices .......................................................... 53
   6.2 Schottky Diode ............................................................................................................. 54
7. Optical Properties of Semiconductors ............................................................................ 62
   7.1 Two-band and Envelope Approximations .............................................................. 64
8. Optics of Bulk and Low-dimensional Semiconductors ................................................ 69
   8.1 Semiconductor Quantum Wells ................................................................................ 71
   8.2 Semiconductor Quantum Wires and Dots ................................................................ 73
9. Models of Excitons ............................................................................................................ 77
   9.1 Wannier Model ............................................................................................................ 81
10. Excitons in Bulk and Two-dimensional Semiconductors ............................................. 85
   10.1 Excitons in Quantum Wells .................................................................................... 88
11. Excitons in Nanowires and Nanotubes ......................................................................... 94
   11.1 1s Excitons in Carbon Nanotubes ......................................................................... 98
12. Semiconductor Lasers and LEDs ................................................................................ 105
   12.1 Gain in Semiconductor Lasers ................................................................................. 108
13. Photonic Band Gap Structures ..................................................................................... 114
   13.1 One Dimensional PBG Structures .......................................................................... 115
   13.2 Two Dimensional PBG Structures .......................................................................... 117
14. Optical Properties of Nanospheres ............................................................................. 123
   14.1 Finding the Fields .................................................................................................... 126
   14.2 Scattering, Absorption and Extinction .................................................................... 129
15. Basic Magnetism ............................................................................................................ 134
   15.1 Isolated Moments .................................................................................................... 136
   15.2 Coupled Moments .................................................................................................... 140
16. Exchange Interaction for Localized Moments ............................................................. 145
17. Itinerant Exchange Interaction ...................................................................................... 153
   17.1 Ferromagnetism of Free Electrons .......................................................................... 153
17.2 Band Model for Ferromagnetism ................................................................. 155
18. Domains and Anisotropy .............................................................................. 160
  18.1 Anisotropy ............................................................................................... 160
  18.2 Domain Boundaries .................................................................................. 162
  18.3 Magnetostatic Energy and the Origin of Domain Formation ............ 163
  18.4 Single Domain Nano particles ................................................................. 165
Introduction

Properties are essentially about cause and effect. A material left completely undisturbed doesn’t display its properties. However, if we probe something the response will reveal the characteristic properties of the object. Here, probing should be understood in its broadest sense. If we look at something it is probed by the light reflected or transmitted by the object. If we put an object on a table it is probed by contact forces. If we place the object on a hot plate it is probed by the heat. An endless list of external “perturbations” serve as probes of properties that, taken together, characterize the object. At a qualitative level we might label the object as shiny, hard, heavy etc. More accurately, however, we should specify its reflectance, hardness, heat capacity and so on as precisely defined properties that can be measured in a specific setup. This also allows us to describe theoretically the phenomenon in a precise manner. Hence, to this end we must construct a model that encompasses the object, the perturbation and the response.

The present set of lecture notes deals only with a small part of all the properties imaginable. We restrict ourselves to the following perturbations: electric potentials, light and magnetic fields. The responses to these stimuli define together the electric, optical and magnetic properties of an object. Moreover, we exclude cases, where any two of these perturbations are present at the same time. Finally, we restrict the analysis to weak disturbances that don’t perturb significantly the object. This might seem as rather severe restrictions but, actually, they are not. They will allow us to understand a wide range of phenomena such as the color of an object. And within this restricted analysis we’ll still be able to explain several important features of advanced devices such as diodes, lasers and magnetic hard discs.

What is characteristic of electric, optical and magnetic properties? To answer this question, we should specify some appropriate experimental setup, in which we wish to measure a given property. Focusing on the perturbations, we might think of something like the sceneries shown in the Fig. I.1. Here, the bar represents a sample that we want to characterize. The electrical setup in the upper panel is probably the most familiar type of setup. In this case, the perturbation is the voltage applied between the end points. The response is the current, which flows in the circuit. Hence, perturbation and response can be determined experimentally by means of a voltmeter and amp meter, respectively. Really, such a measurement is tricky because not only the sample plays a role in determining the current. Resistances in the wires and power supply in general cannot be ignored and so more advanced methods (such as four-point measurements) may be needed. But what is the role of the sample? Well, for a voltage $V$ the current $I$ is limited by the electrical resistance $R = V/I$ or, if we like, we could measure the conductance $G = I/V = 1/R$. The point here is that these quantities depend on both the material in the sample and shape of the sample. For a large homogeneous bar of length $L$ and cross section $A$ the
resistance is expected to vary as \( R = \frac{\rho L}{A} \), where \( \rho \) is the specific resistance of the material. In turn, \( \rho \) is a characteristic of the material and depends only on external parameters such as temperature and pressure and so on.

![Schematic illustration of electric, magnetic and optical perturbations of sample.](image)

Next, we turn to the magnetic response. As shown in the middle panel of the figure, we could imagine placing a sample between the poles of a magnet. Hence, the perturbation in this case is the magnetic field penetrating the sample. What happens inside the sample? The answer to this question depends on the nature of the sample. We consider first the case of so-called non-magnetic materials. Imagine the external magnetic field intensity \( \mathcal{H} \) penetrating the sample. Inside the sample, the electrons act as tiny bar magnets themselves. A characteristic property of non-magnetic materials is that these tiny bar magnets point in all directions with equal probability if the external magnetic field is switched off. However, when the external field \( \mathcal{H} \) is applied they will try to align with this field. The result is that the material becomes magnetized and we say that a certain magnetization \( \mathcal{M} \) has been induced. Since the magnetization is induced by the magnetic field we expect a linear dependence if the
field is not too large: $\mathcal{M} = \chi_M \mathcal{H}$, where $\chi_M$ is the magnetic susceptibility. Hence, in this case, $\chi_M$ is the important material quantity, which we wish to describe. Measuring $\chi_M$ is less simple than measuring e.g. the resistance described above. One possibility is to use a flux meter to record the flux of the total magnetic field $B = \mu_0 (\mathcal{H} + \mathcal{M}) = \mu_0 (1 + \chi_M) \mathcal{H}$ through a wire loop as the external field $\mathcal{H}$ is turned on.

The exception to this behavior of non-magnetic materials is found in magnetic materials. These are substances, in which a finite magnetization can exist even without an external field. The challenge in this case is to understand this phenomenon and to see how such a material will be influenced by an external field. An extremely important aspect of this case is the change in the direction of the magnetization that can be induced by an external field. This forms the basis for magnetic storage devices.

The optical response is, in fact, quite similar to the magnetic one. In this case, a high-frequency electric (and magnetic) field $\mathcal{E}$ is incident on our sample and this field displaces the charges in the material. In the optical regime, the relevant charges are electrons as the nuclei respond primarily to fields of much lower frequency. The displaced electron charges are described by the polarization $\mathcal{P}$ and in perfect analogy with the magnetic case we expect a linear relation $\mathcal{P} = \varepsilon_0 \chi \mathcal{E}$, where $\chi$ is now the electric susceptibility. In turn, $\chi$ determines the dielectric constant of the material $\varepsilon = 1 + \chi$ and also the refractive index $n = \sqrt{1 + \chi}$. Hence, these quantities are the relevant material properties. Measuring the refractive index is in itself a complicated task. The imaginary part reveals itself in absorption measurements, while the real part is responsible for refraction and interference effects. The technique known as ellipsometry is developed for the purpose of accurately measuring these quantities.

So far, the discussion has been quite general and applicable to many circumstances. The focus of these notes, however, will be on nanostructures. The reason is simply that our ability to design and fabricate structures on a nanometer scale has expanded the range of electric, optical and magnetic phenomena in a truly amazing manner. There are several reasons for this. Most importantly, the rules of physics are different on the nanoscale. Pronounced quantization effects appear and, hence, scaling bulk results such as $R = \rho L / A$ into the nanoscale simply doesn’t work if the cross section $A$ becomes sufficiently small. A dramatic consequence in this particular case is the appearance of quantized conductance, in which individual quantum levels determine the resistance. Similarly, electric and magnetic susceptibilities are entirely different in low-dimensional structures. This opens the window to novel phenomena as well as brand new applications. Even if the material properties are almost identical to the bulk values, new effects can appear if the size of the sample is in the nanoscale. An important example is found in nanooptics. Here, optical components of a size comparable to the wavelength are used and this dramatically changes the way light
propagates, diffracts and so on. Actually, completely new metamaterials can be fabricated in this fashion.

Through these lecture notes we hope to display the differences between the properties of bulk materials and nanostructures. We do this by describing both so that a comparison can be made. Our approach consists in the formulation of a very general framework for the response to external perturbations in the bulk as well as in nanostructures. We then turn to all the different electric, optical and magnetic applications of this general framework in the subsequent chapters. The notes are intended for students in the final year of undergraduate study having already established a solid knowledge in quantum mechanics, statistical mechanics, solid state physics as well as optics and electromagnetism.
15. Basic Magnetism

Magnetism is a fundamental property of materials. We will in this chapter review the most important aspects of magnetism and describe para- and ferro-magnetism in some detail. Let us first briefly define a few terms.

\( B \): Magnetic flux density  
\( \mathcal{H} \): Magnetic field strength  
\( \mathcal{M} \): Magnetisation, (dipole moment density)

In free space we have the following relation:  \[ 0 \mu_m = \rho \mathcal{B} \mathcal{H} \], where \( 0 \mu_m \) is the vacuum permeability. In a material we have to take into account the magnetization, thus

\[ \mathcal{B} = \mu_0 \left( \mathcal{H} + \mathcal{M} \right) \quad (15.1) \]

We can now define the magnetic susceptibility \( \chi \), which is the response of the material to an applied magnetic field, via the following relation

\[ \mathcal{M} = \chi \mathcal{H} \quad (15.2) \]

Or more correctly \( \chi = \partial \mathcal{M}/\partial \mathcal{H} \). Strictly speaking \( \chi \) is a tensor and the magnetization is, for some materials, not pointing in the same direction as the applied field.

We thus have \( B = \mu_0 (H + \mathcal{M}) = \mu_0 (H + \chi H) = \mu_0 (1 + \chi) H \), which also defines the relative permeability \( \mu_r = 1 + \chi \). How a material responds to an applied magnetic field can be classified into the following

Paramagnetic materials: \( \chi \sim 10^{-5} \)
Diamagnetic materials: \( \chi \sim 10^{-5} \)
Ferromagnetic materials: \( \chi > 1 \)

The values are orders of magnitude and can vary strongly. Furthermore there is a pronounced temperature variation for para- and ferromagnetic materials which will be discussed in detail later. Note that these values are only valid for static magnetic fields since time-varying applied fields can cause eddy currents, which produce a magnetic field pointing in the opposite direction of the applied field. The material thus behaves strongly diamagnetic. This effect is dependent on the electrical conductivity. Another class of materials is superconductors, which act as perfect
diamagnets, i.e. $\chi = -1$. It is observed that the flux lines of an applied magnetic field are not allowed to penetrate the superconducting material. This is also called the Meissner effect.

We will now establish a microscopic description of magnetism. The essential parameter is the magnetic dipole moment $\vec{\mu}$. Classically, for a current loop, this is given as

$$\vec{\mu} = I A,$$  \hspace{1cm} (15.3)

where $I$ is the current in the loop and $A$ the area. The direction of the vector is given by the “right hand rule”. We can express the current as $I = dq / dt = q / T$, where $T$ is the evolution time of a single charge (an electron, i.e. $q = -e$). Look at the orbit of an electron in the current loop given below

![Fig 15.1. A classical current loop with an orbiting electron](image)

The infinitesimal area of the triangle is given by $dA = \frac{1}{2} |\vec{r} \times d\vec{r}|$ and we can then write

$$\frac{dA}{dt} = \frac{1}{2} \left| \vec{r} \times \frac{d\vec{r}}{dt} \right| = \frac{1}{2} \left| \vec{r} \times \vec{p} \right| = \frac{1}{2} \frac{|\vec{L}|}{2m} = \frac{L}{2m},$$ \hspace{1cm} (15.4)

where $\vec{p}$ is the momentum and $\vec{L}$ the angular momentum of the electron. Furthermore we can write $dA/dt = A/T$ for an elliptic orbit and thus

$$\frac{A}{T} = \frac{L}{2m},$$ \hspace{1cm} (15.5)

which is equal to Kepler’s second law for planetary motion! Inserting Eq. (15.5) and $I = -e / T$ into Eq. (15.3), we can now express the magnetic dipole moment in terms of the angular momentum

$$\vec{\mu} = -\frac{e}{2m} \vec{L}.$$ \hspace{1cm} (15.6)

The origin of magnetism is thus the electrons: orbiting and spinning. We can generalize the above expression and transfer it into a quantum mechanical
description by using the angular momentum operator instead of the classical angular momentum.

\[ \hat{L}^2 \psi = l(l + 1) \hbar^2 \psi \quad \text{and} \quad \hat{L}_z \psi = m_l \hbar \psi \]

where \( l \) is the quantum number describing the angular momentum, \( m_l \) the quantum number describing the projection of \( L \) onto the \( z \)-axis and \( \psi \) the eigenfunction of the operators. The classical angular momentum vector \( \mathbf{L} \) in Eq. (15.6) is then to be replaced by the eigenvalue of the corresponding quantum mechanical operator. For a general orbital angular momentum (spin, orbital or a combination) we can express the magnetic moment as

\[ \vec{\mu} = -\frac{8\mu_B \vec{J}}{\hbar}, \quad (15.7) \]

where \( \mu_B = \frac{e\hbar}{2m} \) is the Bohr magneton and \( \vec{J} = \vec{L} + \vec{S} \) the total, \( \vec{L} \) the orbital and \( \vec{S} \) the spin angular momentum. The relevant quantum numbers are \( j, m_j, l, m_l \) and \( s, m_s \). The so-called Landé \( g \)-factor is given by

\[ g = 1 + \frac{j(j + 1) - l(l + 1) + s(s + 1)}{2j(j + 1)}. \quad (15.8) \]

Note that \( g=1 \) for a pure angular momentum and \( g=2 \) for a pure spin.

The \( z \)-component of the magnetic moment then becomes

\[ \mu_z = -\frac{8\mu_B \mu_j}{\hbar} = -\frac{8\mu_B \mu_l \hbar}{\hbar} = -8\mu_B m_j, \quad (15.9) \]

And specifically for a pure spin or orbital moment we find

\[ \mu_{z}^{\text{spin}} = -2\mu_B m_s = \pm \mu_B \quad \text{and} \quad \mu_{z}^{\text{orbital}} = -\mu_B m_l \]

15.1 Isolated Moments

Let us now look at isolated magnetic moments placed in a magnetic field. It is assumed that there is no interaction between moments, but only interaction between each moment and the applied field. For simplicity we only look at spin moments. The interaction energy depends on the mutual direction of the field and moment as
\[ E = -\vec{\mu} \cdot \vec{B}. \]  

(15.10)

Assuming that the field is in the z-direction we can express the energy as

\[ E = \mu_B g m_B \mathcal{B} = \pm \mu_B \mathcal{B}, \]

(15.11)

where we have used \( g = 2 \) and the projection of our spin operator on the z-axis \( \hat{S}_z \) which has the two eigenvalues \( m_z = \pm \frac{1}{2} \). Our two-level-system described by a “spin up” and a “spin down” state now experiences a splitting in energy depending on the orientation of the dipole moment with respect to the applied magnetic field. This is also known as the Zeeman effect. For a spin-system there are only two orientations possible but for a general angular momentum there can be many (again only those allowed by the quantization conditions of \( J_z : m_J = -j, -j+1, \ldots, j+1, j \)).

The lowest energy is for the magnetic dipole moment aligned parallel to the field (i.e. the spin antiparallel to the field). That all moments do not align in that direction is due to thermal fluctuations which will tend to redistribute the moments. The average moment can be found using simple statistical mechanics

\[ \langle \mu_z \rangle = \frac{\sum_i \mu_i \exp(-E_i/k_B T)}{Z}, \]

(15.12)

where \( k_B \) is Boltzmann’s constant, \( T \) the temperature and \( Z = \sum \exp(-E_i/k_B T) \) the partition function. For \( i=1 \) (spin up) we have \( \mu_i = \mu_B \), \( E_i = -\mu_B \mathcal{B} \) and for \( i=2 \) (spin down) we have \( \mu_i = -\mu_B \), \( E_i = \mu_B \mathcal{B} \). We find that

\[ \langle \mu_z \rangle = \mu_B \tanh(x), \]

(15.13)

where \( x = \mu_B \mathcal{B}/k_B T \).
We see that for $x \to \infty$, i.e. for low temperatures all spins are in the same direction whereas for high temperatures the thermal energy is too high for the spin alignment to be of any favour. We can look at the free energy of the system: $F = E - TS$, where $S$ is the entropy, which is a measure of the disorder of the system. The random distribution of spins thus increases $S$ and the term $TS$ becomes important at increasing $T$ and will reduce the free energy.

The magnetization of a material consisting of atoms (or more precisely: magnetic moments) which can be described by two-level spin states can now be found

$$\mathcal{M}_z = n \langle \mu_z \rangle = n \mu_b \tanh(x),$$  \hspace{1cm} (15.14)

where $n$ is the atom density. The susceptibility can be calculated from $\chi = \partial \mathcal{M}/\partial \mathcal{H}$ and is given as $\chi = n \mu_b \frac{1}{\mathcal{H} \cosh^2(x)}$ plotted below as a function of $1/x$ (proportional to $T$).
The average energy density can be found like the average dipole moment and is given by

\[
\langle E \rangle = -n\mu_B B \tanh(x) .
\]  

(15.15)

We observe that the average energy due to interaction with the applied field approaches 0 as the temperature increases. We can also calculate the heat capacity of this system (see the exercise).

In the limit of high temperatures (or low fields) we expand \( \tanh(x) \approx x \) and find

\[
\chi = \frac{C}{T} .
\]  

(15.16)

This is the Curie law and the constant \( C = \frac{n\mu_B^2}{k_B} \) is called the Curie constant. Below is plotted the simple dependence on temperature.
For a general angular momentum \( J \) we find

\[
\langle \mu_j \rangle = \mu_B \mathcal{B}_j(y),
\]

where

\[
\mathcal{B}_j(y) = \frac{2j(j+1)}{2j} \coth \left( \frac{2j+1}{2j} y \right) - \frac{1}{2j} \coth \left( \frac{y}{2j} \right)
\]

is the Brillouin function, and \( y = \frac{8\mu_B j}{k_B T} B \).

For multi electron atoms it is necessary to use the total, orbital and spin angular momentum as determined by Hund’s three rules. It should be noted though that in solids the orbital momentum is often quenched due to crystal field effects and it can thus be sufficient only to consider the total spin moment.

### 15.2 Coupled Moments

We now introduce a coupling between dipole moments and see how this leads to permanent magnetization describing e.g. ferromagnets. The first coupling to consider is the direct dipole-dipole coupling. One dipole moment (with strength \( \mu_1 \)) creates a magnetic field and a neighbouring dipole moment (\( \mu_2 \)) will experience a change in energy given by Eq. (15.10). The magnetic field from a dipole is on the order of \( B = \frac{\mu_0 \mu_1}{4\pi r^3} \), and the energy is thus \( E = \pm \frac{\mu_0 \mu_1 \mu_2}{4\pi r^3} = \pm \frac{\mu_0^2 \mu_B^2}{4\pi r^3} = \pm 50 \mu\text{eV} \) when using a...
typical next-nearest neighbour distance of $r \sim 1$ Å and a dipole moment of $\mu_\mathcal{B}$. This equals a thermal energy of 0.5 K and is thus negligible at all relevant temperatures. A coupling caused by direct dipole-dipole interaction can thus not explain why the dipole moments in some materials tend to align. The origin has to be found in the so-called exchange coupling, which is a purely quantum mechanical effect. We will describe this in detail in the two following chapters and will here merely write the effect as follows. The exchange energy between two neighbouring particles ($i$ and $j$) is given by

$$E_{\text{ex}} = -2J \vec{S}_i \cdot \vec{S}_j,$$

(15.19)

where $J$ is the so-called exchange integral\(^1\). Following the sign of the dot product between the spins, we find that $J<0$ favours antiparallel spin alignment, thus describing an antiferromagnet and if $J>0$ parallel spin alignment is favoured thus leading to a ferromagnetic configuration. The magnetic order is thus caused by the exchange coupling. For now we simplify it even further and describe the coupling between neighbours in a mean-field model as follows. The total magnetic field seen by one spin is given as

$$\vec{H}_{\text{tot}} = \vec{H} + \vec{H}_{\text{inner}},$$

(15.20)

$$\vec{H}_{\text{inner}} = \lambda \vec{M},$$

(15.21)

where $\vec{H}$ is the applied field and $\vec{H}_{\text{inner}}$ is the field produced by the neighbouring spin. Now, this is not just equal to the field due to the dipole (i.e. $\sim \vec{M}$) which was seen to be far from sufficient, but instead it is described here in a phenomenological way through the coupling parameter $\lambda$. We note that the required inner field is very high ($\vec{B}_{\text{inner}} \sim 10^3$ T), but should not be seen as a real field but the field which would be necessary to achieve the same effect as the quantum mechanical exchange coupling. The model described here is called the mean-field model and is due to Weiss.

Let us first describe our ferromagnet at temperatures above the transition temperature (the so-called Curie temperature $T_C$ below which ferromagnetic order occurs). The magnetization is given by Eq. (15.2) now using the magnetic field of Eq. (15.20)

$$\vec{M} = \chi_p \left( \vec{H} + \lambda \vec{M} \right),$$

(15.22)

\(^1\) For historical reasons the letter $J$ is used for the exchange integral. This is not to be confused with the angular momentum $J$. 

141
where $\chi_p$ is the paramagnetic susceptibility we found earlier. Note that we are looking at the state above $T_C$, where the material is in the paramagnetic state. Still the interaction is taken into account via the $\lambda \vec{M}$ term. Isolating $\vec{M}$ from Eq. (15.22) and using the definition for the susceptibility $\chi = \vec{M}/\vec{H}$ we find the Curie-Weiss law

$$\chi = \frac{\chi_p}{1-\lambda \chi_p} = \frac{C}{T-T_c}.$$  \hfill (15.23)

Here we used $\chi_p = C/T$ (valid at “high temperatures”), where $C$ is the Curie constant and $T_c = \lambda C$, where $T_c$ is the Curie temperature. This can be plotted like in Fig. 15.5 where the graph is simply shifted to the right by $T_c$. By measuring the susceptibility as a function of temperature one can thus make the distinction between a paramagnet and a ferromagnet (or an antiferromagnet, where a shift in the other direction with respect to $T=0$ is expected).

Let us now look at $T<T_c$, and find an expression for the magnetization of the ferromagnetic state. We know that for an ensemble of dipole moments the magnetization is given by

$$\mathcal{M} = n\langle \mu_j \rangle = n\mu_B g_j \mathcal{B}_j(\alpha),$$  \hfill (15.24)

where $\alpha = \mu_0 \mu_B g_j \mathcal{H}_{tot} / k_B T$, with $\mathcal{H}_{tot}$ given by Eq. (15.20). Since the inner field is much larger than the applied field we simplify the equations by setting the applied field $\vec{H} = 0$ and end up with two equations, which both have to be satisfied

$$\mathcal{M} = \mathcal{M}_{\mathcal{B}_j}(\alpha)$$ \hfill (15.25)

and

$$\mathcal{M} = c_1 T \alpha,$$  \hfill (15.26)

where $c_1$ is a constant. We can isolate $\alpha$ from Eq. (15.26), insert it in Eq. (15.25) and solve for $\mathcal{M}$ numerically. Alternatively the combination can be solved graphically (see Fig. 15.6) and has solutions when the Brillouin function intersects the straight line given by Eq. (15.26) (except for the trivial crossing in 0). There will only be solutions for sufficiently low temperatures, i.e. the slope of the straight line has to be smaller than the slope of the Brillouin function at $\alpha = 0$. This also defines the transition temperature between the ordered ferromagnetic state and the disordered state and is given by
Fig. 15.6. Graphical solution of Eq. (15.25) and Eq. (15.26) at the intersection. There are only solutions for temperatures below the transition temperature $T_c$.

The magnetization is thus temperature dependent, saturating at $T=0$ K and decreasing gradually to 0 when $T = T_c$ is approached. Here a sharp phase transition occurs (see Fig. 15.7). We note that there is no abrupt phase transition when an applied field is present. Note that $T_c$ scales directly with the coupling parameter $\lambda$.

The extension of the mean-field model to antiferromagnetic and ferrimagnetic materials is in principle straightforward.

Fig. 15.7. Magnetization of a ferromagnet as a function of temperature.

\[ T_c = \frac{8\mu_B(j+1)\lambda M_s}{3k_B}. \]  

(15.27)
Exercise 15.1

Heat capacity in a two-level system

Look at a system with only two energy levels, where the difference between the energy levels is $2\mu_B B$. The energy splitting thus depends on the applied magnetic field $B$ and equals the system we looked at earlier in this chapter.

The population of the two levels depends on the temperature and the system therefore exhibits a heat capacity. Show that the heat capacity $C$ of the two-level system is given by

$$C = \frac{4}{k_B} \left( \frac{\mu_B B}{T} \right)^2 \frac{e^{-2\mu_B B/k_B T}}{\left(1 + e^{-2\mu_B B/k_B T}\right)^2}$$

and plot the heat capacity as a function of temperature $T$. Discuss the behavior, especially in the limits of low and high temperatures. Assume a constant magnetic field $B$.

Exercise 15.2

Magnetism of a molecule

Look at a system which has a singlet state ($S=0$) and a triplet state ($S=1$) separated by an energy $\Delta$. This could be a molecule. Assume that the excited state is the triplet.

1) Find an expression for the average magnetic moment when the system is placed in a magnetic field $B$, which points in the z-direction.
2) Show that the paramagnetic susceptibility $\chi$ is given by a simple Curie law ($\sim 1/T$) in the limit of high temperatures ($k_B T \gg \Delta, \mu_B B$).
18. Domains and Anisotropy

We will in this chapter investigate three important magnetic energy terms, namely exchange, anisotropy and magnetostatic energy and discuss how they influence the domain structure observed for ferromagnetic materials. The exchange energy forces the moments to point in the same direction thus making a sample which only contains one domain. This on the other hand leads to large stray fields which increases the so-called magnetostatic energy. The latter can be reduced when the sample is broken up into smaller domains pointing in different directions cancelling out the stray fields. The balance between exchange and magnetostatic energy (also called the dipole term) thus determines the domain structure. A third energy term, the so-called anisotropy, plays an important role in the detailed shape and size of the domain boundaries and also in the direction of the magnetization of each domain with respect to the crystal axes.

18.1 Anisotropy

Let us start with the anisotropy which determines the “easy-axis” of magnetization, i.e. the direction in the crystal in which it is easiest to magnetize the material. Fig 18.1 shows the magnetization as a function of applied magnetic field for iron, nickel and cobalt. It is clear that there are certain directions which are easier to magnetize than others. Since the anisotropy energy (also called the magnetocrystalline energy) usually is small compared to the exchange energy the absolute magnitude of the magnetization is independent of the direction.

![Graphs of Magnetization vs. Magnetic Field for Fe, Ni, and Co](image)

Fig. 18.1. Magnetization of Fe, Ni and Co shown for different crystallographic directions as a function of applied magnetic field [18.1].

The origin of the anisotropy lies in the spin-orbit coupling. Due to this the charge distribution is no longer spherical but spheroidal (crude approximation - especially for atoms in a crystal). The asymmetry is tied to the direction of the spin so that a rotation of the spin directions relative to the crystal axis changes the overlap between each atomic orbital and thus the exchange and the electrostatic interaction. This then leads to a change in the total energy. In a crystal the orbital angular momentum is...
quenched due to crystal field interactions which “lock” the orbitals into specific directions and the magnetization of a solid is therefore normally determined by the spin moment. Note that the spin-orbit coupling is mostly small compared to crystal-field effects and the indicated change of the orbital in Fig 18.2 is therefore highly exaggerated.

Fig. 18.2. Asymmetry of the overlap of electron distributions of neighboring atoms provide a mechanism for the magnetocrystalline anisotropy energy [18.1].

How easy it is to magnetize a crystal thus depends on which direction we choose and the crystal is therefore anisotropic. The anisotropy energy thus describes the difference in energy depending upon direction of magnetization. Let us first look at a uniaxial system like hcp Co which has one easy axis along the c-axis. Assume the magnetization $\vec{M}$ points in a direction $\theta$ with respect to the c-axis. We can now project $\vec{M}$ onto the easy and hard axis. The part $M\cos(\theta)$ points in the easy axis direction whereas the part $M\sin(\theta)$ points in the hard axis direction leading to an increase in the total energy of the system being proportional to $\sin(\theta)$. We can express the anisotropy energy in terms of a Taylor expansion in $\sin(\theta)$

$$E = c_1 \sin(\theta) + c_2 \sin^2(\theta) + c_3 \sin^3(\theta) + c_4 \sin^4(\theta) + ...$$ (18.1)

where $c_i$ are constants. Due to the symmetry of the crystal there is no difference in energy with respect to reflection in the close packed planes of the crystal, i.e. $E(\theta) = E(\theta + \pi)$ and all terms with odd order must vanish and we get the following for the anisotropy energy

$$E = K_1 \sin^2(\theta) + K_2 \sin^4(\theta).$$ (18.2)

The constants $K_i$ are temperature dependent, decreasing with increasing temperature such that near the Curie temperature there is no preferred direction for domain magnetization. For Co at room temperature $K_1 = 4 \times 10^5$ J/m$^3$ and $K_2 = 1 \times 10^5$ J/m$^3$. For a cubic crystal like Fe with the easy axis along the cube edges the anisotropy energy is more complicated. We find that
\[ E = K_1 \left( m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2 \right) + K_2 m_x^2 m_y^2 m_z^2, \]  \hspace{1cm} (18.3)

where \( \vec{m} = (m_x, m_y, m_z) = \vec{M}/M \) gives the directions we expand in. Again only even powers are allowed for symmetry reasons. The lowest order term \( m_x^2 + m_y^2 + m_z^2 \) is identical to unity and does not describe anisotropy effects. At room temperature we have for Fe \( K_1 = 4 \times 10^4 \text{ J/m}^3 \) and \( K_2 = 1.5 \times 10^4 \text{ J/m}^3 \) and for Ni \( K_1 = -5.7 \times 10^3 \text{ J/m}^3 \) (note the sign and compare with the easy directions for bcc Fe and fcc Ni shown in Fig 18.1). Anisotropy energies are usually in the range \( 10^2-10^7 \text{ J/m}^3 \) corresponding to an energy per atom of \( 10^{-8}-10^{-3} \text{ eV} \). This is indeed very small compared to the exchange energy.

### 18.2 Domain Boundaries

We will later discuss the energetic advantages upon having more than one domain in a ferromagnetic sample. Here we will look in detail at the boundary between two domains. Below is shown a 90° and a 180° domain boundary.

![Domain Boundaries](image)

**Fig 18.3.** Left: 90° and a 180° domain boundaries. Right: A Bloch domain wall showing the rotation of spins over a 180° domain boundary [18.1].

Let us look at a 180° domain boundary over which the spins have to re-orientate. Between each spin pair the exchange energy is \( E_{\alpha\beta} = -2JS_1 \cdot S_2 = -2JS^2 \cos(\varphi), \) where \( \varphi \) is the angle between two neighboring spins. The exchange interaction will keep the spins aligned and the energy difference due to turning one spin \( \varphi \) is \( \Delta E_{\alpha\beta}(\varphi) = E(\varphi) - E(\varphi = 0) \approx -2JS^2 \left( 1 - \varphi^2/2 \right) - (-2JS^2) = JS^2 \varphi^2, \) where we have expanded the cosine. The total rotation \( \pi \) is taking place over \( N \) atoms, thus \( \varphi = \pi/N \)
and thereby \( \Delta E_{\text{ex}} = JS^2 \pi^2 / N^2 \) for each spin pair. There is 1 line of atoms pr \( a^2 \), where \( a \) is the lattice constant and the energy density (pr area) is thus

\[
\sigma_{\text{ex}} = \frac{JS^2 \pi^2}{Na^2}.
\] (18.4)

Here we have taken into account that there are \( N \) spin pairs in total. We see that \( \sigma_{\text{ex}} \to 0 \) for \( N \to \infty \) and the domain wall will thus tend to be very large by distributing the cost of misaligned spins over as many pairs as possible. This on the other hand leads to many spins pointing in directions where the anisotropy energy is high (Fig 18.1), thus increasing the anisotropy energy given by \( E'_{\text{an}} = K \sin^2(\varphi) \) in the simplest form. In total we get

\[
E_{\text{an}} = \sum_{i=1}^{N} K \sin^2(\theta) \approx \frac{1}{\Delta \theta} \int_{0}^{\pi} K \sin^2(\theta) d\theta = \frac{NK}{2},
\]

where \( \Delta \theta = \pi / N \). Note that this is a volume density and the areal density due to anisotropy is thus found by multiplication with \( a \)

\[
\sigma_{\text{an}} = \frac{NKa}{2}. \] (18.5)

In total we have the domain wall energy density

\[
\sigma_{\text{dw}} = \sigma_{\text{ex}} + \sigma_{\text{an}} = \frac{JS^2 \pi^2}{Na^2} + \frac{NKa}{2}. \] (18.6)

The first term decreases with \( N \) and the second term increases with \( N \). We now just need to minimize \( \sigma_{\text{dw}} \) with respect to \( N \) in order to find the domain wall width \( \delta \). We find

\[
N = S \pi \sqrt{2J/Ka^3} \quad \text{and} \quad \delta = Na
\]

\[
\delta = S \pi \sqrt{2J/Ka}. \] (18.7)

Inserting approximate values: \( S = \frac{1}{2}, J = 10 \text{meV}, a = 2.87 \text{Å}, K = 4 \times 10^4 \text{J/m}^3 \) (Fe) we find \( \delta = 21 \text{ nm} \), thus the wall extends over ca 80 atoms.

**18.3 Magnetostatic Energy and the Origin of Domain Formation**

The reason for domain formation at all has to be found in a third energy term, namely the magnetostatic energy of the particle. We know that \( \vec{B} = \mu_0 (\vec{H} + \vec{M}) \) and \( \nabla \cdot \vec{B} = 0 \) which leads us to
\[ \nabla \cdot \vec{H} = -\nabla \cdot \vec{M}. \]

Look at a homogeneously magnetized sample. At the boundary \( \vec{M} \) diverges and \( \nabla \cdot \vec{M} < 0 \) at the upper and \( \nabla \cdot \vec{M} > 0 \) at the lower boundary respectively. This results in \( \nabla \cdot \vec{H} > 0 \) at the upper and \( \nabla \cdot \vec{H} < 0 \) at the lower boundary, i.e. as if magnetic “charges” (or poles) existed at the surface: positive at the upper and negative at the lower. The resulting field between them is called the demagnetizing field \( \vec{H}_d \). Note that \( \vec{H}_d \) points in the opposite direction as \( \vec{M} \) and thus works against an applied field trying to magnetize the sample. For an elongated sample this effect is more pronounced in the “short” direction, since in the “long” direction the poles are far apart leading to a low \( \vec{H}_d \).

![Fig 18.4. Magnetization (M), demagnetizing field (H_d) and the magnetic “charges” or poles at the boundary [18.2].](image)

We can also look at the stray fields from a ferromagnet. This depends strongly on the number and configuration of domains as seen in the figure below. We see that the magnetic “charges” cancel out when the configuration is favorable (d and e) thus reducing the magnetostatic energy.

![Fig. 18.5. Stray fields around different domain configurations in a ferromagnet [18.1].](image)

In general we can express \( \vec{H}_d \) in terms of the magnetization and a materials shape dependent tensor \( \vec{T} \)

\[ \vec{H}_d = -\vec{T} \cdot \vec{M}. \]

The magnetostatic energy, which is given below, can now be evaluated
\[ E_{ms} = -\frac{\mu_0}{2} \int_V \vec{\mathcal{H}}_g \cdot \vec{\mathcal{M}} dV. \] (18.8)

Note that this looks like a dipole-dipole term integrated up (since \( \mathcal{M} \) is a density). The factor \( \frac{1}{2} \) is to avoid double counting of dipole pairs. For particles with high symmetry, e.g. an ellipsoid, in the overall shape and \( \vec{\mathcal{M}} \) pointing along one of the principal axes we can write the tensor as

\[
\bar{T} = \begin{pmatrix}
T_x & 0 & 0 \\
0 & T_y & 0 \\
0 & 0 & T_z
\end{pmatrix}.
\]

For a sphere we have \( T_x = T_y = T_z = \frac{1}{3} \) and \( \vec{\mathcal{H}}_g = -\frac{\vec{\mathcal{M}}}{3} \). For a very elongated ellipsoid (i.e. a rod which is “long” in the \( z \)-direction) we have \( T_x = T_y = \frac{1}{2}, T_z = 0 \) and \( \vec{\mathcal{H}}_g \) will work against \( \vec{\mathcal{M}} \) only in the \( x \) and \( y \) direction, but not in the \( z \) direction. It is thus easier to magnetize the sample along \( z \) than along \( x \) or \( y \) since \( \vec{\mathcal{H}}_{g,xy} = -\frac{1}{2} \vec{\mathcal{M}} \) and \( \vec{\mathcal{H}}_z = 0 \). This effect is also called shape anisotropy. The difference in easy/hard axis due to shape is used e.g. in data storage where we want magnetic particles with two well defined orientations. An elongated ellipsoid is the perfect choice since the magnetization prefers to be in on of the two “long axis” directions, and not in the orthogonal “short axis” directions. For a flat sample (oblate) we have \( T_x = T_y = 0, T_z = 1 \) leading to an easy axis of magnetization in the plane. This agrees with observations for thin films which can be described by an anisotropy term \( \frac{1}{2} \mu_0 M_s^2 \cos^2(\theta) \), where \( M_s \) is the saturation magnetization and \( \theta \) is the angle between the surface film and the surface normal. It should be noted that surface anisotropy terms can alter this for very thin films.

There is thus a delicate balance between exchange, magnetocrystalline anisotropy and magnetostatic energy (or shape anisotropy) which determines the domain structure of a ferromagnetic particle.

### 18.4 Single Domain Nano particles

Finally we will look at a spherical particle and see when a single domain is favorable. This has many applications in data storage using the magnetic state of a particle (up/down) for storing bits of information. Here it is important to have well defined domain structures which best is achieved when only a single domain exist.
Look at a small ferromagnetic particle with volume $V$ and radius $r$ having either 1 or 2 domains. 

Fig 18.6. A single domain and a two-domain ferromagnetic nano particle

For the single domain particle the energy is given by the magnetostatic energy from Eq. (18.8), where the demagnetizing field for a sphere is given by $\mathcal{H}_d = -\frac{1}{3}\mathcal{M}$.

Inserting and integrating over the volume of a sphere we find

$$E_1 = \frac{2}{3} \mu_0 \pi \mathcal{M}^2 r^3.$$

For the 2-domain particle the magnetostatic energy is roughly halved thus reducing the total energy. On the other hand we have to create a domain wall which costs energy $\sigma_{dw} A$, where the area is $A = \pi r^2$. The total energy is then

$$E_2 = \frac{1}{2} \mu_0 \pi \mathcal{M}^2 r^3 + \sigma_{dw} \pi r^2.$$

Inserting $\sigma_{dw}$ from Eq. (18.6) (with the value of $N$ minimizing $\sigma_{dw}$) we find that the criterion for a single domain particle is

$$E_1 < E_2$$

\[\downarrow\]

$$r < \frac{9\pi S \sqrt{2J/K}}{\mu_0 \mathcal{M}^2}$$

\[\downarrow\]

$$r < 13\text{nm},$$

where we have inserted the parameters from earlier $\sigma_{dw} = 1.2 \times 10^{-3} \text{J/m}^2$ and assumed a magnetization of $\mu_0 \mathcal{M} = 1 \text{T}$. This is actually slightly smaller than the domain wall boundary width of 21 nm and might be confusing, but the above should more be seen as a rough estimate. The transition between single-domain and two-domain structure is gradual and there will thus be an intermediate state where the magnetization exhibits a vortex like structure.

References

Exercise:

Look at a small ferromagnetic particle with either 1 or 2 domains.

\[ \begin{array}{c}
\uparrow \\
\downarrow \\
\end{array} \]

a) At which particle radius is the 1-domain case energetically favorable? (the magnetostatic energy: \( E_{ms} = -\frac{\mu_0}{2} \int \frac{\hat{H}_d}{\rho} \cdot \vec{M} dV \), where the demagnetizing field for a sphere is given by \( \hat{H}_d = -\frac{1}{2} \vec{M} \). \( E_{ms} \) is ca. reduced to half for the 2-domain case. Assume a domain wall energy density of ca. 1.2x10^{-3} J/m^2 and a magnetization \( \mu_0 M = 1 \text{T} \).

Now a 1-domain particle is placed in a magnetic field \( B \) in the z direction. The magnetization \( M \) of the particle points in a direction with an angle \( \theta \) to the z-axis. The particle has volume \( V \).

b) What is the energy of the particle, when taking into account the dipole interaction with the field and the anisotropy which we assume can be described simply by \( K_1 \sin^2(\theta) \)? (where \( K_1 \) is the anisotropy constant, note that the units are J/m^3, i.e. an energy density).

c) Find the first two minima and the first maxima and plot the energy for \( K_1 V = 5MBV \) in the range \( \theta \in [-0.2; \pi + 0.2] \).

d) Assume that the magnetization of the particle will jump between the states described by the two minima in energy. Write down an expression for the rate of that process. Indicate the necessary conditions for the materials parameters (\( M, K_1 \)) if the particle should be used for data storage applications.