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Introduction

The first objective of this chapter is to briefly review some of the basic ideas about the structure of matter, in particular the concepts of microscopic physics, in order to recall the knowledge gained in previous physics (and chemistry) courses and make it more precise. Our review will be very concise, and most statements will be made without any proof or detailed discussion. A second objective is to give a brief description of some of the crucial stages in the early development of quantum physics. We shall not follow the strict historical order of this development or present the arguments used at the beginning of the last century by the founding fathers of quantum mechanics; rather, we shall stress the concepts which we shall find useful later on. Our last objective is to give an elementary introduction to some of the basic ideas, like those of a quantum particle or energy level, that will reappear throughout this text. We shall base our review on the Bohr theory, which provides a simple, though far from convincing, explanation of how energy levels are quantized and how the spectrum of the hydrogen atom arises. This chapter should be reread later on, once the basic ideas of quantum mechanics have been made explicit and illustrated by examples. From the practical point of view, it is possible to skip the general considerations of Sections 1.1 and 1.2 at the first reading and begin with Section 1.3, returning to those two sections later on as needed.

1.1 The structure of matter

1.1.1 Length scales from cosmology to elementary particles

Table 1.1 gives the length scales in meters of some typical objects, ranging from the size of the known Universe to the subatomic scale. A unit of length convenient for measuring astrophysical distances is the light-year (l.y.): $1 \text{ l.y.} = 0.95 \times 10^{16} \text{ m}$. The submeter scales commonly used in physics are the micrometer $1 \,\mu\text{m} = 10^{-6} \text{ m}$, the nanometer $1 \text{ nm} = 10^{-9} \text{ m}$, and the femtometer (or fermi, F) $1 \text{ fm} = 10^{-15} \text{ m}$. Objects at the microscopic scale are often studied using electromagnetic radiation of wavelength of the order of the characteristic size of the object under study (by means of a microscope, X-rays, etc.).¹ It is well known that

¹ Other techniques are neutron scattering (Exercise 1.6.4), electron microscopy, tunneling microscopy (Section 9.4.2), and so on.

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	Size (m)
Known Universe	1.3×10^{26}
Radius of the Milky Way	$\sim 5 imes 10^{20}$
Sun-Earth separation	$1.5 imes 10^{11}$
Radius of the Earth	$6.4 imes 10^6$
Man	~1.7
Insect	0.01 to 0.001
E. coli (bacterium)	$\sim \! 2 \times 10^{-6}$
HIV (virus)	1.1×10^{-7}
Fullerene C ₆₀	0.7×10^{-9}
Atom	$\sim \! 10^{-10}$
Lead nucleus	7×10^{-15}
Proton	0.8×10^{-15}

Table 1.1 Some typical distance scales

the limiting resolution is determined by the wavelength used: it is fractions of a micrometer for a microscope using visible light, or fractions of a nanometer when X-rays are used. The wavelength spectrum of electromagnetic radiation (infrared, visible, etc.) is summarized in Fig. 1.1.

1.1.2 States of matter

We shall be particularly interested in phenomena occurring at the microscopic scale, and so it is useful to recall some of the elementary ideas about the microscopic description of matter. Matter can exist in two different forms: an ordered form, namely a crystalline solid, and a disordered form, namely a liquid, a gas, or an amorphous solid.



Fig. 1.1. Wavelengths of electromagnetic radiation and the corresponding photon energies. The boundaries between different types of radiation (for example, between γ -rays and X-rays) are not strictly defined. A photon of energy E = 1 eV has wavelength $\lambda = 1.24 \times 10^{-6}$ m, frequency $\nu = 2.42 \times 10^{14}$ Hz, and angular frequency $\omega = 1.52 \times 10^{15}$ rad s⁻¹.

1.1 The structure of matter



Fig. 1.2. Arrangement of atoms in a crystal of sodium chloride. The chlorine ions Cl^- are larger than the sodium ions Na^+ .

A crystalline solid possesses long-range order. As an example, in Fig. 1.2 we show the microscopic structure of sodium chloride. The basic crystal pattern is repeated with periodicity l = 0.56 nm, forming the *crystal lattice*. Starting from a chlorine ion or a sodium ion and moving along one of the links of the cubic structure, we again reach a chlorine ion or a sodium ion after a distance $n \times 0.56$ nm, where *n* is an integer. This is what we mean by long-range order.

Liquids, gases, and amorphous solids do not possess long-range order. Let us take as an example a monatomic liquid, namely liquid argon. To a first approximation the argon atoms can be represented as impenetrable spheres of diameter $\sigma \simeq 0.36$ nm. In Fig. 1.3 we schematically show an atomic configuration for a liquid in which the spheres practically touch each other, but are arranged in a disordered fashion. Taking the center of one atom as the origin, the probability p(r) of finding the center of another atom at a distance r from the former is practically zero for $r \lesssim \sigma$. However, this probability reaches a maximum at $r = \sigma, 2\sigma, ...$ and then oscillates before becoming stable at a constant value, whereas in the case of a crystalline solid the function p(r) possesses peaks



Fig. 1.3. (a) Arrangement of atoms in liquid argon. (b) Probability p(r) for a liquid (dashed line) and for a gas (solid line). (c) Probability p(r) for a simple crystal.

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no matter what the distance from the origin is. Argon gas has the same type of atomic configuration as liquid argon, the only difference being that the atoms are much farther apart. The difference between the liquid and the gas vanishes at the critical point, and it is possible to move continuously from the gas to the liquid and back while going around the critical point, whereas such a continuous passage to a solid is impossible because the type of order is qualitatively different.

We have chosen a monatomic gas as an example, but in general the basic object is a combination of atoms in a molecule such as N_2 , O_2 , H_2O , etc. Certain molecules like proteins may contain thousands of atoms. For example, the molecular weight of hemoglobin is something like 64 000. A chemical reaction is a rearrangement of atoms – the atoms of the initial molecules are redistributed to form the final molecules:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

An atom is composed of a positively charged atomic nucleus (or simply nucleus) and negatively charged electrons. More than 99.9% of the mass of the atom is in the nucleus, because the ratio of the electron mass $m_{\rm e}$ to the proton mass $m_{\rm p}$ is $m_{\rm e}/m_{\rm p} \simeq 1/1836$. The atom is ten thousand to a hundred thousand times larger than the nucleus: the typical size of an atom is 1 Å (where 1 Å= 10^{-10} m = 0.1 nm), while that of a nucleus is several fermis (or femtometers).²

An atomic nucleus is composed of protons and neutrons. The former are electrically charged and the latter are neutral. The proton and neutron masses are identical to within 0.1%, and this mass difference can often be neglected in practice. The *atomic number* Z is the number of protons in the nucleus, and also the number of electrons in the corresponding atom, so that the atom is electrically neutral. The *mass number* A is the number of protons plus the number of neutrons N: A = Z + N. The protons and neutrons are referred to collectively as *nucleons*. Nuclear reactions involving protons and neutrons of protons and neutrons involving atoms: a nuclear reaction is a redistribution of protons and neutrons to form nuclei different from the initial ones, while a chemical reaction is a redistribution of a deuterium nucleus (²H, a proton and a neutron) and a tritium nucleus (³H, a proton and two neutrons) to form a helium-4 nucleus (⁴He, two protons and two neutrons) plus a free neutron:

$$^{2}\text{H} + ^{3}\text{H} \rightarrow ^{4}\text{He} + n + 17.6 \text{ MeV}.$$

The reaction releases 17.6 MeV of energy and in the (probably distant) future may be used for large-scale energy production (fusion energy).

An important concept pertaining to an atom formed from a nucleus and electrons, as well as to a nucleus formed from protons and neutrons, is that of the *binding energy*. Let us consider a stable object *C* formed of two objects *A* and *B*. The object *C* is termed a *bound state* of *A* and *B*. The breakup $C \rightarrow A + B$ will not be allowed if the mass m_C

² We shall often use the Ångström (Å), which is the characteristic atomic scale, rather than nm.

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of C is less than the sum of the masses m_A and m_B of A and B, that is, if the binding energy $E_{\rm b}$

$$E_{\rm b} = (m_A + m_B - m_C)c^2 \tag{1.1}$$

is positive.³ Here *c* is the speed of light and E_b is the energy needed to dissociate *C* into A + B. In atomic physics this energy is called the ionization energy, and it is the energy necessary to break up an atom into a positive ion and an electron, or, stated differently, to remove an electron from the atom. In the case of molecules E_b is the dissociation energy, or the energy needed to break up the molecule into atoms. A particle or a nucleus that is unstable in a particular configuration may be perfectly stable in a different configuration. For example, a free neutron (n) is unstable: in about fifteen minutes on average it disintegrates into a proton (p), an electron (e), and an electron antineutrino ($\overline{\nu}_e$); this is the basic decay of β -radioactivity:

$$n^0 \to p^+ + e^- + \overline{\nu}_e^0,$$
 (1.2)

where we have explicitly indicated the charge of each particle. This decay is possible because the masses⁴ of the particles in (1.2) satisfy

$$m_{\rm n}c^2 > (m_{\rm p} + m_{\rm e} + m_{\overline{\nu}})c^2,$$

where

$$m_{\rm n} \simeq 939.5 \,{\rm MeV}\,c^{-2}, \quad m_{\rm p} \simeq 938.3 \,{\rm MeV}\,c^{-2}, \quad m_{\rm e} \simeq 0.51 \,{\rm MeV}\,c^{-2}, \quad m_{\overline{\nu}_{\rm e}} \simeq 0.51 \,{\rm MeV}\,c^{-2},$$

On the other hand, a neutron in a stable atomic nucleus does not decay; taking as an example the deuterium nucleus (the deuteron, ²H), we have

$$m_{^{2}\mathrm{H}}c^{^{2}} \simeq 1875.6 \text{ MeV} < (2m_{p} + m_{e} + m_{\overline{\nu}_{s}})c^{^{2}} \simeq 1878.3 \text{ MeV},$$

and so the decay

$$^{2}\text{H} \rightarrow 2\text{p} + \text{e} + \overline{\nu}_{e}$$

is impossible: the deuteron is a proton-neutron bound state.

1.1.3 Elementary constituents

So far, we have broken up molecules into atoms, atoms into electrons and nuclei, and nuclei into protons and neutrons. Can we go even farther? For example, can we break

³ According to the celebrated Einstein relation $E = mc^2$; by simple dimensional analysis we can relate mass and energy to each other, so that, for example, masses can be expressed in Jc^{-2} or in eV c^{-2} .

⁴ Three recent experiments, those of S. Fukuda *et al.* (SuperKamiokande Collaboration), Solar B8 and hep neutrino measurements from 1258 days of SuperKamiokande data, *Phys. Rev. Lett.* **86**, 5651 (2001), Q. Ahmad *et al.* (SNO Collaboration), Interactions produced by B8 solar neutrinos at the Sudbury Neutrino Observatory, *Phys. Rev. Lett.*, **87**, 071301 (2001), and K. Eguchi *et al.* (Kamland Collaboration), First results from Kamland: evidence from reactor antineutrino disappearance, *Phys. Rev. Lett.* **90**, 021802 (2003), demonstrate convincingly that the neutrino mass is not zero, but is probably of order 10⁻² ev C⁻²; cf. Exercise 4.4.6 on neutrino oscillations. For a review, see D. Wark, Neutrinos: ghosts of matter, *Physics World* **18**(6), 29 (June 2005).

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up a proton or an electron into more elementary constituents? Is it possible, for example, that a neutron is composed of a proton, an electron, and an antineutrino, as Eq. (1.2) suggests? A simple argument based on the Heisenberg inequalities shows that the electron cannot pre-exist inside the neutron (Exercise 9.7.4), but instead is *created* at the moment the decay occurs. Therefore, we cannot say that a neutron is composed of a proton, an electron, and a neutrino. One could also imagine "breaking" a proton or a neutron into more elementary constituents by bombarding it with energetic particles, just as, for example, happens when a deuteron is bombarded by electrons of several MeV in energy:

$$e + {}^{2}H \rightarrow e + p + n.$$

The deuteron 2 H is broken up into its constituents, a proton and a neutron. However, the situation is not repeated when a proton is bombarded by electrons. When low-energy electrons are used, the collisions are elastic:

$$e + p \rightarrow e + p$$
,

and when the electron energy is high enough (several hundred MeV), the proton does not break up; instead, other particles are created, for example in reactions like

$$\begin{split} e+p &\rightarrow e+p+\pi^0, \\ e+p &\rightarrow e+n+\pi^++\pi^0 \\ e+p &\rightarrow e+K^++\Lambda^0, \end{split}$$

where the π and K mesons and the Λ^0 hyperon are new particles whose nature is not important for the present discussion. The crucial point is that these particles do not exist *ab initio* inside the proton, but are created at the instant the reaction occurs.

It therefore appears that at some point it is not possible to decompose matter into constituents which are more and more elementary. We can then ask the following question: what is the criterion for a particle to be elementary? The current idea is that a particle is elementary if it behaves as a point particle in its interactions with other particles. According to this idea, the electron, neutrino, and photon are elementary, while the proton and neutron are not: they are "composed" of quarks. These quotation marks are important, because quarks do not exist as free states,⁵ and the quark "composition" of the proton is very different from the proton and neutron composition of the deuteron. Only indirect (but convincing) evidence of this quark composition exists.

As far as is known at present,⁶ there exist three families of elementary particles or "particles of matter" of spin 1/2.⁷ They are listed in Table 1.2, where the electric charge q is expressed in units of the proton charge. Each family is composed of leptons and quarks,

⁵ What exactly is meant by the quark "mass" is quite complicated, at least for the so-called "light" quarks – the up, down, and strange quarks. Something close to the mass defined in the usual way is obtained for the heavy b and t quarks.

⁶ There is a very strong argument for limiting the number of families to three. In 1992 experiments at CERN showed that the number of families is limited to three on the condition that the neutrino masses are less than 45 GeV c^{-2} . The actual experimental value of the number of families is 2.984±0.008.

⁷ Spin 1/2 is defined in Chapter 3 and spin in general in Chapter 10.

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 Table 1.2 Matter particles. The electric charges are measured in units of the proton charge.

	Lepton $q = -1$	Neutrino $q = 0$	Quark $q = 2/3$	Quark $q = -1/3$
Family 1	electron	neutrino _e	up quark	down quark
Family 2 Family 3	tau	neutrino _{τ}	top quark	bottom quark

and each particle has a corresponding antiparticle of the opposite charge. The leptons of the first family are the electron and its antiparticle the positron e^+ , as well as the electron neutrino v_e and its antiparticle the electron antineutrino \overline{v}_e . The quarks of this family are the up quark u of charge 2/3 and the down quark d of charge -1/3 plus, of course, the corresponding antiquarks \overline{u} and \overline{d} , with charges -2/3 and 1/3, respectively. The proton is the combination uud and the neutron is the combination udd. This first family is sufficient for our everyday life, as all ordinary matter is composed of these particles. The neutrino is essential for the cycle of nuclear reactions occurring in the normally functioning Sun. While the existence of this first family is justified by an anthropocentric argument (if the family did not exist, we would not be here to talk about it), the reason for the existence of the other two families remains obscure.⁸

To these particles we need to add those that "carry" the interactions: the photon for electromagnetic interactions, the W and Z bosons for weak interactions, the gluons for strong interactions, and the graviton for gravitational interactions.⁹ Now let us discuss these interactions.

1.1.4 The fundamental interactions

There are four types of fundamental interaction (forces): strong, electromagnetic, weak, and gravitational.¹⁰ The *electromagnetic interaction* will play a leading role in this book, as it governs the behavior of atoms, molecules, solids, etc. The electrical forces obeying Coulomb's law dominate. We recall that a charge q fixed at the coordinate origin exerts a force on a charge q' at rest located at a point \vec{r}

$$\vec{F} = \frac{qq'}{4\pi\varepsilon_0} \frac{\hat{r}}{r^2},\tag{1.3}$$

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⁸ As I. I. Rabi reputedly said of the muon: "Who ordered that?" Nevertheless, we know that each family must be complete: this is how the existence of the top quark and the value of its mass were predicted several years before its experimental discovery in 1994. Owing to its high mass, about 175 times that of the proton, the top quark was not discovered until the proton-antiproton collider known as the Tevatron was in operation in the USA.

⁹ More rigorously, the electromagnetic and weak interactions have by now been unified as the electroweak interaction. The gluon, just like the quark, does not exist as a free state. Finally, the existence of the graviton is still hypothetical.

¹⁰ Every once in a while a "fifth force" is "discovered," but it soon disappears again!

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where \hat{r} is a unit vector \vec{r}/r , $r = |\vec{r}|$, and ε_0 is the vacuum permittivity.¹¹ If the charges move with speed v, we must also take into account the magnetic forces. However, they are weaker than the Coulomb force by a factor $\sim (v/c)^2$ (we are using \sim in the sense "of the order of"). For the electrons of the outer shells of an atom $(v/c)^2 \approx (1/137)^2 \ll 1$, but, owing to the extremely high precision of atomic physics experiments, the effects of magnetic forces are easily seen in phenomena such as the fine structure or the Zeeman effect (Section 14.2.3). The Coulomb force (1.3) is characterized by

- the $1/r^2$ force law. This is called a *long-range* force law;
- the strength of the force as measured by the *coupling constant* $qq'/4\pi\epsilon_0$.

The modern, field-theoretic, point of view is that electromagnetic forces are generated by the exchange of "virtual" photons between charged particles.¹² Quantum field theory is the result of the (conflicting!¹³) marriage between quantum mechanics and special relativity. The interactions between atoms or between molecules are represented as effective forces, for example van der Waals forces (Exercise 14.6.1). These forces are not fundamental because they are derived from the Coulomb force – they are actually the Coulomb force in disguise in the case of complex, electrically neutral systems.

The *strong interaction* is responsible for the cohesion of the atomic nucleus. In contrast to the Coulomb force, it falls off exponentially with distance according to the law $\simeq (1/r^2) \exp(r/r_0)$ with $r_0 \simeq 1$ F, and therefore is termed a *short-range* force. For $r \lesssim r_0$ this force is very strong, such that the typical energies inside the nucleus are of the order of MeV, while for the outer-shell electrons of an atom they are of the order of eV. In reality, the forces between nucleons are not fundamental, because, as we have seen, nucleons are composite particles. The forces between nucleons are analogous to the van der Waals forces between atoms, and the fundamental forces are actually those between the quarks. However, the quantitative relation between the nucleon–nucleon force and the quark–quark force is far from understood. The gluon, a particle of zero mass and spin 1 like the photon, plays the same role in the strong interaction as the photon plays in the electromagnetic one. The charge is replaced by a property conventionally referred to as color, and the theory of strong interactions is therefore called (*quantum*) *chromodynamics*. The *weak interaction* is responsible for radioactive β -decay:

$$(Z, N) \to (Z+1, N-1) + e^- + \overline{\nu}_e.$$
 (1.4)

A special case is that of (1.2), which is written in the notation of (1.4) as

$$(0,1) \rightarrow (1,0) + e^- + \overline{\nu}_e$$
.

Like the strong interaction, the weak interaction is short-range; however, as suggested by its name, it is much weaker than the former. The carriers of the weak interaction are

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¹¹ We shall systematically use the notation \hat{r} , \hat{n} , \hat{p} etc. for unit vectors in ordinary space.

¹² The term "virtual photons" will be explained in Section 4.2.4.

¹³ The combination of quantum mechanics and special relativity leads to infinities, which must be controlled by a procedure called renormalization. The latter was not fully understood and justified until the 1970s.

1.2 Classical and quantum physics

spin-1 bosons: the charged W^{\pm} and the neutral Z^0 with masses 82 MeV c^{-2} and 91 MeV c^{-2} , respectively (about 100 times the proton mass). The leptons, quarks, spin-1 bosons (also referred to as gauge bosons: the photon, gluons, W^{\pm} , and Z^0 ; see Exercise 11.5.11 for some elementary explanations), as well as a hypothetical spin-0 particle called the Higgs boson which gives masses to all the particles, are the particles of the *Standard Model* of particle physics. This model has been tested experimentally with a precision of better than 0.1% over the past ten years.

Last of all, we have the *gravitational interaction* between two masses m and m', which, in contrast to the Coulomb interaction, is always attractive:

$$\vec{F} = -Gmm' \,\frac{\hat{r}}{r^2}.\tag{1.5}$$

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Here the notation is the same as in (1.2) and G is the gravitational constant. The force law (1.5) is, like the Coulomb law, a long-range law, and since the two forces have the same form we can form the ratio of these forces between an electron and a proton:

$$\frac{F_{\rm C}}{F_{\rm gr}} = \left(\frac{q_{\rm e}^2}{4\pi\varepsilon_0}\right) \left(\frac{1}{Gm_{\rm e}m_{\rm p}}\right) \sim 10^{39}.$$

In the hydrogen atom the gravitational force is negligible; in general, this force is completely negligible for all the phenomena of atomic, molecular, and solid-state physics. General relativity, the relativistic theory of gravity, predicts the existence of gravitational waves.¹⁴ These are the gravitational analog of electromagnetic waves, and the spin-2, massless graviton is the analog of the photon. Nevertheless, at present there is no quantum theory of gravity. The unification of quantum mechanics and general relativity and the explanation of the origin of mass and the three particle families are major challenges of theoretical physics in the twenty-first century.

Let us summarize our presentation of the elementary constituents and the fundamental forces. There exist three families of matter particles, the leptons and quarks, plus the carriers of the fundamental forces: the photon for the electromagnetic interaction, the gluon for the strong interaction, the W and Z bosons for the weak interaction, and, finally, the hypothetical graviton for the gravitational interaction.

1.2 Classical and quantum physics

Before introducing quantum physics, let us briefly review the fundamentals of classical physics. There are three main branches of classical physics, and each has different ramifications.

¹⁴ At present, there is only indirect, but convincing, evidence for gravitational waves from observations of binary pulsars (neutron stars). Such waves may some day be detected on Earth in the VIRGO, LIGO, and LISA experiments. The graviton will probably be observed only in the very distant future.

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1. The first branch is *mechanics*, where the fundamental law is Newton's law. Newton's law is the fundamental law of dynamics; it states that in an inertial frame the force \vec{F} on a point particle of mass *m* is equal to the derivative of its momentum \vec{p} with respect to time:

$$\vec{F} = \frac{\mathrm{d}\vec{p}}{\mathrm{d}t}.\tag{1.6}$$

This form of the fundamental equation of dynamics remains unchanged when the modifications due to special relativity, introduced by Einstein in 1905, are taken into account. In the general form of (1.6) we must use the relativistic expression for the momentum as a function of the particle velocity \vec{v} and mass *m*:

$$\vec{p} = \frac{m\vec{v}}{\sqrt{1 - v^2/c^2}}.$$
 (1.7)

2. The second branch is *electromagnetism*, summarized in the four Maxwell equations which give the electric field \vec{E} and magnetic field \vec{B} as functions of the charge density ρ_{em} and the current density \vec{j}_{em} , which are referred to as the *sources* of the electromagnetic field:

$$\vec{\nabla} \cdot \vec{B} = 0, \qquad \vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t},$$
(1.8)

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho_{\rm em}}{\varepsilon_0}, \quad c^2 \vec{\nabla} \times \vec{B} = \frac{\partial \vec{E}}{\partial t} + \frac{1}{\varepsilon_0} \vec{J}_{\rm em}.$$
 (1.9)

These equations lead to a description of the propagation of electromagnetic waves in a vacuum at the speed of light:

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right) \begin{cases} \vec{E} \\ \vec{B} \end{cases} = 0.$$
(1.10)

Maxwell's equations allow us to make the connection to optics, which becomes a special case of electromagnetism. The connection between mechanics and electromagnetism is supplied by the *Lorentz law* giving the force on a particle of charge q and velocity \vec{v} :

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B}). \tag{1.11}$$

3. The third branch is *thermodynamics*, in which the main consequences are derived from the second law:¹⁵ there exists no transformation whose sole effect is to extract a quantity of heat from a reservoir and convert it entirely to work. This second law leads to the concept of entropy which lies at the base of all of classical thermodynamics. The microscopic origin of the second law was understood at the end of the nineteenth century by Boltzmann and Gibbs, who were able to relate this law to the fact that a macroscopic sample of matter is made up of an enormous ($\sim 10^{23}$) number of atoms; this allows us to use probability arguments, on which statistical mechanics is founded. The principal result of statistical mechanics is the *Boltzmann law*: the

¹⁵ The first law is just energy conservation, while the third is fundamentally of quantum origin.