1 The nature of condensed matter

Condensed matter physics is the study of large numbers of atoms and molecules that are "stuck together." Solids and liquids are examples. In the condensed state many molecules interact with each other. The physics of such a system is quite different from that of the individual molecules because of *collective effects*: qualitatively new things happen because there are many interacting particles. The behavior of most of the objects in our everyday experience is dominated by collective effects. Examples of materials where such effects are important are crystals and magnets.

This is a vast field: the subject matter could be taken to include traditional solid state physics (basically the study of the quantum mechanics of crystalline matter), magnetism, fluid dynamics, elasticity theory, the physics of materials, aspects of polymer science, and some biophysics. In fact, condensed matter is less a field than a collection of fields with some overlapping tools and techniques. Any course in this area must make choices. This is my personal choice.

In this chapter I will discuss orders of magnitude that are important, review ideas from quantum mechanics and chemistry that we will need, outline what holds condensed matter together, and discuss how order arises in condensed systems. The discussion here will be qualitative. Later chapters will fill in the details.

1.1 Some basic orders of magnitude

To fix our ideas, consider a typical bit of condensed matter, a macroscopic piece of solid copper metal. As we will see later it is best to view the system as a collection of cuprous (Cu^+) ions and conduction electrons, one per atom, that are free to move within the metal. We discuss some basic scales that will be important for understanding the physics of this piece of matter.

Lengths A characteristic length that will be important is the distance between the Cu atoms. In a solid this distance will be of order of a chemical bond length:

$$L \approx 3 \text{ Å} \approx 3 \times 10^{-8} \text{cm}. \tag{1.1}$$

Note that this is very tiny on the macroscopic scale. The whole art of condensed matter physics consists in bridging the gap between the atomic scale and the macroscopic properties of condensed matter.

Energies We can ask about the characteristic energy scales for the sample. One important energy scale is the binding energy of the material per atom. A closely related quantity is the melting temperature in energy units:

$$1357 \text{ K} = 0.11 \text{ eV}. \tag{1.2}$$

This is a typical scale to break up the material. If we probe at much larger energies (KeV, for example) we will be probing the inner shells of Cu, namely the domain of atomic physics, or at MeV, the Cu nucleus, i.e. nuclear physics.

Cu has an interesting color (it is copper colored, in fact), so we might expect something interesting at the scale of the energy of ordinary light, namely,

$$E \approx \hbar \omega_{\text{opt}} \sim 3 \text{ eV} \tag{1.3}$$

which is also the strength of a typical chemical bond. A somewhat larger, but comparable scale is that of the Coulomb interaction of two electrons a distance L apart:

$$E \approx e^2/L \approx 5 \text{ eV}. \tag{1.4}$$

These energies are low even for atomic physics. This means that in our study of condensed matter we will always be interested only in the outer (valence electrons) which are least bound.

Speeds When a piece of Cu carries an electrical current of density, $\mathbf{j}$, the conduction electrons move at a drift velocity $\mathbf{v}_d$:

$$\mathbf{j} = ne\,\mathbf{v}_d \tag{1.5}$$

where n is the number density of conduction electrons and e is the charge on the electron. For ordinary sized currents we find a very small speed, $v_d \approx 0.01$ cm/sec.

There is another characteristic speed, the mean thermal speed, v_T of the Cu ions when they vibrate at finite temperature. We estimate v_T as follows. From the Boltzmann equipartition theorem the mean kinetic energy of an ion is:

$$Mv_T^2/2 \sim k_B T. \tag{1.6}$$

Here T is the absolute temperature, k_B is Boltzmann's constant, M is the mass of a Cu ion, and v_T is the mean thermal velocity. At room temperature we get $v_T \sim 3 \times 10^4$ cm/sec.

There is a larger speed associated with the electrons, namely the quantum mechanical speed of the valence electrons. We estimate this speed as [frequency of an optical transition] x length:

$$v \sim (E/\hbar)(L) \approx 10^7 \text{ cm/sec}. \tag{1.7}$$

As we will see below, there is another relevant speed, the magnitude of the Fermi velocity, which is of the same order.

In any case, all of these speeds are small compared to the speed of light. Thus, we seldom need the theory of relativity in condensed matter physics. (An exception is the spin-orbit interaction of heavy elements.)

Large numbers and collective effects The essential point of the subject is that we deal with very large *numbers* of ions and electrons, $\approx 10^{27}$ in a macroscopic sample. In a famous essay P. W. Anderson (1972) pointed out the significance of this fact. When many things interact we often generate new phenomena, sometimes called emergent phenomena. Or, as Anderson put it, "more is different." Some examples of collective effects that we will emphasize in this book are the existence of *order* of various types, e.g. crystalline order, magnetic order, and superconducting order.

1.2 Quantum or classical

We have seen that we are interested in non-relativistic physics. We can go further: for the case of Cu there are conduction electrons and Cu^+ ions. What type of physics is applicable to each? In particular, do we need quantum mechanics? A useful criterion is to compare the de Broglie wavelength of the relevant particle, $\lambda = h/mv$, to the interparticle spacing.

For the ions, the relevant speed is v_T which we estimated above. Thus:

$$\lambda = h/(2Mk_{\mathrm{B}}T)^{1/2} \approx 10^{-9} \text{ cm} << L. \tag{1.8}$$

This is smaller than the spacing by an order of magnitude. For all ions in solids (except for He and H at very low temperatures) we can use classical mechanics. (As we will see, for vibrations of ions at low T, we need quantum mechanics too.)

For the electrons the situation is different because the electron mass, m, is is 63×1800 times smaller than the mass of a Cu ion, so we get

$$\lambda = h/(2mk_{\mathrm{B}}T)^{1/2} \approx 3 \times 10^{-7} \text{ cm} >> L. \tag{1.9}$$

Electrons are quantum mechanical for all temperatures.

1.3 Chemical bonds

Matter condenses because atoms and molecules attract one another. In the condensed state they are connected by chemical bonds. This is the "glue" that holds condensed matter together. We will summarize here some notions from chemistry which we will need in the sequel.

van der Waals' bonds At long ranges the dominant interaction between neutral atoms or molecules is the van der Waals interaction which arises from the interaction of fluctuating induced dipoles. For two neutral molecules (or atoms) a distance d apart this effect gives

rise to a potential energy of interaction given by:

$$V(r) \sim -1/r^6. \tag{1.10}$$

This equation is universally true if the molecules are far apart compared to the size of of their electronic clouds. For closed shell atoms and molecules such as Ar and H_2 that do not chemically react, the van der Waals' interaction is the attractive force that causes condensation. Since this is a weak, short-range force, materials bound this way usually have low melting points.

A rough argument for the r^{-6} dependence is as follows: suppose there is a fluctuation (a quantum fluctuation, in fact) on one of two molecules so that an instantaneous dipole moment, p_1, arises. This gives rise to an electric field of order $E \sim p_1/d^3$ at the other molecule. This electric field polarizes the other atom. To understand this, we introduce a concept that we will use later, the *polarizability*, α, of the molecule. It is defined by:

$$\mathbf{p}_{ind} = \alpha \mathbf{E}, \tag{1.11}$$

where $\mathbf{p}_{ind}$ is the induced dipole moment. Note that in our system of units the polarizability, α, has units of volume. It is roughly the molecular volume. Thus $p_2 \sim \alpha p_1/d^3$. This finally gives for identical molecules the fluctuating dipole-dipole interaction:

$$V \sim p_1 p_2/d^3 \sim \alpha p_1^2/d^6. \tag{1.12}$$

Since this expression depends on p_1^2 there is a time-averaged value for the potential. It is easy to show that the dipoles will be antiparallel so that the interaction is attractive. An actual calculation of the coefficient of r^{-6}, that is, of the average of p_1^2, can be done (in simple cases) using quantum mechanical perturbation theory.

Ionic bonds The chemistry of the valence electrons in a compound can lead to charge transfer, e.g.:

$$Na + Cl \rightarrow Na^+ Cl^-. \tag{1.13}$$

In this case there will be strong forces due to the charges, and the ions will be bound by the Coulomb interaction:

$$V(r) = Zq_1 q_2/r.$$

This is called ionic binding. Solid NaCl, table salt, is bound in this way. Ionic solids often have very large binding, and very large melting points.

Covalent bonds In elements with s and p electrons in the outer shell, covalent sp^3 orbitals give rise to directed bonds where electrons between ions glue together the material. Semiconductors such as Si, Ge, are bonded this way, as well as polymers and many biological materials. There are intermediate cases between the covalent and ionic materials, such as III-V semiconductors like GaAs.

Hydrogen bonds These arise in materials that contain H such as ice. The proton participates in the bonding. This is very important in biological materials.

Metallic bonding For most light metals like Cu or Na, the outer valence electrons are delocalized for quantum mechanical reasons which we will discuss in great detail, later. The electrons act as glue by sitting between the positively charged ions. These essentially free electrons give rise to the electrical conduction of metals such as Cu.

1.4 The exchange interaction

We have talked about bonds between atoms in terms of spatial degrees of freedom of the electrons, but we have not mentioned electron spin. There is another effect, very important for magnetism, which arises from the interplay between the Pauli exclusion principle, the spin degrees of freedom, and the electrostatic repulsion of electrons. It occurs, for example, for atoms which have unpaired spins.

We recall from quantum mechanics that the Pauli principle says that electron wavefunctions must be antisymmetric in the exchange of any two electrons. This implies that when we bring two atoms together the many-electron wavefunction must vanish when two electrons with parallel spins are at the same position. Therefore electrons with parallel spins are likely to be *farther apart* in space than antiparallel ones, and therefore have a smaller electrostatic repulsion. As a result, if the two atoms have parallel spins the energy is lower. Thus spins and therefore magnetic moments tend to line up when electrons from adjacent atoms overlap. This is called the exchange interaction. This is discussed in considerable detail below, Section 9.2.1, or in standard texts on quantum mechanics, e.g. (Landau & Lifshitz 1977, Schiff 1968, Baym 1990).

There are a few comments we should make about this. One is that there needs to be overlap of wavefunctions to have the effect work. The difference in energy between states with parallel and antiparallel spins on adjacent atoms (the strength of the interaction) is dependent on the overlap; the exchange interaction is very short range. Also, the size of the energy difference is basically the electrostatic energy of two electrons an atomic distance apart, a few electron volts.

Spin and symmetry effects need not favor parallel spins; it depends on the nature of the wavefunctions and what energies are most important. A simple example of favoring antiparallel spins is the hydrogen molecule, two electrons and two protons. In one approach to the problem (the Heitler–London approximation) we build up the wavefunction for the molecule from atomic wavefunctions centered on each proton. We can then form symmetric and antisymmetric combinations of these functions, as above. However, since the total wavefunction must be antisymmetric, parallel electron spins (total spin 1) go with the antisymmetric spatial function, and antiparallel spins (total spin 0) go with the symmetric spatial function; for more details see (Baym 1990). The electrostatic interaction with the hydrogen nuclei favors the symmetric state since the electrons spend more time between the nuclei, and the kinetic energy of the symmetric state is lower. As a result the ground (bonding) state of H_2 has total spin 0, and is symmetric in space.

Suggested reading

There are many excellent references and textbooks for this subject that the student can explore. The classic undergraduate text is by

Kittel (2005).

Successive editions of this book (the current one is the eighth) have been used by generations of physicists and engineers.

At the graduate level the following old standards are highly recommended:

Ashcroft & Mermin (1976)

Ziman (1972)

Kittel (1963)

More modern treatments can be found in:

Anderson (1997)

Marder (2000)

Grosso & Pastori Parravicini (2000)

Phillips (2003)

Taylor & Heinonen (2002)

Chaikin & Lubensky (1995)

The last book is particularly good on soft condensed matter such as polymers and liquid crystals, which are not treated in detail in this book.

Problems

1. Calculate the van der Waals' interaction between two H atoms in their ground state. Use the Hamiltonian for two single atoms as a reference: $\hat{\mathcal{H}}_o = p_1^2/2m - e^2/|\mathbf{r}_1 - \mathbf{R}_1| + p_2^2/2m - e^2/|\mathbf{r}_2 - \mathbf{R}_2|$. You can put one nucleus at the origin and the other at distance d along the x axis. Use the rest of the energy as a perturbation in second-order perturbation theory:

   $\hat{\mathcal{H}}_1 = -e^2/|\mathbf{r}_1 - \mathbf{R}_2| - e^2/|\mathbf{r}_2 - \mathbf{R}_1| + e^2/r_{12}$, where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. See (Schiff 1968) Assume $|\mathbf{r}_i| << d$. You may use only the first excited state of H in your perturbation theory.

2. Work out the exchange splitting between the singlet and triplet ($1s2s$) states of He. (a) Use hydrogenic $1s$ and $2s$ states as a basis. Write down symmetric and antisymmetric 2-electron wavefunctions. (b) Show which belongs to the triplet spin state, and which to the singlet. (c) Figure out the energy difference between the two states in terms of the direct and exchange integrals (you need not work out the integrals):

$$I = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{1s}^*(\mathbf{r}_1)\psi_{2s}^*(\mathbf{r}_2)\frac{e^2}{r_{12}}\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)$$

$$J = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{1s}^*(\mathbf{r}_1)\psi_{2s}^*(\mathbf{r}_2)\frac{e^2}{r_{12}}\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1).$$

2   Order and disorder

We have seen in the previous chapter that chemical bonds are the glue for condensed matter. If the temperature is low enough so that thermal fluctuations do not break the bonds, it is no surprise that atoms and molecules condense, i.e. stick together, so that there are large pieces of matter.

However, the precise structure of condensed matter is often quite surprising. For example, we might guess that the typical result of attractive chemical bonds would be a disorderly mass of molecules. This does occur; such materials are called glasses. However, very commonly something else happens: at low enough temperatures the atoms or molecules form a remarkable ordered structure, a *crystal*. A crystal is an ordered, periodic array of atoms or molecules. In the next chapter we will give a precise definition of this concept. For our purposes, it is enough to understand that crystals are made up of identical building blocks that are repeated many times. See Figure 2.1 for an example, the face-centered cubic (fcc) crystal structure.

Chemistry tells us that atoms or ions can have a magnetic moment, either from orbital currents or unpaired spins. However, you might expect that when large numbers of such ions are stuck together that the orientation of the moments would be random. This is not always the case. For some elements, e.g. Fe, Ni, Co, and many compounds the moments line up in regular arrays of various kinds due to the exchange interaction, discussed above.
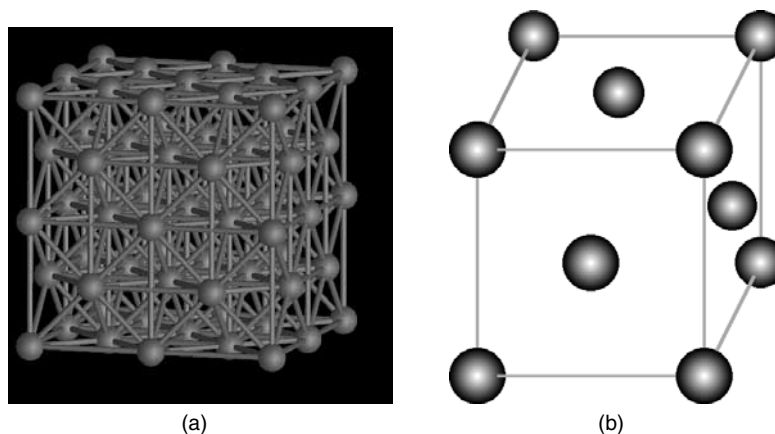

(a)   (b)

Fig. 2.1   **(a) A visualization of the face-centered cubic crystal structure. The nearest and next-nearest neighbor bonds are shown. (b) The structure may be thought of as a collection of cubes with atoms at the corners and the middle of all the faces.**

The large magnetic moment leads to the familiar phenomenon of magnets that pick up nails or stick to your refrigerator. This is called ferromagnetism because it was first noticed in iron and its compounds.

Complicated organic compounds sometimes form liquid crystals. These are liquids that are nevertheless ordered in some way. A nematic liquid crystal, for example, consists of long, rod shaped molecules. In certain temperature ranges the orientation of the molecules lines up, but the positions are random, as in a classical liquid. Nematics are the essential part of many liquid crystal displays such as those in laptop computers.

We will now discuss examples of ordered states in some detail.

2.1 Ferromagnets

Michael Faraday classified materials into three classes according to their magnetic state: there are diamagnets, paramagnets, and ferromagnets. The state can be characterized by the value of the magnetization, **M**, which is defined to be the magnetic moment per unit volume.

In paramagnets there can be non-zero magnetization only if induced by an external field, e.g., by aligning magnetic moments on ions. Diamagnetism is usually a weak effect which gives an induced magnetization antiparallel to the magnetic field due to induced shielding currents described by the Lenz law. The ordered states we are interested in are in the third class where there is a non-zero spontaneous magnetization in the absence of an external magnetic field.

Ordered states of this sort are not uncommon. There are a handful of ferromagnetic elements, and many ferromagnetic compounds. To illustrate a simple case of macroscopic order in condensed matter, we concentrate on magnetic insulators, which may be thought of as a collection of atoms with spin and/or orbital magnetic moments arranged in a crystal. In the ordered state a finite fraction of *all* the moments line up, i.e. point in the same direction, because of strong interactions between the ions. Magnetic metals are a much more subtle phenomenon, and will be discussed later. The interaction that causes ferromagnetism is exchange. The strength of a bond between two magnetic atoms or ions depends on the relative orientation of the spins, as we have seen. If the energy is lower when the spins are parallel, we can have alignment.

A way to parameterize this energy difference was proposed by W. Heisenberg. He noted that the energy is a scalar, but the spins of the atoms are vectors. The simplest way to make a scalar from two vectors is to take their dot product. We expect to be able to write the energy as:

$$E = -2J\mathbf{s}_1 \cdot \mathbf{s}_2. \tag{2.1}$$

This is called the Heisenberg Hamiltonian, and J is called the exchange constant. The minus sign and the factor of 2 are conventional, and J can be positive or negative. It is easy to see for H_2, mentioned above, that J is related to the singlet-triplet energy splitting.

2.1.1 Magnetic order and energies

Suppose we have many magnetic ions in a crystal. We can extend Eq. (2.1) to this case by writing:

$$\mathcal{H} = -\sum_{i \neq j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j. \tag{2.2}$$

J_{ij} is the exchange between ion i and ion j. Recall that the exchange interaction is very short-ranged, so we can suppose that $J_{ij} = 0$ unless i and j are nearest neighbors. In that case we can write:

$$\mathcal{H} = -\sum_{j,\delta} J \mathbf{s}_j \cdot \mathbf{s}_{j+\delta}, \tag{2.3}$$

where $j + \delta$ runs over the nearest neighbors of j.

Suppose that $J > 0$. Now it is clear that the lowest energy state of our model system has all the spins aligned in some direction, so that the magnetization is:

$$\mathbf{M} = n\gamma\hbar\langle\mathbf{s}\rangle \tag{2.4}$$

where $n = N/\Omega$ is the number of ions per unit volume, and $\gamma\hbar\langle\mathbf{s}\rangle$ the average moment of a single spin in the crystal. In this expression γ is the gyromagnetic ratio, the ratio between the moment of a single ion and its angular momentum, $\hbar\mathbf{s}$. Note that $\gamma\hbar = -g\mu_B = -ge\hbar/2mc$ where μ_B is the Bohr magneton, and g the g-factor of the ion. The state will be something like that pictured in Figure 2.2(a).

The difference in energy between the ground state of the system and a random one where the exchange interaction averages out is, from Eq. (2.2), $E_o = -NJs^2z/2$ where z is the *coordination number*, the number of nearest neighbors of a given ion. For example, in Figure 2.2, $z = 4$.
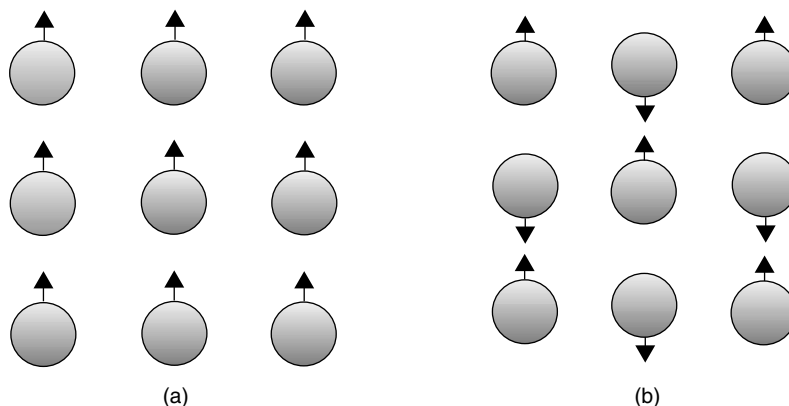

(a)   (b)

Fig. 2.2   **Magnetic order. (a) Ferromagnet (b) Antiferromagnet. The arrow denotes the direction of the magnetic moment.**