# 1

# Introduction

The subject of thermal physics involves studying assemblies of large numbers of atoms. As we will see, it is the large numbers involved in macroscopic systems that allow us to treat some of their properties in a statistical fashion. What do we mean by a large number?

Large numbers turn up in many spheres of life. A book might sell a million ($10^6$) copies (probably not this one), the Earth's population is (at the time of writing) between six and seven billion people ($6$–$7\times10^9$), and the US national debt is currently around ten trillion dollars ($10^{13}$ US\$). But even these large numbers pale into insignificance compared with the numbers involved in thermal physics. The number of atoms in an average-sized piece of matter is usually ten to the power of twenty-something, and this puts extreme limits on what sort of calculations we can make to understand them.

Some large numbers:

| | |
|---|---|
| million | $10^6$ |
| billion | $10^9$ |
| trillion | $10^{12}$ |
| quadrillion | $10^{15}$ |
| quintillion | $10^{18}$ |
| googol | $10^{100}$ |
| googolplex | $10^{10^{100}}$ |

Note: these values assume the US billion, trillion, etc, which are now in general use.

### Example 1.1

One kilogramme of nitrogen gas contains approximately $2 \times 10^{25}$ $N_2$ molecules. Let us see how easy it would be to make predictions about the motion of the molecules in this amount of gas. In one year, there are about $3.2\times10^7$ seconds, so that a 3 GHz personal computer can count molecules at a rate of roughly $10^{17}$ year$^{-1}$, if it counts one molecule every computer clock cycle. Therefore it would take about 0.2 billion years just for this computer to count all the molecules in one kilogramme of nitrogen gas (a time that is roughly a few percent of the age of the Universe!). Counting the molecules is a computationally simpler task than calculating all their movements and collisions with each other. Therefore modelling this quantity of matter by following each and every particle is a hopeless task.[1]

Hence, to make progress in thermal physics it is necessary to make approximations and deal with the statistical properties of molecules, i.e., to study how they behave *on average*. Chapter 3 therefore contains a discussion of probability and statistical methods, which are foundational for understanding thermal physics. In this chapter, we will briefly review the definition of a mole (which will be used throughout the book), consider why very big numbers arise from combinatorial problems in thermal physics and introduce the *thermodynamic limit* and the *ideal gas equation*.

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[1] Still more hopeless would be the task of measuring where each molecule is and how fast it is moving in its initial state!

## 1.1 What is a mole?

A **mole** is, of course, a small burrowing animal, but also a name (first coined about a century ago from the German "Molekül" [molecule]) representing a certain numerical quantity of stuff. It functions in the same way as the word "dozen", which describes a certain number of eggs (12), or "score", which describes a certain number of years (20). It might be easier if we could use the word dozen when describing a certain number of atoms, but a dozen atoms is not many (unless you are building a quantum computer) and since a million, a billion, and even a quadrillion are also too small to be useful, we have ended up with using an even bigger number. Unfortunately, for historical reasons, it isn't a power of ten.

**The mole**
A **mole** is *defined* as the quantity of matter that contains as many objects (for example, atoms, molecules, formula units, or ions) as the number of atoms in exactly 12 g (=0.012 kg) of $^{12}$C.

A mole is also *approximately* the quantity of matter that contains as many objects (for example, atoms, molecules, formula units, ions) as the number of atoms in exactly 1 g (=0.001 kg) of $^{1}$H, but carbon was chosen as a more convenient international standard since solids are easier to weigh accurately.

A mole of atoms is equivalent to an **Avogadro number** $N_A$ of atoms. The Avogadro number, expressed to four significant figures, is

$$\boxed{N_A = 6.022 \times 10^{23}.} \qquad (1.1)$$

One can write $N_A$ as $6.022 \times 10^{23}\ \mathrm{mol}^{-1}$ as a reminder of its definition, but $N_A$ is dimensionless, as are moles. They are both numbers. By the same logic, one would have to define the 'eggbox number' as 12 dozen$^{-1}$.

**Example 1.2**

- 1 mole of carbon is $6.022 \times 10^{23}$ atoms of carbon.
- 1 mole of benzene is $6.022 \times 10^{23}$ molecules of benzene.
- 1 mole of NaCl contains $6.022 \times 10^{23}$ NaCl formula units, etc.

The Avogadro number is an exceedingly large number: a mole of eggs would make an omelette with about half the mass of the Moon!

The **molar mass** of a substance is the mass of one mole of the substance. Thus the molar mass of carbon is 12 g, but the molar mass of water is close to 18 g (because the mass of a water molecule is about $\frac{18}{12}$ times larger than the mass of a carbon atom). The mass $m$ of a single molecule or atom is therefore the molar mass of that substance *divided* by the Avogadro number. Equivalently:

$$\text{molar mass} = mN_A. \qquad (1.2)$$

## 1.2 The thermodynamic limit

In this section, we will explain how the large numbers of molecules in a typical thermodynamic system mean that it is possible to deal with average quantities. Our explanation proceeds using an analogy: imagine that you are sitting inside a tiny hut with a flat roof. It is raining outside, and you can hear the occasional raindrop striking the roof. The raindrops arrive randomly, so sometimes two arrive close together, but sometimes there is quite a long gap between raindrops. Each raindrop transfers its momentum to the roof and exerts an impulse[2] on it. If you knew the mass and terminal velocity of a raindrop, you could estimate the force on the roof of the hut. The force as a function of time would look like that shown in Fig. 1.1(a), each little blip corresponding to the impulse from one raindrop.

Now imagine that you are sitting inside a much bigger hut with a flat roof a thousand times the area of the first roof. Many more raindrops will now be falling on the larger roof area and the force as a function of time would look like that shown in Fig. 1.1(b). Now scale up the area of the flat roof by a further factor of one hundred and the force would look like that shown in Fig. 1.1(c). Notice two key things about these graphs:

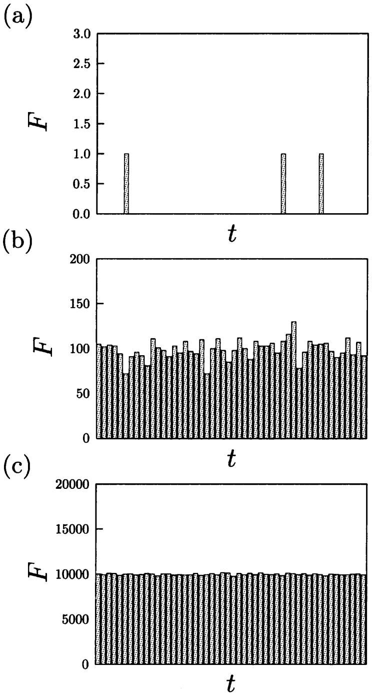

**Fig. 1.1** Graphs of the force on a roof as a function of time due to falling rain drops.

(1) The force, on average, gets bigger as the area of the roof gets bigger. This is not surprising because a bigger roof catches more raindrops.

(2) The *fluctuations* in the force get smoothed out and the force looks like it stays much closer to its average value. In fact, the fluctuations are still big but, as the area of the roof increases, they grow more slowly than the average force does.

The force grows with area, so it is useful to consider the **pressure**, which is defined as

$$\text{pressure} = \frac{\text{force}}{\text{area}}. \tag{1.3}$$

The average pressure due to the falling raindrops will not change as the area of the roof increases, but the fluctuations in the pressure will decrease. In fact, we can completely ignore the fluctuations in the pressure in the limit that the area of the roof *grows to infinity*. This is precisely analogous to the limit we refer to as the **thermodynamic limit**.

Consider now the molecules of a gas which are bouncing around in a container. Each time the molecules bounce off the walls of the container, they exert an impulse on the walls. The net effect of all these impulses is a pressure, a force per unit area, exerted on the walls of the container. If the container were very small, we would have to worry about fluctuations in the pressure (the random arrival of individual molecules on the wall, much like the raindrops in Fig. 1.1(a)). However, in most cases that one meets, the number of molecules in a container of gas is extremely large, so these fluctuations can be ignored and the pressure of the gas appears to be completely uniform. Again, our description of the pressure of this

[2] An impulse is the product of force and a time interval. The impulse is equal to the change of momentum.

system can be said to be "in the thermodynamic limit", where we have let the number of molecules be regarded as tending to infinity in such a way that the density of the gas is a constant.

Suppose that the container of gas has volume $V$, that the temperature is $T$, the pressure is $p$, and the kinetic energy of all the gas molecules adds up to $U$. Imagine slicing the container of gas in half with an imaginary plane, and now just focus your attention on the gas on one side of the plane. The volume of this half of the gas, let's call it $V^*$, is by definition half that of the original container, i.e.,

$$V^* = \frac{V}{2}. \tag{1.4}$$

The kinetic energy of this half of the gas, let's call it $U^*$, is clearly half that of the total kinetic energy, i.e.,

$$U^* = \frac{U}{2}. \tag{1.5}$$

However, the pressure $p^*$ and the temperature $T^*$ of this half of the gas are the same as for the whole container of gas, so that

$$p^* = p, \tag{1.6}$$

$$T^* = T. \tag{1.7}$$

Variables which scale with the system size, like $V$ and $U$, are called **extensive variables**. Those which are independent of system size, like $p$ and $T$, are called **intensive variables**.

Thermal physics evolved in various stages and has left us with various approaches to the subject:

- The subject of **classical thermodynamics** deals with macroscopic properties, such as pressure, volume, and temperature, without worrying about the underlying microscopic physics. It applies to systems that are sufficiently large that microscopic fluctuations can be ignored, and it does not assume that there is an underlying atomic structure to matter.
- The **kinetic theory of gases** tries to determine the properties of gases by considering probability distributions associated with the motions of individual molecules. This was initially somewhat controversial since the existence of atoms and molecules was doubted by many until the late nineteenth and early twentieth centuries.
- The realization that atoms and molecules exist led to the development of **statistical mechanics**. Rather than starting with descriptions of macroscopic properties (as in thermodynamics) this approach begins with trying to describe the individual microscopic states of a system and then uses statistical methods to derive the macroscopic properties from them. This approach received an additional impetus with the development of **quantum theory**, which showed explicitly how to describe the microscopic quantum

states of different systems. The thermodynamic behaviour of a system is then asymptotically approximated by the results of statistical mechanics in the *thermodynamic limit*, i.e., as the number of particles tends to infinity (with intensive quantities such as pressure and density remaining finite).

In the next section, we will state the *ideal gas law*, which was first found experimentally but can be deduced from the kinetic theory of gases (see Chapter 6).

## 1.3 The ideal gas

Experiments on gases show that the pressure $p$ of a volume $V$ of gas depends on its temperature $T$. For example, a fixed amount of gas at constant temperature obeys

$$p \propto 1/V, \tag{1.8}$$

a result which is known as **Boyle's law** (sometimes as the Boyle–Mariotte law); it was discovered experimentally by Robert Boyle (1627–1691) in 1662 and independently by Edmé Mariotte (1620–1684) in 1676. At constant pressure, the gas also obeys

$$V \propto T, \tag{1.9}$$

where $T$ is measured in kelvin. This is known as **Charles' law** and was discovered experimentally, in a crude fashion, by Jacques Charles (1746–1823) in 1787, and more completely by Joseph Louis Gay-Lussac (1778–1850) in 1802, though their work was partly anticipated by Guillaume Amontons (1663–1705) in 1699, who also noticed that a fixed volume of gas obeys

$$p \propto T, \tag{1.10}$$

a result that Gay-Lussac himself found independently in 1809 and is often known as **Gay-Lussac's law**.[3]

These three empirical laws can be combined to give

$$pV \propto T. \tag{1.11}$$

It turns out that, if there are $N$ molecules in the gas, this finding can be expressed as follows:

$$\boxed{pV = Nk_{\mathrm{B}}T.} \tag{1.12}$$

This is known as the **ideal gas equation**, and the constant $k_{\mathrm{B}}$ is known as the **Boltzmann constant**.[4] We now make some comments about the ideal gas equation.

- We have stated this law purely as an empirical law, observed in experiment. We will derive it from first principles using the kinetic theory of gases in Chapter 6. This theory assumes that a gas can be modelled as a collection of individual tiny particles which can bounce off the walls of the container, and each other (see Fig. 1.2).

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[3] Note that none of these scientists expressed temperature in this way, since the kelvin scale and absolute zero had yet to be invented. For example, Gay-Lussac found merely that $V = V_0(1 + \alpha\tilde{T})$, where $V_0$ and $\alpha$ are constants and $\tilde{T}$ is temperature in his scale.

[4] It takes the numerical value $k_{\mathrm{B}} = 1.3807\times10^{-23}\,\mathrm{J\,K^{-1}}$. We will meet this constant again in eqn 4.7.

- Why do we call it "ideal"? The microscopic justification that we will present in Chapter 6 proceeds under various assumptions: (i) we assume that there are no intermolecular forces, so that the molecules are not attracted to each other; (ii) we assume that molecules are point-like and have zero size. These are idealized assumptions and so we do not expect the ideal gas model to describe real gases under all circumstances. However, it does have the virtue of simplicity: eqn 1.12 is simple to write down and remember. Perhaps more importantly, it does describe gases quite well under quite a wide range of conditions.
- The ideal gas equation forms the basis of much of our study of classical thermodynamics. Gases are common in nature: they are encountered in astrophysics and atmospheric physics; it is gases which are used to drive engines, and thermodynamics was invented to try and understand engines. Therefore this equation is fundamental in our treatment of thermodynamics and should be memorized.
- The ideal gas law, however, doesn't describe all important gases, and several chapters in this book are devoted to seeing what happens when various assumptions fail. For example, the ideal gas equation assumes that the gas molecules move non-relativistically. When this is not the case, we have to develop a model of relativistic gases (see Chapter 25). At low temperatures and high densities, gas molecules do attract one another (this must occur for liquids and solids to form) and this is considered in Chapters 26, 27, and 28. Furthermore, when quantum effects are important we need a model of quantum gases, and this is outlined in Chapter 30.
- Of course, thermodynamics applies also to systems which are not gaseous (so the ideal gas equation, though useful, is not a cure for all ills), and we will look at the thermodynamics of rods, bubbles, and magnets in Chapter 17.

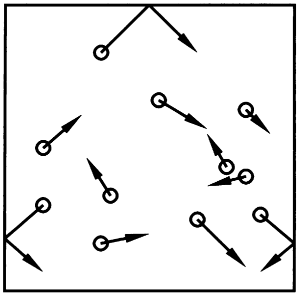

**Fig. 1.2** In the kinetic theory of gases, a gas is modelled as a number of individual tiny particles which can bounce off the walls of the container, and each other.

## 1.4 Combinatorial problems

Even larger numbers than $N_A$ occur in problems involving combinations, and these turn out to be very important in thermal physics. The following example illustrates a simple combinatorial problem which captures the essence of what we are going to have to deal with.

### Example 1.3

Let us imagine that a certain system contains ten atoms. Each of these atoms can exist in one of two states, according to whether it has zero units or one unit of energy. These "units" of energy are called **quanta** of energy. How many distinct arrangements of quanta are possible for this system if you have at your disposal (a) ten quanta of energy; (b) four quanta of energy?

*Solution:*

We can represent the ten atoms by drawing ten boxes; an empty box signifies an atom with zero quanta of energy; a filled box signifies an atom with one quantum of energy (see Fig. 1.3). We give two methods for calculating the number of ways of arranging $r$ quanta among $n$ atoms:

**Fig. 1.3** Ten atoms that can accommodate four quanta of energy. An atom with a single quantum of energy is shown as a filled circle, otherwise it is shown as an empty circle. One configuration is shown here.

(1) In the first method, we realize that the first quantum can be assigned to any of the $n$ atoms, the second quantum can be assigned to any of the remaining atoms (there are $n-1$ of them), and so on until the $r^{\text{th}}$ quantum can be assigned to any of the remaining $n-r+1$ atoms. Thus our first guess for the number of possible arrangements of the $r$ quanta we have assigned is $\Omega_{\text{guess}} = n \times (n-1) \times (n-2) \times \ldots \times (n-r+1)$. This can be simplified as follows:

$$\Omega_{\text{guess}} = \frac{n \times (n-1) \times (n-2) \times \ldots \times 1}{(n-r) \times (n-r-1) \times \ldots \times 1} = \frac{n!}{(n-r)!}. \tag{1.13}$$

However, this assumes that we have labelled the quanta as "the first quantum", "the second quantum" etc. In fact, we don't care which quantum is which because they are indistinguishable. We can rearrange the $r$ quanta in any one of $r!$ arrangements. Hence our answer $\Omega_{\text{guess}}$ needs to be divided by $r!$, so that the number $\Omega$ of unique arrangements is

$$\Omega = \frac{n!}{(n-r)!\,r!} \equiv {}^nC_r, \tag{1.14}$$

where ${}^nC_r$ is the symbol for a **combination**.[5]

(2) In the second method, we recognize that there are $r$ atoms each with one quantum and $n-r$ atoms with zero quanta. The number of arrangements is then simply the number of ways of arranging $r$ ones and $n-r$ zeros. There are $n!$ ways of arranging a sequence of $n$ distinguishable symbols. If $r$ of these symbols are the same (all ones), there are $r!$ ways of arranging these without changing the pattern. If the remaining $n-r$ symbols are all the same (all zeros), there are $(n-r)!$ ways of arranging these without changing the pattern. Hence we again find that

$$\Omega = \frac{n!}{(n-r)!\,r!}. \tag{1.15}$$

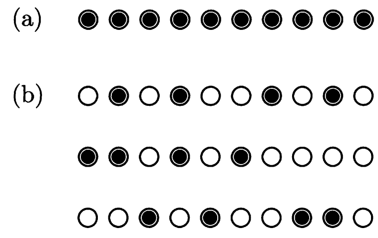

**Fig. 1.4** Each row shows the ten atoms that can accommodate $r$ quanta of energy. An atom with a single quantum of energy is shown as a filled circle, otherwise it is shown as an empty circle. (a) For $r = 10$ there is only one possible configuration. (b) For $r = 4$, there are 210 possibilities, of which three are shown.

For the specific cases shown in Fig. 1.4:

(a) $n = 10$, $r = 10$, so $\Omega = 10!/(10! \times 0!) = 1$. This one possibility, with each atom having a quantum of energy, is shown in Fig. 1.4(a).

(b) $n = 10$, $r = 4$, so $\Omega = 10!/(6! \times 4!) = 210$. A few of these possibilities are shown in Fig. 1.4(b).

If instead we had chosen ten times as many atoms (so $n = 100$) and ten times as many quanta, the numbers for (b) would have come out much much bigger. In this case, we would have $r = 40$, $\Omega \sim 10^{28}$. A further factor of ten sends these numbers up much further, so for $n = 1000$ and $r = 400$, $\Omega \sim 10^{290}$ – a staggeringly large number.

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[5] Other symbols sometimes used for ${}^nC_r$ include ${}^n_rC$ and $\binom{n}{r}$.

The numbers in the above example are so large because factorials increase very quickly. In our example we treated 10 atoms; we are clearly going to run into trouble when we attempt to deal with a mole of atoms, i.e., when $n = 6 \times 10^{23}$.

One way of bringing large numbers down to size is to look at their logarithms.[6] Thus, if $\Omega$ is given by eqn 1.15, we could calculate

$$\ln \Omega = \ln(n!) - \ln((n-r)!) - \ln(r!). \tag{1.16}$$

This expression involves the logarithm of a factorial, and it is going to be very useful to be able to evaluate this. Most pocket calculators have difficulty in evaluating factorials above 69! (because $70! > 10^{100}$ and many pocket calculators give an overflow error for numbers above $9.999 \times 10^{99}$), so some low cunning will be needed to overcome this. Such low cunning is provided by an expression termed **Stirling's formula**:

$$\boxed{\ln n! \approx n \ln n - n.} \tag{1.17}$$

This expression[7] is derived in Appendix C.3.

**Example 1.4**

Estimate the order of magnitude of $10^{23}!$.

*Solution:*

Using Stirling's formula, we can estimate

$$\ln 10^{23}! \approx 10^{23} \ln 10^{23} - 10^{23} = 5.2 \times 10^{24}, \tag{1.18}$$

and hence

$$10^{23}! = \exp(\ln 10^{23}!) \approx \exp(5.20 \times 10^{24}). \tag{1.19}$$

We have our answer in the form $e^x$, but we would really like it as ten to some power. Now if $e^x = 10^y$, then $y = x/\ln 10$ and hence

$$10^{23}! \approx 10^{2.26 \times 10^{24}}. \tag{1.20}$$

Just pause for a moment to take in how big this number is. It is roughly one followed by about $2.26 \times 10^{24}$ zeros! Our claim that combinatorial numbers are big seems to be justified!

## 1.5 Plan of the book

This book aims to introduce the concepts of thermal physics one by one, steadily building up the techniques and ideas that make up the subject. Part I contains various preliminary topics. In Chapter 2 we define heat and introduce the idea of heat capacity. In Chapter 3, the ideas of probability are presented for discrete and continuous distributions. (For

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[6] We will use "ln" to signify log to the base e, i.e., $\ln = \log_e$. This is known as the natural logarithm.

[7] As shown in Appendix C.3, it is slightly more accurate to use the formula $\ln n! \approx n \ln n - n + \frac{1}{2} \ln 2\pi n$, but this only gives a significant advantage when $n$ is not too large.

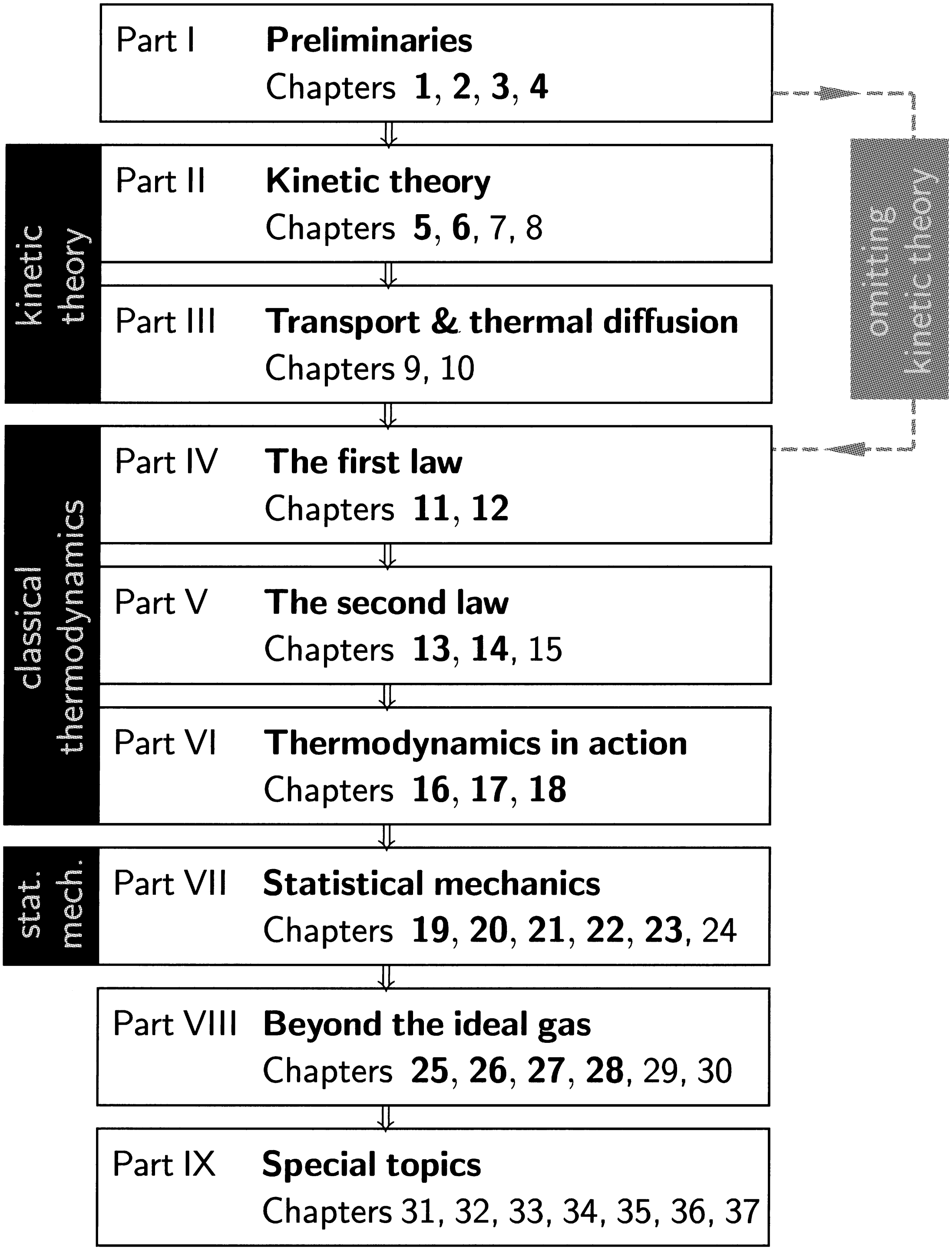

**Fig. 1.5** Organization of the book. The dashed line shows a possible route through the material that avoids the kinetic theory of gases. The numbers of the core chapters are given in bold type. The other chapters can be omitted on a first reading, or for a reduced-content course.

a reader familiar with probability theory, this chapter can be omitted.) We then define temperature in Chapter 4, and this allows us to introduce the Boltzmann distribution, which is the probability distribution for systems in contact with a thermal reservoir.

The plan for the remaining parts of the book is sketched in Fig. 1.5. The following two parts contain a presentation of the kinetic theory of gases, which justifies the ideal gas equation from a microscopic model. Part II presents the Maxwell–Boltzmann distribution of molecular speeds in a gas and the derivation of formulae for pressure, molecular effusion, and mean free path. Part III concentrates on transport and thermal diffusion. Parts II and III can be omitted in courses in which kinetic theory is treated at a later stage.

In Part IV, we begin our introduction to mainstream thermodynamics. The concept of energy is covered in Chapter 11, along with the zeroth and first laws of thermodynamics. These are applied to isothermal and adiabatic processes in Chapter 12.

Part V contains the crucial second law of thermodynamics. The idea of a heat engine is introduced in Chapter 13, which leads to various statements of the second law of thermodynamics. Hence the important concept of entropy is presented in Chapter 14 and its application to information theory is discussed in Chapter 15.

Part VI introduces the rest of the machinery of thermodynamics. Various thermodynamic potentials, such as the enthalpy, Helmholtz function, and Gibbs function, are introduced in Chapter 16, and their usage illustrated. Thermal systems include not only gases, and Chapter 17 looks at other possible systems, such as elastic rods and magnetic systems. The third law of thermodynamics is described in Chapter 18 and provides a deeper understanding of how entropy behaves as the temperature is reduced to absolute zero.

Part VII focuses on statistical mechanics. Following a discussion of the equipartition of energy in Chapter 19, so useful for understanding high temperature limits, the concept of the partition function is presented in some detail in Chapter 20, which is foundational for understanding statistical mechanics. The idea is applied to the ideal gas in Chapter 21. Particle number becomes important when considering different types of particle, so the chemical potential and grand partition function are presented in Chapter 22. Two simple applications where the chemical potential is zero are photons and phonons, discussed in Chapters 23 and 24 respectively.

The discussion up to this point has concentrated on the ideal gas model and we go beyond this in Part VIII: Chapter 25 discusses the effect of relativistic velocities and Chapters 26 and 27 discuss the effect of intermolecular interactions, while phase transitions are discussed in Chapter 28, where the important Clausius–Clapeyron equation for a phase boundary is derived. Another quantum mechanical implication is the existence of identical particles and the difference between fermions and bosons, discussed in Chapter 29; the consequences for the properties of quantum gases are presented in Chapter 30.

The remainder of the book, Part IX, contains more detailed information on various special topics which allow the power of thermal physics to be demonstrated. In Chapters 31 and 32 we describe sound waves and shock waves in fluids. We draw some of the statistical ideas of the book together in Chapter 33 and discuss non-equilibrium thermodynamics and the arrow of time in Chapter 34. Applications of the concepts in the book to astrophysics are described in Chapters 35 and 36 and to atmospheric physics in Chapter 37.

## Chapter summary

- In this chapter, the idea of big numbers has been introduced. These arise in thermal physics for two main reasons:
  1. (1) The number of atoms in a typical macroscopic lump of matter is large. It is measured in the units of the mole. One mole of atoms contains $N_{\mathrm{A}}$ atoms, where $N_{\mathrm{A}} = 6.022 \times 10^{23}$.
  2. (2) Combinatorial problems generate very large numbers. To make these numbers manageable, we often consider their logarithms and use Stirling's approximation: $\ln n! \approx n \ln n - n$.

## Exercises

(1.1) What is the mass of 3 moles of carbon dioxide ($CO_2$)? (1 mole of oxygen atoms has a mass of 16 g.)

(1.2) A typical bacterium has a mass of $10^{-12}$ g. Calculate the mass of a mole of bacteria. (Interestingly, this is about the total number of bacteria living in the guts of all humans resident on planet Earth.) Give your answer in units of elephant-masses (elephants have a mass $\approx$ 5000 kg).

(1.3) (a) How many water molecules are there in your body? (Assume that you are nearly all water.)
(b) How many drops of water are there in all the oceans of the world? (The mass of the world's oceans is about $10^{21}$ kg. Estimate the size of a typical drop of water.)
(c) Which of these two numbers from (a) and (b) is the larger?

(1.4) A system contains $n$ atoms, each of which can only have zero or one quanta of energy. How many ways can you arrange $r$ quanta of energy when (a) $n = 2$, $r = 1$; (b) $n = 20$, $r = 10$; (c) $n = 2 \times 10^{23}$, $r = 10^{23}$?

(1.5) What fractional error do you make when using Stirling's approximation (in the form $\ln n! \approx n \ln n - n$) to evaluate

**(a)** $\ln 10!$,

**(b)** $\ln 100!$, and

**(c)** $\ln 1000!$ ?

(1.6) Show that eqn C.19 is equivalent to writing

$$n! \approx n^n \mathrm{e}^{-n} \sqrt{2\pi n}, \tag{1.21}$$

and

$$n! \approx \sqrt{2\pi} n^{n+\frac{1}{2}} \mathrm{e}^{-n}. \tag{1.22}$$

# Heat

# 2

In this chapter, we will introduce the concepts of heat and heat capacity.

## 2.1 A definition of heat

We all have an intuitive notion of what heat is: sitting next to a roaring fire in winter, we *feel* its heat warming us up, increasing our temperature; lying outside in the sunshine on a warm day, we *feel* the Sun's heat warming us up. In contrast, holding a snowball, we feel heat leaving our hand and transferring to the snowball, making our hand feel cold. Heat seems to be some sort of energy transferred from hot things to cold things when they come into contact. We therefore make the following definition:

**heat** is *thermal energy in transit.*

We now stress a couple of important points about this definition.

(1) Experiments suggest that heat spontaneously transfers from a hotter body to a colder body when they are in contact, and not in the reverse direction. However, there are circumstances when it is possible for heat to go in the reverse direction. A good example of this is a kitchen freezer: you place food, initially at room temperature, into the freezer and shut the door; the freezer then sucks heat out of the food and cools the food down to below freezing point. Heat is being transferred from your warmer food to the colder freezer, apparently in the "wrong" direction. Of course, to achieve this, you have to be paying your electricity bill and therefore be putting energy in to your freezer. If there is a power cut, heat will slowly leak back into the freezer from the warmer kitchen and thaw out all your frozen food. This shows that it is possible to reverse the direction of heat flow, but only if you intervene by putting additional energy in. We will return to this point in Section 13.5 when we consider refrigerators, but for now let us note that we are defining heat as *thermal energy in transit* and not hard-wiring into the definition anything about which direction it goes.

(2) The "in transit" part of our definition is very important. Though you can add heat to an object, you *cannot* say that "an object contains a certain quantity of heat." This is very different from the case of the fuel in your car: you can add fuel to your car,

and you are quite entitled to say that your car "contains a certain quantity of fuel". You even have a gauge for measuring it! But heat is quite different. Objects do not and cannot have gauges which read out how much heat they contain, because heat only makes sense when it is "in transit".[1]

To see this, consider your cold hands on a chilly winter day. You can increase the temperature of your hands in two different ways: (i) by adding heat, for example by putting your hands close to something hot, like a roaring fire; (ii) by rubbing your hands together. In one case you have added heat from the outside, in the other case you have not added any heat but have done some work.[2] In both cases, you end up with the same final situation: hands that have increased in temperature. There is no physical difference between hands that have been warmed by heat and hands that have been warmed by work.[3]

Heat is measured in joules (J). The rate of heating has the units of watts (W), where $1\,\mathrm{W}=1\,\mathrm{J\,s^{-1}}$ (i.e., 1 watt=1 joule per second).

**Example 2.1**

A 1 kW electric heater is switched on for ten minutes. How much heat does it produce?

*Solution:*

Ten minutes equals 600 s, so the heat $Q$ is given by

$$Q = 1\,\mathrm{kW} \times 600\,\mathrm{s} = 600\,\mathrm{kJ}. \tag{2.1}$$

Notice in this last example that the power in the heater is supplied by electrical work. Thus it is possible to produce heat by doing work. We will return to the question of whether one can produce work from heat in Chapter 13.

## 2.2 Heat capacity

In the previous section, we explained that it is not possible for an object to contain a certain quantity of heat, because heat is defined as "thermal energy in transit". It is therefore with a somewhat heavy heart that we turn to the topic of "heat capacity", since we have argued that objects have no capacity for heat! (This is one of those occasions in physics when decades of use of a name have made it completely standard, even though it is really a misleading name to use.) What we are going to derive in this section might be better termed "energy capacity", but to do this would put us at odds with common usage throughout physics. All of this being said, we can proceed quite legitimately by asking the following simple question:

[1] We will see later that objects can contain a certain quantity of *energy*, so it is possible, at least in principle, to have a gauge that reads out how much energy is contained.

[2] Work is also a type of energy in transit, since you always do work *on* something. For example you do work on a mass by lifting it a height $h$. We could define work as "mechanical energy in transit". We will explore how work and heat can be interchanged in Chapter 13.

[3] We have made this point by giving a plausible example, but in Chapter 11 we will show using more mathematical arguments that heat only makes sense as energy "in transit".

*How much heat needs to be supplied to an object to raise its temperature by a small amount* $\mathrm{d}T$*?*

The answer to this question is the heat $\mathrm{d}Q = C\,\mathrm{d}T$, where we define the **heat capacity** $C$ of an object using

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T}. \tag{2.2}$$

As long as we remember that heat capacity tells us simply how much heat is needed to warm an object (and is nothing about the capacity of an object for heat) we shall be on safe ground. As can be inferred from eqn 2.2, the heat capacity $C$ has units $\mathrm{J\,K^{-1}}$.

As shown in the following example, although objects have a heat capacity, one can also express the heat capacity of a particular substance *per unit mass*, or *per unit volume*.[4]

**Example 2.2**

The heat capacity of 0.125 kg of water is measured to be $523\,\mathrm{J\,K^{-1}}$ at room temperature. Hence calculate the heat capacity of water (a) per unit mass and (b) per unit volume.

*Solution:*

(a) The heat capacity per unit mass $c$ is given by dividing the heat capacity by the mass, and hence

$$c = \frac{523\,\mathrm{J\,K^{-1}}}{0.125\,\mathrm{kg}} = 4.184 \times 10^3\,\mathrm{J\,K^{-1}\,kg^{-1}}\ . \tag{2.3}$$

(b) The heat capacity per unit volume $C$ is obtained by multiplying the previous answer by the density of water, namely $1000\,\mathrm{kg\,m^{-3}}$, so that

$$C = 4.184 \times 10^3\,\mathrm{J\,K^{-1}\,kg^{-1}} \times 1000\,\mathrm{kg\,m^{-3}} = 4.184 \times 10^6\,\mathrm{J\,K^{-1}\,m^{-3}}. \tag{2.4}$$

The heat capacity per unit mass $c$ occurs quite frequently, and it is given a special name: the **specific heat capacity**.

**Example 2.3**

Calculate the specific heat capacity of water.

*Solution:*

This is given in answer (a) from the previous example: the specific heat capacity of water is $4.184 \times 10^3\,\mathrm{J\,K^{-1}\,kg^{-1}}$ .

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[4] We will use the symbol $C$ to represent a heat capacity, whether of an object, or per unit volume, or per mole. We will always state which is being used. The heat capacity per unit mass is distinguished by the use of the lower-case symbol $c$. We will usually reserve the use of subscripts on the heat capacity to denote the constraint being applied (see eqns 2.6 and 2.7).

Also useful is the **molar heat capacity**, which is the heat capacity of one mole of the substance.

### Example 2.4

Calculate the molar heat capacity of water. (The molar mass of water is 18 g.)
*Solution:*
The molar heat capacity is obtained by multiplying the specific heat capacity by the molar mass, and hence

$$C = 4.184 \times 10^3\,\mathrm{J\,K^{-1}\,kg^{-1}} \times 0.018\,\mathrm{kg} = 75.2\,\mathrm{J\,K^{-1}\,mol^{-1}}. \tag{2.5}$$

When we think about the heat capacity of a gas, there is a further complication.[5] We are trying to ask the question: how much heat should you add to raise the temperature of our gas by one kelvin? But we can imagine doing the experiment in two ways (see also Fig. 2.1):

1. Place our gas in a sealed box and add heat (Fig. 2.1(a)). As the temperature rises, the gas will not be allowed to expand because its volume is fixed, so its pressure will increase. This method is known as heating *at constant volume.*
2. Place our gas in a chamber connected to a piston and heat it (Fig. 2.1(b)). The piston is well lubricated, and so will slide in and out to maintain the pressure in the chamber to be identical to that in the lab. As the temperature rises, the piston is forced out (doing work against the atmosphere) and the gas is allowed to expand, keeping its pressure constant. This method is known as heating *at constant pressure.*

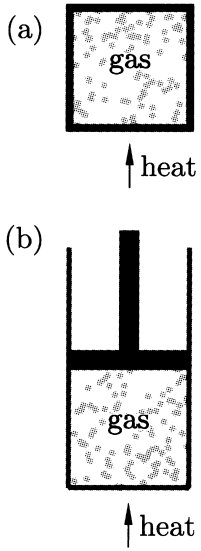

**Fig. 2.1** Two methods of heating a gas: (a) constant volume, (b) constant pressure.

In both cases, we are applying a **constraint** to the system, either constraining the volume of the gas to be fixed, or constraining the pressure of the gas to be fixed. We need to modify our definition of heat capacity given in eqn 2.2, and hence we define two new quantities: $C_V$ is the heat capacity *at constant volume* and $C_p$ is the heat capacity *at constant pressure.* We can write them using partial differentials as follows:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \tag{2.6}$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p. \tag{2.7}$$

We expect that $C_p$ will be bigger than $C_V$ for the simple reason that more heat will need to be added when heating at constant pressure than when heating at constant volume. This is because in the latter case additional energy will be expended on doing work on the atmosphere as the gas expands. It turns out that indeed $C_p$ is bigger than $C_V$ in practice.[6]

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[5] This complication is there for liquids and solids, but doesn't make such a big difference.

[6] We will *calculate* the relative sizes of $C_V$ and $C_p$ in Section 11.3.

**Example 2.5**

The specific heat capacity of helium gas is measured to be $3.12\,\mathrm{kJ\,K^{-1}\,kg^{-1}}$ at constant volume and $5.19\,\mathrm{kJ\,K^{-1}\,kg^{-1}}$ at constant pressure. Calculate the molar heat capacities. (The molar mass of helium is 4 g.)

*Solution:*

The molar heat capacity is obtained by multiplying the specific heat capacity by the molar mass, and hence

$$\begin{aligned} C_V &= 12.48\,\mathrm{J\,K^{-1}\,mol^{-1}}, & (2.8)\\ C_p &= 20.76\,\mathrm{J\,K^{-1}\,mol^{-1}}. & (2.9) \end{aligned}$$

(Interestingly, these answers are almost exactly $\frac{3}{2}R$ and $\frac{5}{2}R$ where $R$ is the gas constant.[7] We will see why in Section 11.3.)

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[7] $R = 8.31447\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is known as the gas constant and is equal to the product of the Avogadro number $N_A$ and the Boltzmann constant $k_B$ (see Section 6.2).

## Chapter summary

- In this chapter, the concepts of heat and heat capacity have been introduced.
- Heat is "thermal energy in transit".
- The heat capacity $C$ of an object is given by $C = \mathrm{d}Q/\mathrm{d}T$. The heat capacity of a substance can also be expressed per unit volume or per unit mass (in the latter case it is called *specific heat capacity*).

## Exercises

(2.1) Using data from this chapter, estimate the energy needed to (a) boil enough tap water to make a cup of tea, (b) heat the water for a bath.

(2.2) The world's oceans contain approximately $10^{21}$ kg of water. Estimate the total heat capacity of the world's oceans.

(2.3) The world's power consumption is currently about 13 TW, and growing! (1 TW= $10^{12}$ W.) Burning one ton of crude oil (which is nearly seven barrels worth) produces about 42 GJ (1 GJ= $10^9$ J). If the world's total power needs were to come from burning oil (a large fraction currently does), how much oil would we be burning per second?

(2.4) The molar heat capacity of gold is $25.4\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Its density is $19.3\times10^3\,\mathrm{kg\,m^{-3}}$. Calculate the specific heat capacity of gold and the heat capacity per unit volume. What is the heat capacity of $4\times10^6$ kg of gold? (This is roughly the holdings of Fort Knox.)

(2.5) Two bodies, with heat capacities $C_1$ and $C_2$ (assumed independent of temperature) and initial temperatures $T_1$ and $T_2$ respectively, are placed in thermal contact. Show that their final temperature $T_f$ is given by $T_f = (C_1T_1 + C_2T_2)/(C_1 + C_2)$. If $C_1$ is much larger than $C_2$, show that $T_f \approx T_1 + C_2(T_2 - T_1)/C_1$.