Thermodynamics & Statistical Mechanics:

An intermediate level course

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1 Introduction

1.1 Intended audience

These lecture notes outline a single semester course intended for upper division undergraduates.

1.2 Major sources

The textbooks which I have consulted most frequently whilst developing course material are:

Fundamentals of statistical and thermal physics: F. Reif (McGraw-Hill, New York NY, 1965).

Introduction to quantum theory: D. Park, 3rd Edition (McGraw-Hill, New York NY, 1992).

1.3 Why study thermodynamics?

Thermodynamics is essentially the study of the internal motions of many body systems. Virtually all substances which we encounter in everyday life are many body systems of some sort or other (*e.g.*, solids, liquids, gases, and light). Not surprisingly, therefore, thermodynamics is a discipline with an exceptionally wide range of applicability. Thermodynamics is certainly the most ubiquitous subfield of Physics outside Physics Departments. Engineers, Chemists, and Material Scientists do not study relatively or particle physics, but thermodynamics is an integral, and very important, part of their degree courses.

Many people are drawn to Physics because they want to understand why the world around us is like it is. For instance, why the sky is blue, why raindrops are spherical, why we do not fall through the floor, *etc*. It turns out that statistical thermodynamics can explain more things about the world around us than all of the other physical theories studied in the undergraduate Physics curriculum put together. For instance, in this course we shall explain why heat flows from hot to cold bodies, why the air becomes thinner and colder at higher altitudes, why the Sun appears yellow whereas colder stars appear red and hotter stars appear bluish-white, why it is impossible to measure a temperature below -273° centigrade, why there is a maximum theoretical efficiency of a power generation unit which can never be exceeded no matter what the design, why high mass stars must ultimately collapse to form black-holes, and much more!

1.4 The atomic theory of matter

According to the well-known *atomic* theory of matter, the familiar objects which make up the world around us, such as tables and chairs, are themselves made up of a great many microscopic particles.

Atomic theory was invented by the ancient Greek philosophers Leucippus and Democritus, who speculated that the world essentially consists of myriads of tiny indivisible particles, which they called *atoms*, from the Greek *atomon*, meaning "uncuttable." They speculated, further, that the observable properties of everyday materials can be explained either in terms of the different *shapes* of the atoms which they contain, or the different *motions* of these atoms. In some respects modern atomic theory differs substantially from the primitive theory of Leucippus and Democritus, but the central ideas have remained essentially unchanged. In particular, Leucippus and Democritus were right to suppose that the properties of materials depend not only on the nature of the constituent atoms or molecules, but also on the relative motions of these particles.

1.5 Thermodynamics

In this course, we shall focus almost exclusively on those physical properties of everyday materials which are associated with the *motions* of their constituent atoms or molecules. In particular, we shall be concerned with the type of motion which we normally call "heat." We shall try to establish what controls the flow of heat from one body to another when they are brought into thermal contact. We shall also attempt to understand the relationship between heat and mechanical work. For instance, does the heat content of a body increase when mechanical work is done on it? More importantly, can we extract heat from a body in order to do useful work? This subject area is called "thermodynamics," from the Greek roots *thermos*, meaning "heat," and *dynamis*, meaning "power."

1.6 The need for a statistical approach

It is necessary to emphasize from the very outset that this is a *difficult* subject. In fact, this subject is so difficult that we are forced to adopt a radically different approach to that employed in other areas of Physics.

In all of the Physics courses which you have taken up to now, you were eventually able to formulate some *exact*, or nearly exact, set of equations which governed the system under investigation. For instance, Newton's equations of motion, or Maxwell's equations for electromagnetic fields. You were then able to analyze the system by solving these equations, either exactly or approximately.

In thermodynamics we have no problem formulating the governing equations. The motions of atoms and molecules are described *exactly* by the laws of quantum mechanics. In many cases, they are also described to a reasonable approximation by the much simpler laws of classical mechanics. We shall not be dealing with systems sufficiently energetic for atomic nuclei to be disrupted, so we can forget about nuclear forces. Also, in general, the gravitational forces between atoms and molecules are completely negligible. This means that the forces between atoms and molecules are predominantly electromagnetic in origin, and are, therefore, very well understood. So, in principle, we could write down the exact laws of motion for a thermodynamical system, including all of the inter-atomic forces. The problem is the sheer complexity of this type of system. In one mole of a substance (*e.g.*, in twelve grams of carbon, or eighteen grams of water) there are

Avagadro's number of atoms or molecules. That is, about

$$N_A = 6 \times 10^{23}$$

particles, which is a *gigantic* number of particles! To solve the system exactly we would have to write down about 10^{24} coupled equations of motion, with the same number of initial conditions, and then try to integrate the system. Quite plainly, this is impossible. It would also be complete overkill. We are not at all interested in knowing the position and velocity of *every* particle in the system as a function of time. Instead, we want to know things like the volume of the system, the temperature, the pressure, the heat capacity, the coefficient of expansion, *etc*. We would certainly be hard put to specify more than about fifty, say, properties of a thermodynamic system in which we are really interested. So, the number of pieces of information we require is absolutely minuscule compared to the number of degrees of freedom of the system. That is, the number of pieces of information needed to completely specify the internal motion. Moreover, the quantities which we are interested in do not depend on the motions of individual particles, or some some small subset of particles, but, instead, depend on the average motions of *all* the particles in the system. In other words, these quantities depend on the *statistical* properties of the atomic or molecular motion.

The method adopted in this subject area is essentially dictated by the enormous complexity of thermodynamic systems. We start with some statistical information about the motions of the constituent atoms or molecules, such as their average kinetic energy, but we possess virtually no information about the motions of individual particles. We then try to deduce some other properties of the system from a statistical treatment of the governing equations. If fact, our approach *has* to be statistical in nature, because we lack most of the information required to specify the internal state of the system. The best we can do is to provide a few overall constraints, such as the average volume and the average energy.

Thermodynamic systems are ideally suited to a statistical approach because of the enormous numbers of particles they contain. As you probably know already, statistical arguments actually get *more exact* as the numbers involved get larger. For instance, whenever I see an opinion poll published in a newspaper, I immediately look at the small print at the bottom where it says how many people were interviewed. I know that even if the polling was done without bias, which is extremely unlikely, the laws of statistics say that there is a intrinsic error of order one over the square root of the number of people questioned. It follows that if a thousand people were interviewed, which is a typical number, then the error is at least three percent. Hence, if the headline says that so and so is ahead by one percentage point, and only a thousand people were polled, then I know the result is statistically meaningless. We can easily appreciate that if we do statistics on a thermodynamic system containing 10^{24} particles then we are going to obtain results which are valid to incredible accuracy. In fact, in most situations we can forget that the results are statistical at all, and treat them as exact laws of Physics. For instance, the familiar equation of state of an ideal gas,

$$P V = \nu R T,$$

is actually a statistical result. In other words, it relates the *average* pressure and the average volume to the average temperature. However, for one mole of gas the statistical deviations from average values are only about 10^{-12}, according to the $1/\sqrt{N}$ law. Actually, it is virtually impossible to measure the pressure, volume, or temperature of a gas to such accuracy, so most people just forget about the fact that the above expression is a statistical result, and treat it as a law of Physics interrelating the actual pressure, volume, and temperature of an ideal gas.

1.7 Microscopic and macroscopic systems

It is useful, at this stage, to make a distinction between the different sizes of the systems that we are going to examine. We shall call a system *microscopic* if it is roughly of atomic dimensions, or smaller. On the other hand, we shall call a system *macroscopic* when it is large enough to be visible in the ordinary sense. This is a rather inexact definition. The exact definition depends on the number of particles in the system, which we shall call N. A system is macroscopic if

$$\frac{1}{\sqrt{N}} \ll 1,$$

which means that statistical arguments can be applied to reasonable accuracy. For instance, if we wish to keep the statistical error below one percent then a macroscopic system would have to contain more than about ten thousand particles. Any system containing less than this number of particles would be regarded as essentially microscopic, and, hence, statistical arguments could not be applied to such a system without unacceptable error.

1.8 Thermodynamics and statistical thermodynamics

In this course, we are going to develop some machinery for interrelating the statistical properties of a system containing a very large number of particles, via a statistical treatment of the laws of atomic or molecular motion. It turns out that once we have developed this machinery, we can obtain some very general results which do not depend on the exact details of the statistical treatment. These results can be described without reference to the underlying statistical nature of the system, but their validity depends ultimately on statistical arguments. They take the form of general statements regarding heat and work, and are usually referred to as *classical thermodynamics*, or just *thermodynamics*, for short. Historically, classical thermodynamics was the first sort of thermodynamics to be discovered. In fact, for many years the laws of classical thermodynamics seemed rather mysterious, because their statistical justification had yet to be discovered. The strength of classical thermodynamics is its great *generality*, which comes about because it does not depend on any detailed assumptions about the statistical properties of the system under investigation. This generality is also the principle weakness of classical thermodynamics. Only a relatively few statements can be made on such general grounds, so many interesting properties of the system remain outside the scope of this theory.

If we go beyond classical thermodynamics, and start to investigate the statistical machinery which underpins it, then we get all of the results of classical thermodynamics, plus a large number of other results which enable the macroscopic parameters of the system to be calculated from a knowledge of its microscopic constituents. This approach is known as *statistical thermodynamics*, and is extremely powerful. The only drawback is that the further we delve inside the statistical machinery of thermodynamics, the harder it becomes to perform the necessary calculations.

Note that both classical and statistical thermodynamics are only valid for systems in *equilibrium*. If the system is not in equilibrium then the problem becomes considerably more difficult. In fact, the thermodynamics of non-equilibrium systems, which is generally called *irreversible thermodynamics*, is a graduate level subject.

1.9 Classical and quantum approaches

We mentioned earlier that the motions (by which we really meant the translational motions) of atoms and molecules are described exactly by quantum mechanics, and only approximately by classical mechanics. It turns out that the non-translational motions of molecules, such as their rotation and vibration, are very poorly described by classical mechanics. So, why bother using classical mechanics at all? Unfortunately, quantum mechanics deals with the translational motions of atoms and molecules (via wave mechanics) in a rather awkward manner. The classical approach is far more straightforward, and, under most circumstances, yields the same statistical results. Hence, in the bulk of this course, we shall use classical mechanics, as much as possible, to describe translational motions, and reserve quantum mechanics for dealing with non-translational motions. However, towards the end of this course, we shall switch to a purely quantum mechanical approach.

2 Probability theory

2.1 Introduction

The first part of this course is devoted to a brief, and fairly low level, introduction to a branch of mathematics known as *probability theory*. In fact, we do not need to know very much about probability theory in order to understand statistical thermodynamics, since the probabilistic "calculation" which underpins all of this subject is extraordinarily simple.

2.2 What is probability?

What is the *scientific* definition of probability? Well, let us consider an observation made on a general system S. This can result in any one of a number of different possible outcomes. We want to find the probability of some general outcome X. In order to ascribe a probability, we have to consider the system as a member of a large set Σ of similar systems. Mathematicians have a fancy name for a large group of similar systems. They call such a group an *ensemble*, which is just the French for "group." So, let us consider an ensemble Σ of similar systems S. The probability of the outcome X is defined as the ratio of the number of systems in the ensemble which exhibit this outcome to the total number of systems, in the limit where the latter number tends to infinity. We can write this symbolically as

$$P(X) = {}_{\mathrm{lt}\,\Omega(\Sigma)\to\infty}\frac{\Omega(X)}{\Omega(\Sigma)}, \tag{2.1}$$

where $\Omega(\Sigma)$ is the total number of systems in the ensemble, and $\Omega(X)$ is the number of systems exhibiting the outcome X. We can see that the probability $P(X)$ must be a number between 0 and 1. The probability is *zero* if no systems exhibit the outcome X, even when the number of systems goes to infinity. This is just another way of saying that there is *no chance* of the outcome X. The probability is *unity* if all systems exhibit the outcome X in the limit as the number of systems goes to infinity. This is another way of saying that the outcome X is *bound* to occur.

2.3 Combining probabilities

Consider two *distinct* possible outcomes, X and Y, of an observation made on the system S, with probabilities of occurrence $P(X)$ and $P(Y)$, respectively. Let us determine the probability of obtaining the outcome X *or* Y, which we shall denote $P(X \mid Y)$. From the basic definition of probability

$$P(X \mid Y) = {\rm lt}_{\,\Omega(\Sigma)\rightarrow\infty} \frac{\Omega(X \mid Y)}{\Omega(\Sigma)}, \tag{2.2}$$

where $\Omega(X \mid Y)$ is the number of systems in the ensemble which exhibit either the outcome X or the outcome Y. It is clear that

$$\Omega(X \mid Y) = \Omega(X) + \Omega(Y) \tag{2.3}$$

if the outcomes X and Y are mutually exclusive (which they must be the case if they are two distinct outcomes). Thus,

$$P(X \mid Y) = P(X) + P(Y). \tag{2.4}$$

So, the probability of the outcome X *or* the outcome Y is just the *sum* of the individual probabilities of X and Y. For instance, with a six sided die the probability of throwing any particular number (one to six) is $1/6$, because all of the possible outcomes are considered to be equally likely. It follows from what has just been said that the probability of throwing either a one or a two is simply $1/6 + 1/6$, which equals $1/3$.

Let us denote all of the M, say, possible outcomes of an observation made on the system S by X_i, where i runs from 1 to M. Let us determine the probability of obtaining any of these outcomes. This quantity is clearly unity, from the basic definition of probability, because every one of the systems in the ensemble must exhibit one of the possible outcomes. But, this quantity is also equal to the sum of the probabilities of all the individual outcomes, by (2.4), so we conclude that this sum is equal to unity. Thus,

$$\sum_{i=1}^{M} P(X_i) = 1, \tag{2.5}$$

which is called the *normalization condition*, and must be satisfied by any complete set of probabilities. This condition is equivalent to the self-evident statement that an observation of a system must definitely result in one of its possible outcomes.

There is another way in which we can combine probabilities. Suppose that we make an observation on a state picked at random from the ensemble and then pick a second state *completely independently* and make another observation. We are assuming here that the first observation does not influence the second observation in any way. The fancy mathematical way of saying this is that the two observations are *statistically independent*. Let us determine the probability of obtaining the outcome X in the first state *and* the outcome Y in the second state, which we shall denote $P(X \otimes Y)$. In order to determine this probability, we have to form an ensemble of all of the possible pairs of states which we could choose from the ensemble Σ. Let us denote this ensemble $\Sigma \otimes \Sigma$. It is obvious that the number of pairs of states in this new ensemble is just the square of the number of states in the original ensemble, so

$$\Omega(\Sigma \otimes \Sigma) = \Omega(\Sigma)\,\Omega(\Sigma). \tag{2.6}$$

It is also fairly obvious that the number of pairs of states in the ensemble $\Sigma \otimes \Sigma$ which exhibit the outcome X in the first state and Y in the second state is just the product of the number of states which exhibit the outcome X and the number of states which exhibit the outcome Y in the original ensemble, so

$$\Omega(X \otimes Y) = \Omega(X)\,\Omega(Y). \tag{2.7}$$

It follows from the basic definition of probability that

$$P(X \otimes Y) = {}_{\mathrm{lt}\,\Omega(\Sigma)\to\infty}\frac{\Omega(X \otimes Y)}{\Omega(\Sigma \otimes \Sigma)} = P(X)\,P(Y). \tag{2.8}$$

Thus, the probability of obtaining the outcomes X *and* Y in two statistically independent observations is just the *product* of the individual probabilities of X and Y. For instance, the probability of throwing a one and then a two on a six sided die is $1/6 \times 1/6$, which equals $1/36$.

2.4 The two-state system

The simplest non-trivial system which we can investigate using probability theory is one for which there are only *two* possible outcomes. There would obviously be little point in investigating a one outcome system. Let us suppose that there are two possible outcomes to an observation made on some system S. Let us denote these outcomes 1 and 2, and let their probabilities of occurrence be

$$P(1) = p, \tag{2.9}$$

$$P(2) = q. \tag{2.10}$$

It follows immediately from the normalization condition (2.5) that

$$p + q = 1, \tag{2.11}$$

so $q = 1 - p$. The best known example of a two-state system is a tossed coin. The two outcomes are “heads” and “tails,” each with equal probabilities $1/2$. So, $p = q = 1/2$ for this system.

Suppose that we make N statistically independent observations of S. Let us determine the probability of n_1 occurrences of the outcome 1 and $N - n_1$ occurrences of the outcome 2, *with no regard to the order of these occurrences*. Denote this probability $P_N(n_1)$. This type of calculation crops up again and again in probability theory. For instance, we might want to know the probability of getting nine “heads” and only one “tails” in an experiment where a coin is tossed ten times, or where ten coins are tossed simultaneously.

Consider a simple case in which there are only three observations. Let us try to evaluate the probability of two occurrences of the outcome 1 and one occurrence of the outcome 2. There are three different ways of getting this result. We could get the outcome 1 on the first two observations and the outcome 2 on the third. Or, we could get the outcome 2 on the first observation and the outcome 1 on the latter two observations. Or, we could get the outcome 1 on the first and last observations and the outcome 2 on the middle observation. Writing this symbolically

$$P_3(2) = P(1 \otimes 1 \otimes 2 \mid 2 \otimes 1 \otimes 1 \mid 1 \otimes 2 \otimes 1). \tag{2.12}$$

This formula looks a bit scary, but all we have done here is to write out symbolically what was just said in words. Where we said "and" we have written the symbolic operator $\otimes$, and where we said "or" we have written the symbolic operator $|$. This symbolic representation is helpful because of the two basic rules for combining probabilities which we derived earlier

$$P(X\,|\,Y) = P(X) + P(Y), \tag{2.13}$$

$$P(X \otimes Y) = P(X)\,P(Y). \tag{2.14}$$

The straightforward application of these rules gives

$$P_3(2) = p\,p\,q + q\,p\,p + p\,q\,p = 3\,p^2\,q \tag{2.15}$$

in the case under consideration.

The probability of obtaining n_1 occurrences of the outcome 1 in N observations is given by

$$P_N(n_1) = C^N_{n_1,\,N-n_1}\,p^{n_1}\,q^{N-n_1}, \tag{2.16}$$

where $C^N_{n_1,\,N-n_1}$ is the number of ways of arranging two distinct sets of n_1 and $N - n_1$ indistinguishable objects. Hopefully, that this is, at least, plausible from the example we just discussed. There, the probability of getting two occurrences of the outcome 1 and one occurrence of the outcome 2 was obtained by writing out all of the possible arrangements of two p s (the probability of outcome 1) and one q (the probability of outcome 2), and then added them all together.

2.5 Combinatorial analysis

The branch of mathematics which studies the number of different ways of arranging things is called *combinatorial analysis*. We need to know how many different ways there are of arranging N objects which are made up of two groups of n_1 and $N - n_1$ indistinguishable objects. This is a pretty tough problem! Let us try something a little easier to begin with. How many ways are there of arranging N *distinguishable* objects? For instance, suppose that we have six pool balls, numbered one through six, and we pot one each into every one of the six pockets of a pool table (that is, top-left, top-right, middle-left, middle-right, bottom-left, and bottom-right). How many different ways are there of doing this? Well, let us start with the top-left pocket. We could pot any one of the six balls into this pocket, so there are 6 possibilities. For the top-right pocket we only have 5 possibilities, because we have already potted a ball into the top-left pocket, and it cannot be in two pockets simultaneously. So, our 6 original possibilities combined with these 5 new possibilities gives 6×5 ways of potting two balls into the top two pockets. For the middle-left pocket we have 4 possibilities, because we have already potted two balls. These possibilities combined with our 6×5 possibilities gives $6 \times 5 \times 4$ ways of potting three balls into three pockets. At this stage, it should be clear that the final answer is going to be $6 \times 5 \times 4 \times 3 \times 2 \times 1$. Well, $6 \times 5 \times 4 \times 3 \times 2 \times 1$ is a bit of a mouthful, so to prevent us having to say (or write) things like this, mathematicians have invented a special function called a *factorial*. The factorial of a general positive integer n is defined

$$n! = n(n-1)(n-2)\cdots 3 \cdot 2 \cdot 1. \tag{2.17}$$

So, $1! = 1$, and $2! = 2 \times 1 = 2$, and $3! = 3 \times 2 \times 1 = 6$, and so on. Clearly, the number of ways of potting six pool balls into six pockets is 6! (which incidentally equals 720). Since there is nothing special about pool balls, or the number six, we can safely infer that the number of different ways of arranging N distinguishable objects, denoted C^N, is given by

$$C^N = N!\,. \tag{2.18}$$

Suppose that we take the number four ball off the pool table and replace it by a second number five ball. How many different ways are there of potting the balls now? Well, consider a previous arrangement in which the number five ball was potted into the top-left pocket and the number four ball was potted into the top-right pocket, and then consider a second arrangement which only differs from the first because the number four and five balls have been swapped around. These arrangements are now indistinguishable, and are therefore counted as a single arrangement, whereas previously they were counted as two separate arrangements. Clearly, the previous arrangements can be divided into two groups, containing equal numbers of arrangements, which differ only by the permutation of the number four and five balls. Since these balls are now indistinguishable, we conclude that there are only half as many different arrangements as there were before. If we take the number three ball off the table and replace it by a third number five ball, we can split the original arrangements into six equal groups of arrangements which differ only by the permutation of the number three, four, and five balls. There are six groups because there are $3! = 6$ separate permutations of these three balls. Since the number three, four, and five balls are now indistinguishable, we conclude that there are only $1/6$ the number of original arrangements. Generalizing this result, we conclude that the number of arrangements of n_1 *indistinguishable* and $N - n_1$ *distinguishable* objects is

$$C^N_{n_1} = \frac{N!}{n_1!}. \tag{2.19}$$

We can see that if all the balls on the table are replaced by number five balls then there is only $N!/N! = 1$ possible arrangement. This corresponds, of course, to a number five ball in each pocket. A further straightforward generalization tells us that the number of arrangements of two groups of n_1 and $N-n_1$ indistinguishable objects is

$$C^N_{n_1,\,N-n_1} = \frac{N!}{n_1!\,(N-n_1)!}. \tag{2.20}$$

2.6 The binomial distribution

It follows from Eqs. (2.16) and (2.20) that the probability of obtaining n_1 occurrences of the outcome 1 in N statistically independent observations of a two-state system is

$$P_N(n_1) = \frac{N!}{n_1!\,(N-n_1)!}\,p^{n_1}\,q^{N-n_1}. \tag{2.21}$$

This probability function is called the *binomial distribution* function. The reason for this is obvious if we tabulate the probabilities for the first few possible values of N (see Tab. 1). Of course, we immediately recognize these expressions: they appear in the standard algebraic expansions of $(p+q)$, $(p+q)^2$, $(p+q)^3$, and $(p+q)^4$, respectively. In algebra, the expansion of $(p+q)^N$ is called the *binomial expansion* (hence, the name given to the probability distribution function), and

		n_1				
		0	1	2	3	4
	1	q	p			
N	2	q^2	$2\,p\,q$	p^2		
	3	q^3	$3\,p\,q^2$	$3\,p^2\,q$	p^3	
	4	q^4	$4\,p\,q^3$	$6\,p^2\,q^2$	$4\,p^3\,q$	p^4

Table 1: *The binomial probability distribution*

can be written

$$(p+q)^N \equiv \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\,p^n\,q^{N-n}. \tag{2.22}$$

Equations (2.21) and (2.22) can be used to establish the normalization condition for the binomial distribution function:

$$\sum_{n_1=0}^{N} P_N(n_1) = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\,p^{n_1}\,q^{N-n_1} \equiv (p+q)^N = 1, \tag{2.23}$$

since $p+q=1$.

2.7 The mean, variance, and standard deviation

What is meant by the mean or average of a quantity? Well, suppose that we wanted to calculate the average age of undergraduates at the University of Texas at Austin. We could go to the central administration building and find out how many eighteen year-olds, nineteen year-olds, *etc*. were currently enrolled. We would then write something like

$$\text{Average Age} \simeq \frac{N_{18}\times 18 + N_{19}\times 19 + N_{20}\times 20 + \cdots}{N_{18}+N_{19}+N_{20}\cdots}, \tag{2.24}$$

where N_{18} is the number of enrolled eighteen year-olds, *etc*. Suppose that we were to pick a student *at random* and then ask “What is the probability of this student being eighteen?” From what we have already discussed, this probability is defined

$$P_{18} = \frac{N_{18}}{N_{\text{students}}}, \tag{2.25}$$

where $N_{\rm students}$ is the total number of enrolled students. We can now see that the average age takes the form

$$\text{Average Age} \simeq P_{18} \times 18 + P_{19} \times 19 + P_{20} \times 20 + \cdots. \tag{2.26}$$

Well, there is nothing special about the age distribution of students at UT Austin. So, for a general variable u, which can take on any one of M possible values $u_1, u_2, \cdots, u_M$, with corresponding probabilities $P(u_1)$, $P(u_2), \cdots, P(u_M)$, the mean or average value of u, which is denoted $\bar{u}$, is defined as

$$\bar{u} \equiv \sum_{i=1}^{M} P(u_i)\, u_i. \tag{2.27}$$

Suppose that $f(u)$ is some function of u. Then, for each of the M possible values of u, there is a corresponding value of $f(u)$ which occurs with the same probability. Thus, $f(u_1)$ corresponds to u_1 and occurs with the probability $P(u_1)$, and so on. It follows from our previous definition that the mean value of $f(u)$ is given by

$$\overline{f(u)} \equiv \sum_{i=1}^{M} P(u_i)\, f(u_i). \tag{2.28}$$

Suppose that $f(u)$ and $g(u)$ are two general functions of u. It follows that

$$\overline{f(u) + g(u)} = \sum_{i=1}^{M} P(u_i)\, [f(u_i) + g(u_i)] = \sum_{i=1}^{M} P(u_i)\, f(u_i) + \sum_{i=1}^{M} P(u_i)\, g(u_i), \tag{2.29}$$

so

$$\overline{f(u) + g(u)} = \overline{f(u)} + \overline{g(u)}. \tag{2.30}$$

Finally, if c is a general constant then it is clear that

$$\overline{c\, f(u)} = c\, \overline{f(u)}. \tag{2.31}$$

We now know how to define the mean value of the general variable u. But, how can we characterize the scatter around the mean value? We could investigate the deviation of u from its mean value $\bar{u}$, which is denoted

$$\Delta u \equiv u - \bar{u}. \tag{2.32}$$

In fact, this is not a particularly interesting quantity, since its average is obviously zero:

$$\overline{\Delta u} = \overline{(u - \bar{u})} = \bar{u} - \bar{u} = 0. \tag{2.33}$$

This is another way of saying that the average deviation from the mean vanishes. A more interesting quantity is the square of the deviation. The average value of this quantity,

$$\overline{(\Delta u)^2} = \sum_{i=1}^{M} P(u_i)\,(u_i - \bar{u})^2, \tag{2.34}$$

is usually called the *variance*. The variance is clearly a *positive* number, unless there is no scatter at all in the distribution, so that all possible values of u correspond to the mean value $\bar{u}$, in which case it is *zero*. The following general relation is often useful

$$\overline{(u - \bar{u})^2} = \overline{(u^2 - 2\,u\,\bar{u} + \bar{u}^2)} = \overline{u^2} - 2\,\bar{u}\,\bar{u} + \bar{u}^2, \tag{2.35}$$

giving

$$\overline{(u - \bar{u})^2} = \overline{u^2} - \bar{u}^2. \tag{2.36}$$

The variance of u is proportional to the square of the scatter of u around its mean value. A more useful measure of the scatter is given by the square root of the variance,

$$\Delta^* u = \left[\overline{(\Delta u)^2}\right]^{1/2}, \tag{2.37}$$

which is usually called the *standard deviation* of u. The standard deviation is essentially the width of the range over which u is distributed around its mean value $\bar{u}$.

2.8 Application to the binomial distribution

Let us now apply what we have just learned about the mean, variance, and standard deviation of a general distribution function to the specific case of the binomial distribution function. Recall, that if a simple system has just two possible outcomes, denoted 1 and 2, with respective probabilities p and $q = 1 - p$, then the probability of obtaining n_1 occurrences of outcome 1 in N observations is

$$P_N(n_1) = \frac{N!}{n_1!\,(N-n_1)!}\,p^{n_1}\,q^{N-n_1}. \tag{2.38}$$

Thus, the mean number of occurrences of outcome 1 in N observations is given by

$$\overline{n_1} = \sum_{n_1=0}^{N} P_N(n_1)\,n_1 = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\,p^{n_1}\,q^{N-n_1}\,n_1. \tag{2.39}$$

This is a rather nasty looking expression! However, we can see that if the final factor n_1 were absent, it would just reduce to the binomial expansion, which we know how to sum. We can take advantage of this fact by using a rather elegant mathematical sleight of hand. Observe that since

$$n_1\,p^{n_1} \equiv p\,\frac{\partial}{\partial p}\,p^{n_1}, \tag{2.40}$$

the summation can be rewritten as

$$\sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\,p^{n_1}\,q^{N-n_1}\,n_1 \equiv p\,\frac{\partial}{\partial p}\left[\sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\,p^{n_1}\,q^{N-n_1}\right]. \tag{2.41}$$

This is just algebra, and has nothing to do with probability theory. The term in square brackets is the familiar binomial expansion, and can be written more succinctly as $(p+q)^N$. Thus,

$$\sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\,p^{n_1}\,q^{N-n_1}\,n_1 \equiv p\,\frac{\partial}{\partial p}\,(p+q)^N \equiv p\,N\,(p+q)^{N-1}. \tag{2.42}$$

However, $p + q = 1$ for the case in hand, so

$$\overline{n_1} = N\,p. \tag{2.43}$$

In fact, we could have guessed this result. By definition, the probability p is the number of occurrences of the outcome 1 divided by the number of trials, in the limit as the number of trials goes to infinity:

$$p = {\rm lt}_{N\to\infty}\,\frac{n_1}{N}. \tag{2.44}$$

If we think carefully, however, we can see that taking the limit as the number of trials goes to infinity is equivalent to taking the mean value, so that

$$p = \overline{\left(\frac{n_1}{N}\right)} = \frac{\overline{n_1}}{N}. \tag{2.45}$$

But, this is just a simple rearrangement of Eq. (2.43).

Let us now calculate the variance of n_1. Recall that

$$\overline{(\Delta n_1)^2} = \overline{(n_1)^2} - (\overline{n_1})^2. \tag{2.46}$$

We already know $\overline{n_1}$, so we just need to calculate $\overline{(n_1)^2}$. This average is written

$$\overline{(n_1)^2} = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\, p^{n_1}\, q^{N-n_1}\, (n_1)^2. \tag{2.47}$$

The sum can be evaluated using a simple extension of the mathematical trick we used earlier to evaluate $\overline{n_1}$. Since

$$(n_1)^2\, p^{n_1} \equiv \left(p\,\frac{\partial}{\partial p}\right)^2 p^{n_1}, \tag{2.48}$$

then

$$\begin{aligned} \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\, p^{n_1}\, q^{N-n_1}\, (n_1)^2 &\equiv \left(p\,\frac{\partial}{\partial p}\right)^2 \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\, p^{n_1} q^{N-n_1} \\ &\equiv \left(p\,\frac{\partial}{\partial p}\right)^2 (p+q)^N \\ &\equiv \left(p\,\frac{\partial}{\partial p}\right) \left[p\, N\, (p+q)^{N-1}\right] \\ &\equiv p\left[N\,(p+q)^{N-1} + p\, N\,(N-1)\,(p+q)^{N-2}\right]. \end{aligned} \tag{2.49}$$

Using $p + q = 1$ yields

$$\begin{aligned} \overline{(n_1)^2} &= p\,[N + p\, N\,(N-1)] = N\, p\,[1 + p\, N - p] \\ &= (N\, p)^2 + N\, p\, q = (\overline{n_1})^2 + N\, p\, q, \end{aligned} \tag{2.50}$$

since $\overline{n_1} = N\, p$. It follows that the variance of n_1 is given by

$$\overline{(\Delta n_1)^2} = \overline{(n_1)^2} - (\overline{n_1})^2 = N\, p\, q. \tag{2.51}$$

The standard deviation of n_1 is just the square root of the variance, so

$$\Delta^* n_1 = \sqrt{N\,p\,q}. \tag{2.52}$$

Recall that this quantity is essentially the width of the range over which n_1 is distributed around its mean value. The relative width of the distribution is characterized by

$$\frac{\Delta^* n_1}{\overline{n_1}} = \frac{\sqrt{N\,p\,q}}{N\,p} = \sqrt{\frac{q}{p}}\frac{1}{\sqrt{N}}. \tag{2.53}$$

It is clear from this formula that the relative width decreases like $N^{-1/2}$ with increasing N. So, the greater the number of trials, the more likely it is that an observation of n_1 will yield a result which is relatively close to the mean value $\overline{n_1}$. This is a very important result.

2.9 The Gaussian distribution

Consider a very large number of observations, $N \gg 1$, made on a system with two possible outcomes. Suppose that the probability of outcome 1 is sufficiently large that the average number of occurrences after N observations is much greater than unity:

$$\overline{n_1} = N\,p \gg 1. \tag{2.54}$$

In this limit, the standard deviation of n_1 is also much greater than unity,

$$\Delta^* n_1 = \sqrt{N\,p\,q} \gg 1, \tag{2.55}$$

implying that there are very many probable values of n_1 scattered about the mean value $\overline{n_1}$. This suggests that the probability of obtaining n_1 occurrences of outcome 1 does not change significantly in going from one possible value of n_1 to an adjacent value:

$$\frac{|P_N(n_1+1) - P_N(n_1)|}{P_N(n_1)} \ll 1. \tag{2.56}$$

In this situation, it is useful to regard the probability as a smooth function of n_1. Let n be a continuous variable which is interpreted as the number of occurrences of outcome 1 (after N observations) whenever it takes on a positive integer value. The probability that n lies between n and $n + dn$ is defined

$$P(n, n + dn) = \mathcal{P}(n)\, dn, \tag{2.57}$$

where $\mathcal{P}(n)$ is called the *probability density*, and is independent of dn. The probability can be written in this form because $P(n, n + dn)$ can always be expanded as a Taylor series in dn, and must go to zero as $dn \to 0$. We can write

$$\int_{n_1-1/2}^{n_1+1/2} \mathcal{P}(n)\, dn = P_N(n_1), \tag{2.58}$$

which is equivalent to smearing out the discrete probability $P_N(n_1)$ over the range $n_1 \pm 1/2$. Given Eq. (2.56), the above relation can be approximated

$$\mathcal{P}(n) \simeq P_N(n) = \frac{N!}{n!\,(N-n)!}\, p^n\, q^{N-n}. \tag{2.59}$$

For large N, the *relative* width of the probability distribution function is small:

$$\frac{\Delta^* n_1}{\overline{n_1}} = \sqrt{\frac{q}{p}} \frac{1}{\sqrt{N}} \ll 1. \tag{2.60}$$

This suggests that $\mathcal{P}(n)$ is strongly peaked around the mean value $\overline{n} = \overline{n_1}$. Suppose that $\ln \mathcal{P}(n)$ attains its maximum value at $n = \tilde{n}$ (where we expect $\tilde{n} \sim \overline{n}$). Let us Taylor expand $\ln \mathcal{P}$ around $n = \tilde{n}$. Note that we expand the slowly varying function $\ln \mathcal{P}(n)$, instead of the rapidly varying function $\mathcal{P}(n)$, because the Taylor expansion of $\mathcal{P}(n)$ does not converge sufficiently rapidly in the vicinity of $n = \tilde{n}$ to be useful. We can write

$$\ln \mathcal{P}(\tilde{n} + \eta) \simeq \ln \mathcal{P}(\tilde{n}) + \eta\, B_1 + \frac{\eta^2}{2}\, B_2 + \cdots, \tag{2.61}$$

where

$$B_k = \left.\frac{d^k \ln \mathcal{P}}{dn^k}\right|_{n=\tilde{n}}. \tag{2.62}$$

By definition,

$$B_1 = 0, \tag{2.63}$$
$$B_2 < 0, \tag{2.64}$$

if $n = \tilde{n}$ corresponds to the *maximum* value of $\ln\mathcal{P}(n)$.

It follows from Eq. (2.59) that

$$\ln\mathcal{P} = \ln N! - \ln n! - \ln(N-n)! + n\ln p + (N-n)\ln q. \tag{2.65}$$

If n is a large integer, such that $n \gg 1$, then $\ln n!$ is almost a continuous function of n, since $\ln n!$ changes by only a relatively small amount when n is incremented by unity. Hence,

$$\frac{d\ln n!}{dn} \simeq \frac{\ln(n+1)! - \ln n!}{1} = \ln\left[\frac{(n+1)!}{n!}\right] = \ln(n+1), \tag{2.66}$$

giving

$$\frac{d\ln n!}{dn} \simeq \ln n, \tag{2.67}$$

for $n \gg 1$. The integral of this relation

$$\ln n! \simeq n\,\ln n - n + \mathcal{O}(1), \tag{2.68}$$

valid for $n \gg 1$, is called *Stirling's approximation*, after the Scottish mathematician James Stirling who first obtained it in 1730.

According to Eq. (2.65),

$$B_1 = -\ln\tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q. \tag{2.69}$$

Hence, if $B_1 = 0$ then

$$(N-\tilde{n})\,p = \tilde{n}\,q, \tag{2.70}$$

giving

$$\tilde{n} = N\,p = \overline{n_1}, \tag{2.71}$$

since $p + q = 1$. Thus, the maximum of $\ln\mathcal{P}(n)$ occurs *exactly* at the mean value of n, which equals $\overline{n_1}$.

Further differentiation of Eq. (2.65) yields

$$B_2 = -\frac{1}{\tilde{n}} - \frac{1}{N-\tilde{n}} = -\frac{1}{Np} - \frac{1}{N(1-p)} = -\frac{1}{N\,p\,q}, \tag{2.72}$$

since $p + q = 1$. Note that $B_2 < 0$, as required. The above relation can also be written

$$B_2 = -\frac{1}{(\Delta^* n_1)^2} \tag{2.73}$$

It follows from the above that the Taylor expansion of $\ln \mathcal{P}$ can be written

$$\ln \mathcal{P}(\overline{n_1} + \eta) \simeq \ln \mathcal{P}(\overline{n_1}) - \frac{\eta^2}{2\,(\Delta^* n_1)^2} + \cdots. \tag{2.74}$$

Taking the exponential of both sides yields

$$\mathcal{P}(n) \simeq \mathcal{P}(\overline{n_1}) \exp\left[-\frac{(n - \overline{n_1})^2}{2\,(\Delta^* n_1)^2}\right]. \tag{2.75}$$

The constant $\mathcal{P}(\overline{n_1})$ is most conveniently fixed by making use of the normalization condition

$$\sum_{n_1=0}^{N} P_N(n_1) = 1, \tag{2.76}$$

which translates to

$$\int_0^N \mathcal{P}(n)\, dn \simeq 1 \tag{2.77}$$

for a continuous distribution function. Since we only expect $\mathcal{P}(n)$ to be significant when n lies in the relatively narrow range $\overline{n_1} \pm \Delta^* n_1$, the limits of integration in the above expression can be replaced by $\pm\infty$ with negligible error. Thus,

$$\mathcal{P}(\overline{n_1}) \int_{-\infty}^{\infty} \exp\left[-\frac{(n - \overline{n_1})^2}{2\,(\Delta^* n_1)^2}\right] dn = \mathcal{P}(\overline{n_1})\, \sqrt{2}\, \Delta^* n_1 \int_{-\infty}^{\infty} \exp(-x^2)\, dx \simeq 1. \tag{2.78}$$

As is well-known,

$$\int_{-\infty}^{\infty} \exp(-x^2)\, dx = \sqrt{\pi}, \tag{2.79}$$

so it follows from the normalization condition (2.78) that

$$\mathcal{P}(\overline{n_1}) \simeq \frac{1}{\sqrt{2\pi}\, \Delta^* n_1}. \tag{2.80}$$

Finally, we obtain

$$\mathcal{P}(n) \simeq \frac{1}{\sqrt{2\pi}\,\Delta^* n_1}\,\exp\left[-\frac{(n-\overline{n_1})^2}{2\,(\Delta^* n_1)^2}\right]. \tag{2.81}$$

This is the famous *Gaussian distribution function*, named after the German mathematician Carl Friedrich Gauss, who discovered it whilst investigating the distribution of errors in measurements. The Gaussian distribution is only valid in the limits $N \gg 1$ and $\overline{n_1} \gg 1$.

Suppose we were to plot the probability $P_N(n_1)$ against the integer variable n_1, and then fit a continuous curve through the discrete points thus obtained. This curve would be equivalent to the continuous probability density curve $\mathcal{P}(n)$, where n is the continuous version of n_1. According to Eq. (2.81), the probability density attains its *maximum* value when n equals the *mean* of n_1, and is also *symmetric* about this point. In fact, when plotted with the appropriate ratio of vertical to horizontal scalings, the Gaussian probability density curve looks rather like the outline of a *bell* centred on $n = \overline{n_1}$. Hence, this curve is sometimes called a *bell curve*. At one standard deviation away from the mean value, *i.e.*, $n = \overline{n_1} \pm \Delta^* n_1$, the probability density is about 61% of its peak value. At two standard deviations away from the mean value, the probability density is about 13.5% of its peak value. Finally, at three standard deviations away from the mean value, the probability density is only about 1% of its peak value. We conclude that there is very little chance indeed that n_1 lies more than about three standard deviations away from its mean value. In other words, n_1 is almost certain to lie in the relatively narrow range $\overline{n_1} \pm 3\,\Delta^* n_1$. This is a very well-known result.

In the above analysis, we have gone from a *discrete* probability function $P_N(n_1)$ to a *continuous* probability density $\mathcal{P}(n)$. The normalization condition becomes

$$1 = \sum_{n_1=0}^{N} P_N(n_1) \simeq \int_{-\infty}^{\infty} \mathcal{P}(n)\,dn \tag{2.82}$$

under this transformation. Likewise, the evaluations of the mean and variance of the distribution are written

$$\overline{n_1} = \sum_{n_1=0}^{N} P_N(n_1)\,n_1 \simeq \int_{-\infty}^{\infty} \mathcal{P}(n)\,n\,dn, \tag{2.83}$$

and

$$\overline{(\Delta n_1)^2} \equiv (\Delta^* n_1)^2 = \sum_{n_1=0}^{N} P_N(n_1)\,(n_1 - \overline{n_1})^2 \simeq \int_{-\infty}^{\infty} \mathcal{P}(n)\,(n - \overline{n_1})^2\,dn, \tag{2.84}$$

respectively. These results follow as simple generalizations of previously established results for the discrete function $P_N(n_1)$. The limits of integration in the above expressions can be approximated as $\pm\infty$ because $\mathcal{P}(n)$ is only non-negligible in a relatively narrow range of n. Finally, it is easily demonstrated that Eqs. (2.82)–(2.84) are indeed true by substituting in the Gaussian probability density, Eq. (2.81), and then performing a few elementary integrals.

2.10 The central limit theorem

Now, you may be thinking that we got a little carried away in our discussion of the Gaussian distribution function. After all, this distribution only seems to be relevant to two-state systems. In fact, as we shall see, the Gaussian distribution is of crucial importance to statistical physics because, under certain circumstances, it applies to *all* systems.

Let us briefly review how we obtained the Gaussian distribution function in the first place. We started from a very simple system with only two possible outcomes. Of course, the probability distribution function (for n_1) for this system did not look anything like a Gaussian. However, when we combined very many of these simple systems together, to produce a complicated system with a great number of possible outcomes, we found that the resultant probability distribution function (for n_1) reduced to a Gaussian in the limit as the number of simple systems tended to infinity. We started from a two outcome system because it was easy to calculate the final probability distribution function when a *finite* number of such systems were combined together. Clearly, if we had started from a more complicated system then this calculation would have been far more difficult.

Let me now tell you something which is quite astonishing! Suppose that we start from *any* system, with *any* distribution function (for some measurable quantity x). If we combine a sufficiently large number of such systems together, the resultant distribution function (for x) is *always* Gaussian. This proposition is known as the *central limit theorem*. As far as Physics is concerned, it is one of the most important theorems in the whole of mathematics.

Unfortunately, the central limit theorem is notoriously difficult to prove. A somewhat restricted proof is presented in Sections 1.10 and 1.11 of Reif.

The central limit theorem guarantees that the probability distribution of *any* measurable quantity is Gaussian, provided that a sufficiently large number of statistically independent observations are made. We can, therefore, confidently predict that Gaussian distributions are going to crop up all over the place in statistical thermodynamics.

3 Statistical mechanics

3.1 Introduction

Let us now analyze the internal motions of a many particle system using probability theory. This subject area is known as *statistical mechanics*.

3.2 Specification of the state of a many particle system

How do we determine the state of a many particle system? Well, let us, first of all, consider the simplest possible many particle system, which consists of a single spinless particle moving classically in one dimension. Assuming that we know the particle's equation of motion, the state of the system is fully specified once we simultaneously measure the particle's position q and momentum p. In principle, if we know q and p then we can calculate the state of the system at all subsequent times using the equation of motion. In practice, it is impossible to specify q and p exactly, since there is always an intrinsic error in any experimental measurement.

Consider the time evolution of q and p. This can be visualized by plotting the point $(q,\ p)$ in the q-p plane. This plane is generally known as *phase-space*. In general, the point $(q,\ p)$ will trace out some very complicated pattern in phase-space. Suppose that we divide phase-space into rectangular cells of uniform dimensions δq and δp. Here, δq is the intrinsic error in the position measurement, and δp the intrinsic error in the momentum measurement. The "area" of each cell is

$$\delta q\,\delta p = h_0, \tag{3.1}$$

where h_0 is a small constant having the dimensions of angular momentum. The coordinates q and p can now be conveniently specified by indicating the cell in phase-space into which they plot at any given time. This procedure automatically ensures that we do not attempt to specify q and p to an accuracy greater than our experimental error, which would clearly be pointless.

Let us now consider a single spinless particle moving in three dimensions. In order to specify the state of the system we now need to know three q-p pairs: *i.e.*, q_x-p_x, q_y-p_y, and q_z-p_z. Incidentally, the number of q-p pairs needed to specify the state of the system is usually called the *number of degrees of freedom* of the system. Thus, a single particle moving in one dimension constitutes a one degree of freedom system, whereas a single particle moving in three dimensions constitutes a three degree of freedom system.

Consider the time evolution of $\mathbf{q}$ and $\mathbf{p}$, where $\mathbf{q} = (q_x, q_y, q_z)$, *etc.* This can be visualized by plotting the point ($\mathbf{q}$, $\mathbf{p}$) in the six dimensional $\mathbf{q}$-$\mathbf{p}$ phase-space. Suppose that we divide the q_x-p_x plane into rectangular cells of uniform dimensions δq and δp, and do likewise for the q_y-p_y and q_z-p_z planes. Here, δq and δp are again the intrinsic errors in our measurements of position and momentum, respectively. This is equivalent to dividing phase-space up into regular six dimensional cells of volume $h_0^{\,3}$. The coordinates $\mathbf{q}$ and $\mathbf{p}$ can now be conveniently specified by indicating the cell in phase-space into which they plot at any given time. Again, this procedure automatically ensures that we do not attempt to specify $\mathbf{q}$ and $\mathbf{p}$ to an accuracy greater than our experimental error.

Finally, let us consider a system consisting of N spinless particles moving classically in three dimensions. In order to specify the state of the system, we need to specify a large number of q-p pairs. The requisite number is simply the number of degrees of freedom, f. For the present case, $f = 3\,N$. Thus, phase-space (*i.e.*, the space of all the q-p pairs) now possesses $2\,f = 6\,N$ dimensions. Consider a particular pair of conjugate coordinates, q_i and p_i. As before, we divide the q_i-p_i plane into rectangular cells of uniform dimensions δq and δp. This is equivalent to dividing phase-space into regular $2\,f$ dimensional cells of volume $h_0^{\,f}$. The state of the system is specified by indicating which cell it occupies in phase-space at any given time.

In principle, we can specify the state of the system to arbitrary accuracy by taking the limit $h_0 \rightarrow 0$. In reality, we know from quantum mechanics that it is impossible to simultaneously measure a coordinate q_i and its conjugate momentum p_i to greater accuracy than $\delta q_i\,\delta p_i = \hbar$. This implies that

$$h_0 \geq \hbar. \tag{3.2}$$

In other words, the uncertainty principle sets a lower limit on how finely we can chop up classical phase-space.

In quantum mechanics we can specify the state of the system by giving its wave-function at time t,

$$\psi(q_1, \cdots, q_f, s_1, \cdots, s_g, t), \tag{3.3}$$

where f is the number of translational degrees of freedom, and g the number of internal (*e.g.*, spin) degrees of freedom. For instance, if the system consists of N spin-one-half particles then there will be $3\,N$ translational degrees of freedom, and N spin degrees of freedom (*i.e.*, the spin of each particle can either point up or down along the z-axis). Alternatively, if the system is in a *stationary state* (*i.e.*, an eigenstate of the Hamiltonian) then we can just specify $f+g$ *quantum numbers*. Either way, the future time evolution of the wave-function is fully determined by Schrödinger's equation.

In reality, this approach does not work because the Hamiltonian of the system is only known approximately. Typically, we are dealing with a system consisting of many *weakly interacting* particles. We usually know the Hamiltonian for completely non-interacting particles, but the component of the Hamiltonian associated with particle interactions is either impossibly complicated, or not very well known (often, it is both!). We can define approximate stationary eigenstates using the Hamiltonian for non-interacting particles. The state of the system is then specified by the quantum numbers identifying these eigenstates. In the absence of particle interactions, if the system starts off in a stationary state then it stays in that state for ever, so its quantum numbers never change. The interactions allow the system to make transitions between different "stationary" states, causing its quantum numbers to change in time.

3.3 The principle of equal *a priori* probabilities

We now know how to specify the instantaneous state of a many particle system. In principle, such a system is completely deterministic. Once we know the initial state and the equations of motion (or the Hamiltonian) we can evolve the system forward in time and, thereby, determine all future states. In reality, it is quite impossible to specify the initial state or the equations of motion to sufficient accuracy for this method to have any chance of working. Furthermore, even if it were possible, it would still not be a practical proposition to evolve the equations of motion. Remember that we are typically dealing with systems containing Avogadro's number of particles: *i.e.*, about 10^{24} particles. We cannot evolve 10^{24} simultaneous differential equations! Even if we could, we would not want to. After all, we are not particularly interested in the motions of *individual* particles. What we really want is *statistical* information regarding the motions of *all* particles in the system.

Clearly, what is required here is a statistical treatment of the problem. Instead of focusing on a single system, let us proceed in the usual manner and consider a *statistical ensemble* consisting of a large number of identical systems. In general, these systems are distributed over many different states at any given time. In order to evaluate the probability that the system possesses a particular property, we merely need to find the number of systems in the ensemble which exhibit this property, and then divide by the total number of systems, in the limit as the latter number tends to infinity.

We can usually place some general constraints on the system. Typically, we know the total energy E, the total volume V, and the total number of particles N. To be more honest, we can only really say that the total energy lies between E and $E + \delta E$, *etc.*, where δE is an experimental error. Thus, we only need concern ourselves with those systems in the ensemble exhibiting states which are consistent with the known constraints. We call these the *states accessible to the system*. In general, there are a great many such states.

We now need to calculate the probability of the system being found in each of its accessible states. Well, perhaps "calculate" is the wrong word. The only way we could calculate these probabilities would be to evolve all of the systems in the ensemble and observe how long on average they spend in each accessible state. But, as we have already mentioned, such a calculation is completely out of the question. So what do we do instead? Well, we effectively *guess* the probabilities.

Let us consider an isolated system in *equilibrium*. In this situation, we would expect the probability of the system being found in one of its accessible states to be independent of time. This implies that the statistical ensemble does not evolve with time. Individual systems in the ensemble will constantly change state, but the average number of systems in any given state should remain constant. Thus, all macroscopic parameters describing the system, such as the energy and the volume, should also remain constant. There is nothing in the laws of mechanics which would lead us to suppose that the system will be found more often in one of its accessible states than in another. We assume, therefore, that *the system is equally likely to be found in any of its accessible states*. This is called the assumption of *equal a priori probabilities*, and lies at the very heart of statistical mechanics.

In fact, we use assumptions like this all of the time without really thinking about them. Suppose that we were asked to pick a card at random from a well-shuffled pack. I think that most people would accept that we have an equal probability of picking any card in the pack. There is nothing which would favour one particular card over all of the others. So, since there are fifty-two cards in a normal pack, we would expect the probability of picking the Ace of Spades, say, to be 1/52. We could now place some constraints on the system. For instance, we could only count red cards, in which case the probability of picking the Ace of Hearts, say, would be 1/26, by the same reasoning. In both cases, we have used the principle of equal *a priori* probabilities. People really believe that this principle applies to games of chance such as cards, dice, and roulette. In fact, if the principle were found not to apply to a particular game most people would assume that the game was “crooked.” But, imagine trying to prove that the principle actually does apply to a game of cards. This would be very difficult! We would have to show that the way most people shuffle cards is effective at randomizing their order. A convincing study would have to be part mathematics and part psychology!

In statistical mechanics, we treat a many particle system a bit like an extremely large game of cards. Each accessible state corresponds to one of the cards in the pack. The interactions between particles cause the system to continually change state. This is equivalent to constantly shuffling the pack. Finally, an observation of the state of the system is like picking a card at random from the pack. The principle of equal *a priori* probabilities then boils down to saying that we have an equal chance of choosing any particular card.

It is, unfortunately, *impossible* to prove with mathematical rigor that the principle of equal *a priori* probabilities applies to many-particle systems. Over the years, many people have attempted this proof, and all have failed miserably. Not surprisingly, therefore, statistical mechanics was greeted with a great deal of scepticism when it was first proposed just over one hundred years ago. One of the its main proponents, Ludvig Boltzmann, got so fed up with all of the criticism that he eventually threw himself off a bridge! Nowadays, statistical mechanics is completely accepted into the cannon of physics. The reason for this is quite simple: *it works!*

It *is* actually possible to formulate a reasonably convincing scientific case for the principle of equal *a priori* probabilities. To achieve this we have to make use of the so-called H *theorem*.

3.4 The H theorem

Consider a system of weakly interacting particles. In quantum mechanics we can write the Hamiltonian for such a system as

$$H = H_0 + H_1, \tag{3.4}$$

where H_0 is the Hamiltonian for completely non-interacting particles, and H_1 is a small correction due to the particle interactions. We can define *approximate* stationary eigenstates of the system using H_0. Thus,

$$H_0 \Psi_r = E_r \Psi_r, \tag{3.5}$$

where the index r labels a state of energy E_r and eigenstate Ψ_r. In general, there are many different eigenstates with the same energy: these are called *degenerate* states.

For example, consider N non-interacting spinless particles of mass m confined in a cubic box of dimension L. According to standard wave-mechanics, the energy levels of the ith particle are given by

$$e_i = \frac{\hbar^2\pi^2}{2\,m\,L^2}\left(n_{i1}^{\,2} + n_{i2}^{\,2} + n_{i3}^{\,2}\right), \tag{3.6}$$

where n_{i1}, n_{i2}, and n_{i3} are three (positive integer) quantum numbers. The overall energy of the system is the sum of the energies of the individual particles, so that for a general state r

$$E_r = \sum_{i=1}^{N} e_i. \tag{3.7}$$

The overall state of the system is thus specified by $3N$ quantum numbers (*i.e.*, three quantum numbers per particle). There are clearly very many different arrangements of these quantum numbers which give the same overall energy.

Consider, now, a statistical ensemble of systems made up of weakly interacting particles. Suppose that this ensemble is initially very far from equilibrium. For instance, the systems in the ensemble might only be distributed over a very small subset of their accessible states. If each system starts off in a particular stationary state (*i.e.*, with a particular set of quantum numbers) then, in the absence of particle interactions, it will remain in that state for ever. Hence, the ensemble will always stay far from equilibrium, and the principle of equal *a priori* probabilities will never be applicable. In reality, particle interactions cause each system in the ensemble to make transitions between its accessible “stationary” states. This allows the overall state of the ensemble to change in time.

Let us label the accessible states of our system by the index r. We can ascribe a time dependent probability $P_r(t)$ of finding the system in a particular approximate stationary state r at time t. Of course, $P_r(t)$ is proportional to the number of systems in the ensemble in state r at time t. In general, P_r is time dependent because the ensemble is evolving towards an equilibrium state. We assume that the probabilities are properly normalized, so that the sum over all accessible states always yields

$$\sum_r P_r(t) = 1. \tag{3.8}$$

Small interactions between particles cause transitions between the approximate stationary states of the system. There then exists some transition probability per unit time W_{rs} that a system originally in state r ends up in state s as a result of these interactions. Likewise, there exists a probability per unit time W_{sr} that a system in state s makes a transition to state r. These transition probabilities are meaningful in quantum mechanics provided that the particle interaction strength is sufficiently small, there is a nearly continuous distribution of accessible energy levels, and we consider time intervals which are not too small. These conditions are easily satisfied for the types of systems usually analyzed via statistical mechanics (*e.g.*, nearly ideal gases). One important conclusion of quantum mechanics is that the forward and inverse transition probabilities between two states are the same, so that

$$W_{rs} = W_{sr} \tag{3.9}$$

for any two states r and s. This result follows from the *time reversal symmetry* of quantum mechanics. On the microscopic scale of individual particles, all fundamental laws of physics (in particular, classical and quantum mechanics) possess this symmetry. So, if a certain motion of particles satisfies the classical equations of motion (or Schrödinger's equation) then the reversed motion, with all particles starting off from their final positions and then retracing their paths exactly until they reach their initial positions, satisfies these equations just as well.

Suppose that we were to "film" a microscopic process, such as two classical particles approaching one another, colliding, and moving apart. We could then gather an audience together and show them the film. To make things slightly more interesting we could play it either forwards or backwards. Because of the time reversal symmetry of classical mechanics, the audience would not be able to tell which way the film was running (unless we told them!). In both cases, the film would show completely plausible physical events.

We can play the same game for a quantum process. For instance, we could "film" a group of photons impinging on some atoms. Occasionally, one of the atoms will *absorb* a photon and make a transition to an "excited" state (*i.e.*, a state with higher than normal energy). We could easily estimate the rate constant for this process by watching the film carefully. If we play the film backwards then it will appear to show excited atoms occasionally *emitting* a photon and decaying back to their unexcited state. If quantum mechanics possesses time reversal symmetry (which it certainly does!) then both films should appear equally plausible.

This means that the rate constant for the absorption of a photon to produce an excited state must be the same as the rate constant for the excited state to decay by the emission of a photon. Otherwise, in the backwards film the excited atoms would appear to emit photons at the wrong rate, and we could then tell that the film was being played backwards. It follows, therefore, that as a consequence of time reversal symmetry, the rate constant for any process in quantum mechanics must equal the rate constant for the inverse process.

The probability P_r of finding the systems in the ensemble in a particular state r changes with time for two reasons. Firstly, systems in another state s can make transitions to the state r. The rate at which this occurs is P_s, the probability that the systems are in the state s to begin with, times the rate constant of the transition W_{sr}. Secondly, systems in the state r can make transitions to other states such as s. The rate at which this occurs is clearly P_r times W_{rs}. We can write a simple differential equation for the time evolution of P_r:

$$\frac{dP_r}{dt} = \sum_{s\neq r} P_s W_{sr} - \sum_{s\neq r} P_r W_{rs}, \tag{3.10}$$

or

$$\frac{dP_r}{dt} = \sum_{s} W_{rs}(P_s - P_r), \tag{3.11}$$

where use has been made of the symmetry condition (3.9). The summation is over all accessible states.

Consider now the quantity H (from which the H theorem derives its name), which is the mean value of $\ln P_r$ over all accessible states:

$$H \equiv \overline{\ln P_r} \equiv \sum_r P_r \ln P_r. \tag{3.12}$$

This quantity changes as the individual probabilities P_r vary in time. Straightforward differentiation of the above equation yields

$$\frac{dH}{dt} = \sum_r \left(\frac{dP_r}{dt}\ln P_r + \frac{dP_r}{dt}\right) = \sum_r \frac{dP_r}{dt}\,(\ln P_r + 1). \tag{3.13}$$

According to Eq. (3.11), this can be written

$$\frac{dH}{dt} = \sum_r \sum_s W_{rs}\,(P_s - P_r)\,(\ln P_r + 1). \tag{3.14}$$

We can now interchange the dummy summations indices r and s to give

$$\frac{dH}{dt} = \sum_r \sum_s W_{sr}\,(P_r - P_s)\,(\ln P_s + 1). \tag{3.15}$$

We can write dH/dt in a more symmetric form by adding the previous two equations and making use of Eq. (3.9):

$$\frac{dH}{dt} = -\frac{1}{2}\sum_r \sum_s W_{rs}\,(P_r - P_s)\,(\ln P_r - \ln P_s). \tag{3.16}$$

Note, however, that $\ln P_r$ is a monotonically increasing function of P_r. It follows that $\ln P_r > \ln P_s$ whenever $P_r > P_s$, and *vice versa*. Thus, in general, the right-hand side of the above equation is the sum of many *negative* contributions. Hence, we conclude that

$$\frac{dH}{dt} \leq 0. \tag{3.17}$$

The equality sign only holds in the special case where all accessible states are equally probable, so that $P_r = P_s$ for all r and s. This result is called the H theorem, and was first proved by the unfortunate Professor Boltzmann.

The H theorem tells us that if an isolated system is initially not in equilibrium then it will evolve under the influence of particle interactions in such a manner that the quantity H always *decreases*. This process will continue until H reaches its minimum possible value, at which point $dH/dt = 0$, and there is no further evolution of the system. According to Eq. (3.16), in this final equilibrium state the system is equally likely to be found in any one of its accessible states. This is, of course, the situation predicted by the principle of equal *a priori* probabilities.

You may be wondering why the above argument does not constitute a mathematically rigorous proof that the principle of equal *a priori* probabilities applies to many particle systems. The answer is that we tacitly made an unwarranted assumption: *i.e.*, we assumed that the probability of the system making a transition from some state r to another state s is *independent* of the past history of the system. In general, this is not the case in physical systems, although there are many situations in which it is a pretty good approximation. Thus, the epistemological status of the principle of equal *a priori* probabilities is that it is *plausible*, but remains *unproven*. As we have already mentioned, the ultimate justification for this principle is *empirical*: *i.e.*, it leads to theoretical predictions which are in accordance with experimental observations.

3.5 The relaxation time

The H theorem guarantees that an isolated many particle system will eventually reach equilibrium, irrespective of its initial state. The typical time-scale for this process is called the *relaxation time*, and depends in detail on the nature of the inter-particle interactions. The principle of equal *a priori* probabilities is only valid for equilibrium states. It follows that we can only safely apply this principle to systems which have remained undisturbed for many relaxation times since they were setup, or last interacted with the outside world. The relaxation time for the air in a typical classroom is very much less than one second. This suggests that such air is probably in equilibrium most of the time, and should, therefore, be governed by the principle of equal *a priori* probabilities. In fact, this is known to be the case. Consider another example. Our galaxy, the "Milky Way," is an isolated dynamical system made up of about 10^{11} stars. In fact, it can be thought of as a self-gravitating "gas" of stars. At first sight, the "Milky Way" would seem to be an ideal system on which to test out the ideas of statistical mechanics. Stars in the Galaxy interact via occasional "near miss" events in which they exchange energy and momentum. Actual collisions are very rare indeed. Unfortunately, such interactions take place very infrequently, because there is an awful lot of empty space between stars. The best estimate for the relaxation time of the "Milky Way" is about 10^{13} years. This should be compared with the estimated age of the Galaxy, which is only about 10^{10} years. It is clear that, despite its great age, the "Milky Way" has not been around long enough to reach an equilibrium state. This suggests that the principle of equal *a priori* probabilities cannot be used to describe stellar dynamics. Not surprisingly, the observed velocity distribution of the stars in the vicinity of the Sun is not governed by this principle.

3.6 Reversibility and irreversibility

Previously, we mentioned that on a microscopic level the laws of physics are invariant under time reversal. In other words, microscopic phenomena look physically plausible when run in reverse. We usually say that these phenomena are *reversible*. What about macroscopic phenomena? Are they reversible? Well, consider an isolated many particle system which starts off far from equilibrium. According to the H theorem, it will evolve towards equilibrium and, as it does so, the macroscopic quantity H will *decrease*. But, if we run this process backwards the system will appear to evolve away from equilibrium, and the quantity H will *increase*. This type of behaviour is not physical because it violates the H theorem. So, if we saw a film of a macroscopic process we could very easily tell if it was being run backwards. For instance, suppose that by some miracle we were able to move all of the Oxygen molecules in the air in some classroom to one side of the room, and all of the Nitrogen molecules to the opposite side. We would not expect this state to persist for very long. Pretty soon the Oxygen and Nitrogen molecules would start to intermingle, and this process would continue until they were thoroughly mixed together throughout the room. This, of course, is the equilibrium state for air. In reverse, this process looks crazy! We would start off from perfectly normal air, and suddenly, for no good reason, the Oxygen and Nitrogen molecules would appear to separate and move to opposite sides of the room. This scenario is not impossible, but, from everything we know about the world around us, it is spectacularly unlikely! We conclude, therefore, that macroscopic phenomena are generally *irreversible*, because they look “wrong” when run in reverse.

How does the irreversibility of macroscopic phenomena arise? It certainly does not come from the fundamental laws of physics, because these laws are all reversible. In the previous example, the Oxygen and Nitrogen molecules got mixed up by continually scattering off one another. Each individual scattering event would look perfectly reasonable viewed in reverse, but when we add them all together we obtain a process which would look stupid run backwards. How can this be? How can we obtain an irreversible process from the combined effects of very many reversible processes? This is a vitally important question. Unfortunately, we are not quite at the stage where we can formulate a convincing answer. Note, however, that the essential irreversibility of macroscopic phenomena is one of the key results of statistical thermodynamics.

3.7 Probability calculations

The principle of equal *a priori* probabilities is fundamental to all statistical mechanics, and allows a complete description of the properties of macroscopic systems in equilibrium. In principle, statistical mechanics calculations are very simple. Consider a system in equilibrium which is isolated, so that its total energy is known to have a constant value somewhere in the range E to $E + \delta E$. In order to make statistical predictions, we focus attention on an ensemble of such systems, all of which have their energy in this range. Let $\Omega(E)$ be the total number of different states of the system with energies in the specified range. Suppose that among these states there are a number $\Omega(E; y_k)$ for which some parameter y of the system assumes the discrete value y_k. (This discussion can easily be generalized to deal with a parameter which can assume a continuous range of values). The principle of equal *a priori* probabilities tells us that all the $\Omega(E)$ accessible states of the system are equally likely to occur in the ensemble. It follows that the probability $P(y_k)$ that the parameter y of the system assumes the value y_k is simply

$$P(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)}. \tag{3.18}$$

Clearly, the mean value of y for the system is given by

$$\bar{y} = \frac{\sum_k \Omega(E; y_k)\, y_k}{\Omega(E)}, \tag{3.19}$$

where the sum is over all possible values that y can assume. In the above, it is tacitly assumed that $\Omega(E) \to \infty$, which is generally the case in thermodynamic systems.

It can be seen that, using the principle of equal *a priori* probabilities, all calculations in statistical mechanics reduce to simply *counting states*, subject to various constraints. In principle, this is fairly straightforward. In practice, problems arise if the constraints become too complicated. These problems can usually be overcome with a little mathematical ingenuity. Nevertheless, there is no doubt that this type of calculation is far easier than trying to solve the classical equations of motion (or Schrödinger's equation) directly for a many-particle system.

3.8 Behaviour of the density of states

Consider an isolated system in equilibrium whose volume is V, and whose energy lies in the range E to $E+\delta E$. Let $\Omega(E, V)$ be the total number of microscopic states which satisfy these constraints. It would be useful if we could estimate how this number typically varies with the macroscopic parameters of the system. The easiest way to do this is to consider a specific example. For instance, an ideal gas made up of spinless monatomic particles. This is a particularly simple example, because for such a gas the particles possess translational but no internal (*e.g.*, vibrational, rotational, or spin) degrees of freedom. By definition, interatomic forces are negligible in an *ideal* gas. In other words, the individual particles move in an approximately uniform potential. It follows that the energy of the gas is just the total translational kinetic energy of its constituent particles. Thus,

$$E = \frac{1}{2\,m}\sum_{i=1}^{N}\mathbf{p}_i^{\,2}, \tag{3.20}$$

where m is the particle mass, N the total number of particles, and $\mathbf{p}_i$ the vector momentum of the ith particle.

Consider the system in the limit in which the energy E of the gas is much greater than the ground-state energy, so that all of the quantum numbers are large. The classical version of statistical mechanics, in which we divide up phase-space into cells of equal volume, is valid in this limit. The number of states $\Omega(E, V)$ lying between the energies E and $E+\delta E$ is simply equal to the number of cells in phase-space contained between these energies. In other words, $\Omega(E, V)$ is proportional to the *volume* of phase-space between these two energies:

$$\Omega(E, V) \propto \int_{E}^{E+\delta E} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N\, d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N. \tag{3.21}$$

Here, the integrand is the element of volume of phase-space, with

$$d^3\mathbf{r} \equiv dx_i\, dy_i\, dz_i, \tag{3.22}$$

$$d^3\mathbf{p} \equiv dp_{i\,x}\, dp_{i\,y}\, dp_{i\,z}, \tag{3.23}$$

where $(x_i,\, y_i,\, z_i)$ and $(p_{i\,x},\, p_{i\,y},\, p_{i\,z})$ are the Cartesian coordinates and momentum components of the ith particle, respectively. The integration is over all coordinates and momenta such that the total energy of the system lies between E and $E + \delta E$.

For an ideal gas, the total energy E does not depend on the positions of the particles [see Eq. (3.20)]. This means that the integration over the position vectors $\mathbf{r}_i$ can be performed immediately. Since each integral over $\mathbf{r}_i$ extends over the volume of the container (the particles are, of course, not allowed to stray outside the container), $\int d^3\mathbf{r}_i = V$. There are N such integrals, so Eq. (3.21) reduces to

$$\Omega(E, V) \propto V^N \chi(E), \tag{3.24}$$

where

$$\chi(E) \propto \int_E^{E+\delta E} d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N \tag{3.25}$$

is a momentum space integral which is independent of the volume.

The energy of the system can be written

$$E = \frac{1}{2\,m} \sum_{i=1}^{N} \sum_{\alpha=1}^{3} p_{i\,\alpha}^{\;2}, \tag{3.26}$$

since $\mathbf{p}_i^{\,2} = p_{i\,1}^{\;2} + p_{i\,2}^{\;2} + p_{i\,3}^{\;2}$, denoting the $(x,\, y,\, z)$ components by (1, 2, 3), respectively. The above sum contains 3N square terms. For $E =$ constant, Eq. (3.26) describes the locus of a sphere of radius $R(E) = (2\,m\,E)^{1/2}$ in the $3\,N$-dimensional space of the momentum components. Hence, $\chi(E)$ is proportional to the volume of momentum phase-space contained in the spherical shell lying between the sphere of radius $R(E)$ and that of slightly larger radius $R(E + \delta E)$. This volume is proportional to the *area* of the inner sphere multiplied by $\delta R \equiv R(E+\delta E) - R(E)$. Since the area varies like $R^{\,3N-1}$, and $\delta R \propto \delta E/E^{\,1/2}$, we have

$$\chi(E) \propto R^{\,3N-1}/E^{\,1/2} \propto E^{\,3N/2-1}. \tag{3.27}$$

Combining this result with (3.24) yields

$$\Omega(E,V) = B\,V^N E^{\,3N/2}, \tag{3.28}$$

where B is a constant independent of V or E, and we have also made use of $N \gg 1$. Note that, since the number of degrees of freedom of the system is $f = 3\,N$, the above relation can be very approximately written

$$\Omega(E,V) \propto V^f E^f. \tag{3.29}$$

In other words, the density of states varies like the *extensive* macroscopic parameters of the system raised to the power of the number of degrees of freedom. An extensive parameter is one which scales with the size of the system (*e.g.*, the volume). Since thermodynamic systems generally possess a very large number of degrees of freedom, this result implies that the density of states is an exceptionally rapidly increasing function of the energy and volume. This result, which turns out to be quite general, is very useful in statistical thermodynamics.

4 Heat and work

4.1 A brief history of heat and work

In 1789 the French scientist Antoine Lavoisier published a famous treatise on Chemistry which, amongst other things, demolished the then prevalent theory of combustion. This theory, known to history as the *phlogiston theory*, is so extraordinary stupid that it is not even worth describing. In place of phlogiston theory, Lavoisier proposed the first reasonably sensible scientific interpretation of heat. Lavoisier pictured heat as an invisible, tasteless, odourless, weightless fluid, which he called *calorific fluid*. He postulated that hot bodies contain more of this fluid than cold bodies. Furthermore, he suggested that the constituent particles of calorific fluid repel one another, causing heat to flow from hot to cold bodies when they are placed in thermal contact.

The modern interpretation of heat is, or course, somewhat different to Lavoisier's *calorific theory*. Nevertheless, there is an important subset of problems involving heat flow for which Lavoisier's approach is rather useful. These problems often crop up as examination questions. For example: "A clean dry copper calorimeter contains 100 grams of water at 30° degrees centigrade. A 10 gram block of copper heated to 60° centigrade is added. What is the final temperature of the mixture?". How do we approach this type of problem? Well, according to Lavoisier's theory, there is an analogy between heat flow and incompressible fluid flow under gravity. The same volume of liquid added to containers of different cross-sectional area fills them to different heights. If the volume is V, and the cross-sectional area is A, then the height is $h = V/A$. In a similar manner, the same quantity of heat added to different bodies causes them to rise to different temperatures. If Q is the heat and θ is the (absolute) temperature then $\theta = Q/C$, where the constant C is termed the *heat capacity*. [This is a somewhat oversimplified example. In general, the heat capacity is a function of temperature, so that $C = C(\theta)$.] Now, if two containers filled to different heights with a free flowing incompressible fluid are connected together at the bottom, via a small pipe, then fluid will flow under gravity, from one to the other, until the two heights are the same. The final height is easily calculated by equating the total fluid volume in the initial and final states. Thus,

$$h_1 A_1 + h_2 A_2 = h A_1 + h A_2, \tag{4.1}$$

giving

$$h = \frac{h_1 A_1 + h_2 A_2}{A_1 + A_2}. \tag{4.2}$$

Here, h_1 and h_2 are the initial heights in the two containers, A_1 and A_2 are the corresponding cross-sectional areas, and h is the final height. Likewise, if two bodies, initially at different temperatures, are brought into thermal contact then heat will flow, from one to the other, until the two temperatures are the same. The final temperature is calculated by equating the total heat in the initial and final states. Thus,

$$\theta_1 C_1 + \theta_2 C_2 = \theta C_1 + \theta C_2, \tag{4.3}$$

giving

$$\theta = \frac{\theta_1 C_1 + \theta_2 C_2}{C_1 + C_2}, \tag{4.4}$$

where the meaning of the various symbols should be self-evident.

The analogy between heat flow and fluid flow works because in Lavoisier's theory heat is a *conserved* quantity, just like the volume of an incompressible fluid. In fact, Lavoisier postulated that heat was an element. Note that atoms were thought to be indestructible before nuclear reactions were discovered, so the total amount of each element in the Universe was assumed to be a constant. If Lavoisier had cared to formulate a law of thermodynamics from his calorific theory then he would have said that the total amount of heat in the Universe was a constant.

In 1798 Benjamin Thompson, an Englishman who spent his early years in pre-revolutionary America, was minister for war and police in the German state of Bavaria. One of his jobs was to oversee the boring of cannons in the state arsenal. Thompson was struck by the enormous, and seemingly inexhaustible, amount of heat generated in this process. He simply could not understand where all this heat was coming from. According to Lavoisier's calorific theory, the heat must flow into the cannon from its immediate surroundings, which should, therefore, become colder. The flow should also eventually cease when all of the available heat has been extracted. In fact, Thompson observed that the surroundings of the cannon got hotter, not colder, and that the heating process continued unabated as long as the boring machine was operating. Thompson postulated that some of the mechanical work done on the cannon by the boring machine was being converted into heat. At the time, this was quite a revolutionary concept, and most people were not ready to accept it. This is somewhat surprising, since by the end of the eighteenth century the conversion of heat into work, by steam engines, was quite commonplace. Nevertheless, the conversion of work into heat did not gain broad acceptance until 1849, when an English physicist called James Prescott Joule published the results of a long and painstaking series of experiments. Joule confirmed that work could indeed be converted into heat. Moreover, he found that the same amount of work always generates the same quantity of heat. This is true regardless of the nature of the work (*e.g.*, mechanical, electrical, *etc*.). Joule was able to formulate what became known as the *work equivalent of heat*. Namely, that 1 newton meter of work is equivalent to 0.241 calories of heat. A calorie is the amount of heat required to raise the temperature of 1 gram of water by 1 degree centigrade. Nowadays, we measure both heat and work in the same units, so that one newton meter, or joule, of work is equivalent to one joule of heat.

In 1850, the German physicist Clausius correctly postulated that the essential conserved quantity is neither heat nor work, but some combination of the two which quickly became known as *energy*, from the Greek *energia* meaning “in work.” According to Clausius, the change in the internal energy of a macroscopic body can be written

$$\Delta E = Q - W, \tag{4.5}$$

where Q is the heat *absorbed* from the surroundings, and W is the work done *on* the surroundings. This relation is known as *the first law of thermodynamics*.

4.2 Macrostates and microstates

In describing a system made up of a great many particles, it is usually possible to specify some macroscopically measurable independent parameters $x_1, x_2, \cdots, x_n$

which affect the particles' equations of motion. These parameters are termed the *external parameters* the system. Examples of such parameters are the volume (this gets into the equations of motion because the potential energy becomes infinite when a particle strays outside the available volume) and any applied electric and magnetic fields. A *microstate* of the system is defined as a state for which the motions of the individual particles are completely specified (subject, of course, to the unavoidable limitations imposed by the uncertainty principle of quantum mechanics). In general, the overall energy of a given microstate r is a function of the external parameters:

$$E_r \equiv E_r(x_1, x_2, \cdots, x_n). \tag{4.6}$$

A *macrostate* of the system is defined by specifying the external parameters, and any other constraints to which the system is subject. For example, if we are dealing with an isolated system (*i.e.*, one that can neither exchange heat with nor do work on its surroundings) then the macrostate might be specified by giving the values of the volume and the constant total energy. For a many-particle system, there are generally a very great number of microstates which are consistent with a given macrostate.

4.3 The microscopic interpretation of heat and work

Consider a macroscopic system A which is known to be in a given macrostate. To be more exact, consider an ensemble of similar macroscopic systems A, where each system in the ensemble is in one of the many microstates consistent with the given macrostate. There are two fundamentally different ways in which the average energy of A can change due to interaction with its surroundings. If the external parameters of the system remain constant then the interaction is termed a purely *thermal* interaction. Any change in the average energy of the system is attributed to an exchange of *heat* with its environment. Thus,

$$\Delta\bar{E} = Q, \tag{4.7}$$

where Q is the heat absorbed by the system. On a microscopic level, the energies of the individual microstates are unaffected by the absorption of heat. In fact, it is the *distribution* of the systems in the ensemble over the various microstates which is modified.

Suppose that the system A is thermally insulated from its environment. This can be achieved by surrounding it by an *adiabatic* envelope (*i.e.*, an envelope fabricated out of a material which is a poor conductor of heat, such a fiber glass). Incidentally, the term adiabatic is derived from the Greek *adiabatos* which means “impassable.” In scientific terminology, an adiabatic process is one in which there is no exchange of heat. The system A is still capable of interacting with its environment via its external parameters. This type of interaction is termed *mechanical* interaction, and any change in the average energy of the system is attributed to work done on it by its surroundings. Thus,

$$\Delta\bar{E} = -W, \tag{4.8}$$

where W is the work done by the system on its environment. On a microscopic level, the energy of the system changes because the energies of the individual microstates are functions of the external parameters [see Eq. (4.6)]. Thus, if the external parameters are changed then, in general, the energies of all of the systems in the ensemble are modified (since each is in a specific microstate). Such a modification usually gives rise to a redistribution of the systems in the ensemble over the accessible microstates (without any heat exchange with the environment). Clearly, from a microscopic viewpoint, performing work on a macroscopic system is quite a complicated process. Nevertheless, macroscopic work is a quantity which can be readily measured experimentally. For instance, if the system A exerts a force $\mathbf{F}$ on its immediate surroundings, and the change in external parameters corresponds to a displacement $\mathbf{x}$ of the center of mass of the system, then the work done *by* A on its surroundings is simply

$$W = \mathbf{F}\cdot\mathbf{x} \tag{4.9}$$

i.e., the product of the force and the displacement along the line of action of the force. In a general interaction of the system A with its environment there is both heat exchange and work performed. We can write

$$Q \equiv \Delta\bar{E} + W, \tag{4.10}$$

which serves as the general definition of the absorbed heat Q (hence, the equivalence sign). The quantity Q is simply the change in the mean energy of the system which is not due to the modification of the external parameters. Note that the notion of a quantity of heat has no independent meaning apart from Eq. (4.10). The mean energy $\bar{E}$ and work performed W are both physical quantities which can be determined experimentally, whereas Q is merely a derived quantity.

4.4 Quasi-static processes

Consider the special case of an interaction of the system A with its surroundings which is carried out so slowly that A remains arbitrarily close to equilibrium at all times. Such a process is said to be *quasi-static* for the system A. In practice, a quasi-static process must be carried out on a time-scale which is much longer than the relaxation time of the system. Recall that the relaxation time is the typical time-scale for the system to return to equilibrium after being suddenly disturbed (see Sect. 3.5).

A finite quasi-static change can be built up out of many infinitesimal changes. The infinitesimal heat $đQ$ absorbed by the system when infinitesimal work $đW$ is done on its environment and its average energy changes by $d\bar{E}$ is given by

$$đQ \equiv d\bar{E} + đW. \tag{4.11}$$

The special symbols $đW$ and $đQ$ are introduced to emphasize that the work done and heat absorbed are infinitesimal quantities which do *not* correspond to the difference between two works or two heats. Instead, the work done and heat absorbed depend on the interaction *process* itself. Thus, it makes no sense to talk about the work in the system before and after the process, or the difference between these.

If the external parameters of the system have the values $x_1, \cdots, x_n$ then the energy of the system in a definite microstate r can be written

$$E_r = E_r(x_1, \cdots, x_n). \tag{4.12}$$

Hence, if the external parameters are changed by infinitesimal amounts, so that $x_\alpha \rightarrow x_\alpha + dx_\alpha$ for α in the range 1 to n, then the corresponding change in the energy of the microstate is

$$dE_r = \sum_{\alpha=1}^{n} \frac{\partial E_r}{\partial x_\alpha}\, dx_\alpha. \tag{4.13}$$

The work $đW$ done *by* the system when it remains in this particular state r is

$$đW_r = -dE_r = \sum_{\alpha=1}^{n} X_{\alpha\, r}\, dx_\alpha, \tag{4.14}$$

where

$$X_{\alpha\, r} \equiv -\frac{\partial E_r}{\partial x_\alpha} \tag{4.15}$$

is termed the *generalized force* (conjugate to the external parameter x_α) in the state r. Note that if x_α is a displacement then $X_{\alpha\, r}$ is an ordinary force.

Consider now an ensemble of systems. Provided that the external parameters of the system are changed quasi-statically, the generalized forces $X_{\alpha\, r}$ have well defined mean values which are calculable from the distribution of systems in the ensemble characteristic of the instantaneous macrostate. The macroscopic work $đW$ resulting from an infinitesimal quasi-static change of the external parameters is obtained by calculating the decrease in the mean energy resulting from the parameter change. Thus,

$$đW = \sum_{\alpha=1}^{n} \bar{X}_\alpha\, dx_\alpha, \tag{4.16}$$

where

$$\bar{X}_\alpha \equiv -\overline{\frac{\partial E_r}{\partial x_\alpha}} \tag{4.17}$$

is the *mean* generalized force conjugate to x_α. The mean value is calculated from the equilibrium distribution of systems in the ensemble corresponding to the external parameter values x_α. The macroscopic work W resulting from a finite quasi-static change of external parameters can be obtained by integrating Eq. (4.16).

The most well-known example of quasi-static work in thermodynamics is that done by pressure when the volume changes. For simplicity, suppose that the volume V is the only external parameter of any consequence. The work done in changing the volume from V to $V + dV$ is simply the product of the force and the displacement (along the line of action of the force). By definition, the mean equilibrium pressure $\bar{p}$ of a given macrostate is equal to the normal force per unit area acting on any surface element. Thus, the normal force acting on a surface element $d\mathbf{S}_i$ is $\bar{p}\ d\mathbf{S}_i$. Suppose that the surface element is subject to a displacement $d\mathbf{x}_i$. The work done by the element is $\bar{p}\ d\mathbf{S}_i \cdot d\mathbf{x}_i$. The total work done by the system is obtained by summing over all of the surface elements. Thus,

$$đW = \bar{p}\ dV, \tag{4.18}$$

where

$$dV = \sum_i d\mathbf{S}_i \cdot d\mathbf{x}_i \tag{4.19}$$

is the infinitesimal volume change due to the displacement of the surface. It follows from (4.17) that

$$\bar{p} = -\frac{\partial \bar{E}}{\partial V}, \tag{4.20}$$

so the mean pressure is the generalized force conjugate to the volume V.

Suppose that a quasi-static process is carried out in which the volume is changed from V_i to V_f. In general, the mean pressure is a function of the volume, so $\bar{p} = \bar{p}(V)$. It follows that the macroscopic work done by the system is given by

$$W_{if} = \int_{V_i}^{V_f} đW = \int_{V_i}^{V_f} \bar{p}(V)\, dV. \tag{4.21}$$

This quantity is just the "area under the curve" in a plot of $\bar{p}(V)$ versus V.

4.5 Exact and inexact differentials

In our investigation of heat and work we have come across various infinitesimal objects such as $d\bar{E}$ and $đW$. It is instructive to examine these infinitesimals more closely.

Consider the purely mathematical problem where $F(x, y)$ is some general function of two independent variables x and y. Consider the change in F in going from the point (x, y) in the x-y plane to the neighbouring point $(x + dx, y + dy)$. This is given by

$$dF = F(x + dx, y + dy) - F(x, y), \tag{4.22}$$

which can also be written

$$dF = X(x, y)\, dx + Y(x, y)\, dy, \tag{4.23}$$

where $X = \partial F/\partial x$ and $Y = \partial F/\partial y$. Clearly, dF is simply the infinitesimal difference between two adjacent values of the function F. This type of infinitesimal quantity is termed an *exact differential* to distinguish it from another type to be discussed presently. If we move in the x-y plane from an initial point $i \equiv (x_i, y_i)$ to a final point $f \equiv (x_f, y_f)$ then the corresponding change in F is given by

$$\Delta F = F_f - F_i = \int_i^f dF = \int_i^f (X\, dx + Y\, dy). \tag{4.24}$$

Note that since the difference on the left-hand side depends only on the initial and final points, the integral on the right-hand side can only depend on these points as well. In other words, the value of the integral is independent of the path taken in going from the initial to the final point. This is the distinguishing feature of an exact differential. Consider an integral taken around a closed circuit in the x-y plane. In this case, the initial and final points correspond to the same point, so the difference $F_f - F_i$ is clearly zero. It follows that the integral of an exact differential over a closed circuit is always zero:

$$\oint dF \equiv 0. \tag{4.25}$$

Of course, not every infinitesimal quantity is an exact differential. Consider the infinitesimal object

$$đG \equiv X'(x, y)\, dx + Y'(x, y)\, dz, \tag{4.26}$$

where X' and Y' are two general functions of x and y. It is easy to test whether or not an infinitesimal quantity is an exact differential. Consider the expression

(4.23). It is clear that since $X = \partial F/\partial x$ and $Y = \partial F/\partial y$ then

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x} = \frac{\partial^2 F}{\partial x \partial y}. \tag{4.27}$$

Thus, if

$$\frac{\partial X'}{\partial y} \neq \frac{\partial Y'}{\partial x} \tag{4.28}$$

(as is assumed to be the case), then $đG$ cannot be an exact differential, and is instead termed an *inexact differential*. The special symbol $đ$ is used to denote an inexact differential. Consider the integral of $đG$ over some path in the x-y plane. In general, it is not true that

$$\int_i^f đG = \int_i^f (X'\,dx + Y'\,dy) \tag{4.29}$$

is independent of the path taken between the initial and final points. This is the distinguishing feature of an inexact differential. In particular, the integral of an inexact differential around a closed circuit is not necessarily zero, so

$$\oint đG \neq 0. \tag{4.30}$$

Consider, for the moment, the solution of

$$đG = 0, \tag{4.31}$$

which reduces to the ordinary differential equation

$$\frac{dy}{dx} = -\frac{X'}{Y'}. \tag{4.32}$$

Since the right-hand side is a known function of x and y, the above equation defines a definite direction (*i.e.*, gradient) at each point in the x-y plane. The solution simply consists of drawing a system of curves in the x-y plane such that at any point the tangent to the curve is as specified in Eq. (4.32). This defines a set of curves which can be written $\sigma(x, y) = c$, where c is a labeling parameter. It follows that

$$\frac{d\sigma}{dx} \equiv \frac{\partial \sigma}{\partial x} + \frac{\partial \sigma}{\partial y}\frac{dy}{dx} = 0. \tag{4.33}$$

The elimination of dy/dx between Eqs. (4.32) and (4.33) yields

$$Y' \frac{\partial \sigma}{\partial x} = X' \frac{\partial \sigma}{\partial y} = \frac{X' Y'}{\tau}, \tag{4.34}$$

where $\tau(x, y)$ is function of x and y. The above equation could equally well be written

$$X' = \tau \frac{\partial \sigma}{\partial x}, \qquad Y' = \tau \frac{\partial \sigma}{\partial y}. \tag{4.35}$$

Inserting Eq. (4.35) into Eq. (4.26) gives

$$đG = \tau \left(\frac{\partial \sigma}{\partial x}\, dx + \frac{\partial \sigma}{\partial y}\, dy \right) = \tau\, d\sigma, \tag{4.36}$$

or

$$\frac{đG}{\tau} = d\sigma. \tag{4.37}$$

Thus, dividing the inexact differential $đG$ by τ yields the exact differential $d\sigma$. A factor τ which possesses this property is termed an *integrating factor*. Since the above analysis is quite general, it is clear that an inexact differential involving *two* independent variables always admits of an integrating factor. Note, however, this is not generally the case for inexact differentials involving more than two variables.

After this mathematical excursion, let us return to physical situation of interest. The macrostate of a macroscopic system can be specified by the values of the external parameters (*e.g.*, the volume) and the mean energy $\bar{E}$. This, in turn, fixes other parameters such as the mean pressure $\bar{p}$. Alternatively, we can specify the external parameters and the mean pressure, which fixes the mean energy. Quantities such as $d\bar{p}$ and $d\bar{E}$ are infinitesimal differences between well-defined quantities: *i.e.*, they are exact differentials. For example, $d\bar{E} = \bar{E}_f - \bar{E}_i$ is just the difference between the mean energy of the system in the final macrostate f and the initial macrostate i, in the limit where these two states are nearly the same. It follows that if the system is taken from an initial macrostate i to any final macrostate f the mean energy change is given by

$$\Delta\bar{E} = \bar{E}_f - \bar{E}_i = \int_i^f d\bar{E}. \tag{4.38}$$

However, since the mean energy is just a function of the macrostate under consideration, $\bar{E}_f$ and $\bar{E}_i$ depend only on the initial and final states, respectively. Thus, the integral $\int d\bar{E}$ depends only on the initial and final states, and not on the particular process used to get between them.

Consider, now, the infinitesimal work done by the system in going from some initial macrostate i to some neighbouring final macrostate f. In general, $đW = \sum \bar{X}_\alpha \, dx_\alpha$ is *not* the difference between two numbers referring to the properties of two neighbouring macrostates. Instead, it is merely an infinitesimal quantity characteristic of the process of going from state i to state f. In other words, the work $đW$ is in general an inexact differential. The total work done by the system in going from any macrostate i to some other macrostate f can be written as

$$W_{if} = \int_i^f đW, \tag{4.39}$$

where the integral represents the sum of the infinitesimal amounts of work $đW$ performed at each stage of the process. In general, the value of the integral *does* depend on the particular process used in going from macrostate i to macrostate f.

Recall that in going from macrostate i to macrostate f the change $\Delta\bar{E}$ *does not* depend on the process used whereas the work W, in general, *does*. Thus, it follows from the first law of thermodynamics, Eq. (4.10), that the heat Q, in general, also depends on the process used. It follows that

$$đQ \equiv d\bar{E} + đW \tag{4.40}$$

is an inexact differential. However, by analogy with the mathematical example discussed previously, there must exist some integrating factor, T, say, which converts the inexact differential $đQ$ into an exact differential. So,

$$\frac{đQ}{T} \equiv dS. \tag{4.41}$$

It will be interesting to find out what physical quantities correspond to the functions T and S.

Suppose that the system is thermally insulated, so that $Q = 0$. In this case, the first law of thermodynamics implies that

$$W_{if} = -\Delta\bar{E}. \tag{4.42}$$

Thus, in this special case, the work done depends only on the energy difference between in the initial and final states, and is independent of the process. In fact, when Clausius first formulated the first law in 1850 this is how he expressed it:

> If a thermally isolated system is brought from some initial to some final state then the work done by the system is independent of the process used.

If the external parameters of the system are kept fixed, so that no work is done, then $đW = 0$, Eq. (4.11) reduces to

$$đQ = d\bar{E}, \tag{4.43}$$

and $đQ$ becomes an exact differential. The amount of heat Q absorbed in going from one macrostate to another depends only on the mean energy difference between them, and is independent of the process used to effect the change. In this situation, heat is a conserved quantity, and acts very much like the invisible indestructible fluid of Lavoisier's calorific theory.

5 Statistical thermodynamics

5.1 Introduction

Let us briefly review the material which we have covered so far in this course. We started off by studying the mathematics of probability. We then used probabilistic reasoning to analyze the dynamics of many particle systems, a subject area known as *statistical mechanics*. Next, we explored the physics of heat and work, the study of which is termed *thermodynamics*. The final step in our investigation is to combine statistical mechanics with thermodynamics: in other words, to investigate heat and work via statistical arguments. This discipline is called *statistical thermodynamics*, and forms the central subject matter of this course. This section is devoted to the study of the fundamental concepts of statistical thermodynamics. The remaining sections will then explore the application and elucidation of these concepts.

5.2 Thermal interaction between macrosystems

Let us begin our investigation of statistical thermodynamics by examining a purely thermal interaction between two macroscopic systems, A and A', from a microscopic point of view. Suppose that the energies of these two systems are E and E', respectively. The external parameters are held fixed, so that A and A' cannot do work on one another. However, we assume that the systems are free to exchange heat energy (*i.e.*, they are in thermal contact). It is convenient to divide the energy scale into small subdivisions of width δE. The number of microstates of A consistent with a macrostate in which the energy lies in the range E to $E + \delta E$ is denoted $\Omega(E)$. Likewise, the number of microstates of A' consistent with a macrostate in which the energy lies between E' and $E' + \delta E$ is denoted $\Omega'(E')$.

The combined system $A^{(0)} = A + A'$ is assumed to be isolated (*i.e.*, it neither does work on nor exchanges heat with its surroundings). It follows from the first law of thermodynamics that the total energy $E^{(0)}$ is constant. When speaking of thermal contact between two *distinct* systems, we usually assume that the mutual interaction is sufficiently weak for the energies to be additive. Thus,

$$E + E' \simeq E^{(0)} = \text{constant}. \tag{5.1}$$

Of course, in the limit of zero interaction the energies are strictly additive. However, a small residual interaction is always required to enable the two systems to exchange heat energy and, thereby, eventually reach thermal equilibrium (see Sect. 3.4). In fact, if the interaction between A and A' is too strong for the energies to be additive then it makes little sense to consider each system in isolation, since the presence of one system clearly strongly perturbs the other, and *vice versa*. In this case, the smallest system which can realistically be examined in isolation is $A^{(0)}$.

According to Eq. (5.1), if the energy of A lies in the range E to $E+\delta E$ then the energy of A' must lie between $E^{(0)} - E - \delta E$ and $E^{(0)} - E$. Thus, the number of microstates accessible to each system is given by $\Omega(E)$ and $\Omega'(E^{(0)} - E)$, respectively. Since every possible state of A can be combined with every possible state of A' to form a distinct microstate, the total number of distinct states accessible to $A^{(0)}$ when the energy of A lies in the range E to $E + \delta E$ is

$$\Omega^{(0)} = \Omega(E)\,\Omega'(E^{(0)} - E). \tag{5.2}$$

Consider an ensemble of pairs of thermally interacting systems, A and A', which are left undisturbed for many relaxation times so that they can attain thermal equilibrium. The principle of equal *a priori* probabilities is applicable to this situation (see Sect. 3). According to this principle, the probability of occurrence of a given macrostate is proportional to the number of accessible microstates, since all microstates are equally likely. Thus, the probability that the system A has an energy lying in the range E to $E + \delta E$ can be written

$$P(E) = C\,\Omega(E)\,\Omega'(E^{(0)} - E), \tag{5.3}$$

where C is a constant which is independent of E.

We know, from Sect. 3.8, that the typical variation of the number of accessible states with energy is of the form

$$\Omega \propto E^{f}, \tag{5.4}$$

where f is the number of degrees of freedom. For a macroscopic system f is an exceedingly large number. It follows that the probability $P(E)$ in Eq. (5.3) is the product of an extremely rapidly increasing function of E and an extremely rapidly decreasing function of E. Hence, we would expect the probability to exhibit a very pronounced maximum at some particular value of the energy.

Let us Taylor expand the logarithm of $P(E)$ in the vicinity of its maximum value, which is assumed to occur at $E = \tilde{E}$. We expand the relatively slowly varying logarithm, rather than the function itself, because the latter varies so rapidly with the energy that the radius of convergence of its Taylor expansion is too small for this expansion to be of any practical use. The expansion of $\ln\Omega(E)$ yields

$$\ln\Omega(E) = \ln\Omega(\tilde{E}) + \beta(\tilde{E})\,\eta - \frac{1}{2}\,\lambda(\tilde{E})\,\eta^2 + \cdots, \tag{5.5}$$

where

$$\eta = E - \tilde{E}, \tag{5.6}$$

$$\beta = \frac{\partial \ln\Omega}{\partial E}, \tag{5.7}$$

$$\lambda = -\frac{\partial^2 \ln\Omega}{\partial E^2} = -\frac{\partial\beta}{\partial E}. \tag{5.8}$$

Now, since $E' = E^{(0)} - E$, we have

$$E' - \tilde{E}' = -(E - \tilde{E}) = -\eta. \tag{5.9}$$

It follows that

$$\ln\Omega'(E') = \ln\Omega'(\tilde{E}') + \beta'(\tilde{E}')\,(-\eta) - \frac{1}{2}\,\lambda'(\tilde{E}')\,(-\eta)^2 + \cdots, \tag{5.10}$$

where β' and λ' are defined in an analogous manner to the parameters β and λ. Equations (5.5) and (5.10) can be combined to give

$$\ln\,[\Omega(E)\,\Omega'(E')] = \ln\,[\Omega(\tilde{E})\,\Omega'(\tilde{E}')] + [\beta(\tilde{E}) - \beta'(\tilde{E}')]\,\eta - \frac{1}{2}\,[\lambda(\tilde{E}) + \lambda'(\tilde{E}')]\,\eta^2 + \cdots. \tag{5.11}$$

At the maximum of $\ln\,[\Omega(E)\,\Omega'(E')]$ the linear term in the Taylor expansion must vanish, so

$$\beta(\tilde{E}) = \beta'(\tilde{E}'), \tag{5.12}$$

which enables us to determine $\tilde{E}$. It follows that

$$\ln P(E) = \ln P(\tilde{E}) - \frac{1}{2}\,\lambda_0\,\eta^2, \tag{5.13}$$

or

$$P(E) = P(\tilde{E})\,\exp\left[-\frac{1}{2}\,\lambda_0\,(E-\tilde{E})^2\right], \tag{5.14}$$

where

$$\lambda_0 = \lambda(\tilde{E}) + \lambda'(\tilde{E}'). \tag{5.15}$$

Now, the parameter λ_0 must be positive, otherwise the probability $P(E)$ does not exhibit a pronounced maximum value: *i.e.*, the combined system $A^{(0)}$ does not possess a well-defined equilibrium state as, physically, we know it must. It is clear that $\lambda(\tilde{E})$ must also be positive, since we could always choose for A' a system with a negligible contribution to λ_0, in which case the constraint $\lambda_0 > 0$ would effectively correspond to $\lambda(\tilde{E}) > 0$. [A similar argument can be used to show that $\lambda'(\tilde{E}')$ must be positive.] The same conclusion also follows from the estimate $\Omega \propto E^f$, which implies that

$$\lambda(\tilde{E}) \sim \frac{f}{\tilde{E}^2} > 0. \tag{5.16}$$

According to Eq. (5.14), the probability distribution function $P(E)$ is a Gaussian. This is hardly surprising, since the central limit theorem ensures that the probability distribution for any macroscopic variable, such as E, is Gaussian in nature (see Sect. 2.10). It follows that the mean value of E corresponds to the situation of maximum probability (*i.e.*, the peak of the Gaussian curve), so that

$$\bar{E} = \tilde{E}. \tag{5.17}$$

The standard deviation of the distribution is

$$\Delta^* E = \lambda_0^{-1/2} \sim \frac{\bar{E}}{\sqrt{f}}, \tag{5.18}$$

where use has been made of Eq. (5.4) (assuming that system A makes the dominant contribution to λ_0). It follows that the fractional width of the probability distribution function is given by

$$\frac{\Delta^* E}{\bar{E}} \sim \frac{1}{\sqrt{f}}. \tag{5.19}$$

Hence, if A contains 1 mole of particles then $f \sim N_A \simeq 10^{24}$ and $\Delta^* E/\bar{E} \sim 10^{-12}$. Clearly, the probability distribution for E has an exceedingly sharp maximum. Experimental measurements of this energy will almost always yield the mean value, and the underlying statistical nature of the distribution may not be apparent.

5.3 Temperature

Suppose that the systems A and A' are initially thermally isolated from one another, with respective energies E_i and E_i'. (Since the energy of an isolated system cannot fluctuate, we do not have to bother with mean energies here.) If the two systems are subsequently placed in thermal contact, so that they are free to exchange heat energy, then, in general, the resulting state is an extremely improbable one [*i.e.*, $P(E_i)$ is much less than the peak probability]. The configuration will, therefore, tend to change in time until the two systems attain final mean energies $\bar{E}_f$ and $\bar{E}_f'$ which are such that

$$\beta_f = \beta_f', \tag{5.20}$$

where $\beta_f \equiv \beta(\bar{E}_f)$ and $\beta_f' \equiv \beta'(\bar{E}_f')$. This corresponds to the state of maximum probability (see Sect. 5.2). In the special case where the initial energies, E_i and E_i', lie very close to the final mean energies, $\bar{E}_f$ and $\bar{E}_f'$, respectively, there is no change in the two systems when they are brought into thermal contact, since the initial state already corresponds to a state of maximum probability.

It follows from energy conservation that

$$\bar{E}_f + \bar{E}_f' = E_i + E_i'. \tag{5.21}$$

The mean energy change in each system is simply the net heat absorbed, so that

$$Q \equiv \bar{E}_f - E_i, \tag{5.22}$$

$$Q' \equiv \bar{E}_f' - E_i'. \tag{5.23}$$

The conservation of energy then reduces to

$$Q + Q' = 0: \tag{5.24}$$

i.e., the heat given off by one system is equal to the heat absorbed by the other (in our notation absorbed heat is positive and emitted heat is negative).

It is clear that if the systems A and A' are suddenly brought into thermal contact then they will only exchange heat and evolve towards a new equilibrium state if the final state is more probable than the initial one. In other words, if

$$P(\bar{E}_f) > P(E_i), \tag{5.25}$$

or

$$\ln P(\bar{E}_f) > \ln P(E_i), \tag{5.26}$$

since the logarithm is a monotonic function. The above inequality can be written

$$\ln \Omega(\bar{E}_f) + \ln \Omega'(\bar{E}_f') > \ln \Omega(E_i) + \ln \Omega'(E_i'), \tag{5.27}$$

with the aid of Eq. (5.3). Taylor expansion to first order yields

$$\frac{\partial \ln \Omega(E_i)}{\partial E}\,(\bar{E}_f - E_i) + \frac{\partial \ln \Omega'(E_i')}{\partial E'}\,(\bar{E}_f' - E_i') > 0, \tag{5.28}$$

which finally gives

$$(\beta_i - \beta_i')\,Q > 0, \tag{5.29}$$

where $\beta_i \equiv \beta(E_i)$, $\beta_i' \equiv \beta'(E_i')$, and use has been made of Eq. (5.24).

It is clear, from the above, that the parameter β, defined

$$\beta = \frac{\partial \ln \Omega}{\partial E}, \tag{5.30}$$

has the following properties:

1. If two systems separately in equilibrium have the same value of β then the systems will remain in equilibrium when brought into thermal contact with one another.
2. If two systems separately in equilibrium have different values of β then the systems will not remain in equilibrium when brought into thermal contact with one another. Instead, the system with the *higher* value of β will *absorb* heat from the other system until the two β values are the same [see Eq. (5.29)].

Incidentally, a partial derivative is used in Eq. (5.30) because in a purely thermal interaction the external parameters of the system are held constant whilst the energy changes.

Let us define the dimensionless parameter T, such that

$$\frac{1}{k\,T} \equiv \beta \equiv \frac{\partial \ln \Omega}{\partial E}, \tag{5.31}$$

where k is a positive constant having the dimensions of energy. The parameter T is termed the *thermodynamic temperature*, and controls heat flow in much the same manner as a conventional temperature. Thus, if two isolated systems in equilibrium possess the same thermodynamic temperature then they will remain in equilibrium when brought into thermal contact. However, if the two systems have different thermodynamic temperatures then heat will flow from the system with the higher temperature (*i.e.*, the "hotter" system) to the system with the lower temperature until the temperatures of the two systems are the same. In addition, suppose that we have three systems A, B, and C. We know that if A and B remain in equilibrium when brought into thermal contact then their temperatures are the same, so that $T_A = T_B$. Similarly, if B and C remain in equilibrium when brought into thermal contact, then $T_B = T_C$. But, we can then conclude that $T_A = T_C$, so systems A and C will also remain in equilibrium when brought into thermal contact. Thus, we arrive at the following statement, which is sometimes called the *zeroth law of thermodynamics*:

> If two systems are separately in thermal equilibrium with a third system then they must also be in thermal equilibrium with one another.

The thermodynamic temperature of a macroscopic body, as defined in Eq. (5.31), depends only on the rate of change of the number of accessible microstates with the total energy. Thus, it is possible to define a thermodynamic temperature for systems with radically different microscopic structures (*e.g.*, matter and radiation). The thermodynamic, or *absolute*, scale of temperature is measured in degrees *kelvin*. The parameter k is chosen to make this temperature scale accord as much as possible with more conventional temperature scales. The choice

$$k = 1.381 \times 10^{-23} \text{ joules/kelvin}, \tag{5.32}$$

ensures that there are 100 degrees kelvin between the freezing and boiling points of water at atmospheric pressure (the two temperatures are 273.15 and 373.15 degrees kelvin, respectively). The above number is known as the *Boltzmann constant*. In fact, the Boltzmann constant is fixed by international convention so as to make the *triple point* of water (*i.e.*, the unique temperature at which the three phases of water co-exist in thermal equilibrium) exactly 273.16° K. Note that the zero of the thermodynamic scale, the so called *absolute zero* of temperature, does not correspond to the freezing point of water, but to some far more physically significant temperature which we shall discuss presently.

The familiar $\Omega \propto E^f$ scaling for translational degrees of freedom yields

$$k\,T \sim \frac{\bar{E}}{f}, \tag{5.33}$$

using Eq. (5.31), so $k\,T$ is a rough measure of the mean energy associated with each degree of freedom in the system. In fact, for a classical system (*i.e.*, one in which quantum effects are unimportant) it is possible to show that the mean energy associated with each degree of freedom is *exactly* $(1/2)\,k\,T$. This result, which is known as the *equipartition theorem*, will be discussed in more detail later on in this course.

The absolute temperature T is usually positive, since $\Omega(E)$ is ordinarily a very rapidly increasing function of energy. In fact, this is the case for all conventional systems where the kinetic energy of the particles is taken into account, because there is no upper bound on the possible energy of the system, and $\Omega(E)$ consequently increases roughly like E^f. It is, however, possible to envisage a situation in which we ignore the translational degrees of freedom of a system, and concentrate only on its *spin* degrees of freedom. In this case, there is an upper bound to the possible energy of the system (*i.e.*, all spins lined up anti-parallel to an applied magnetic field). Consequently, the total number of states available to the system is finite. In this situation, the density of spin states $\Omega_{\rm spin}(E)$ first increases with increasing energy, as in conventional systems, but then reaches a maximum and decreases again. Thus, it is possible to get absolute spin temperatures which are *negative*, as well as positive.

In Lavoisier's calorific theory, the basic mechanism which forces heat to flow from hot to cold bodies is the supposed mutual repulsion of the constituent particles of calorific fluid. In statistical mechanics, the explanation is far less contrived. Heat flow occurs because statistical systems tend to evolve towards their most probable states, subject to the imposed physical constraints. When two bodies at different temperatures are suddenly placed in thermal contact, the initial state corresponds to a spectacularly improbable state of the overall system. For systems containing of order 1 mole of particles, the only reasonably probable final equilibrium states are such that the two bodies differ in temperature by less than 1 part in 10^{12}. The evolution of the system towards these final states (*i.e.*, towards thermal equilibrium) is effectively driven by *probability*.

5.4 Mechanical interaction between macrosystems

Let us now examine a purely mechanical interaction between macrostates, where one or more of the external parameters is modified, but there is no exchange of heat energy. Consider, for the sake of simplicity, a situation where only one external parameter x of the system is free to vary. In general, the number of microstates accessible to the system when the overall energy lies between E and $E + \delta E$ depends on the particular value of x, so we can write $\Omega \equiv \Omega(E, x)$.

When x is changed by the amount dx, the energy $E_r(x)$ of a given microstate r changes by $(\partial E_r/\partial x)\,dx$. The number of states $\sigma(E, x)$ whose energy is changed from a value less than E to a value greater than E when the parameter changes from x to $x + dx$ is given by the number of microstates per unit energy range multiplied by the *average* shift in energy of the microstates. Hence,

$$\sigma(E, x) = \frac{\Omega(E, x)}{\delta E}\,\overline{\frac{\partial E_r}{\partial x}}\,dx, \tag{5.34}$$

where the mean value of $\partial E_r/\partial x$ is taken over all accessible microstates (*i.e.*, all states where the energy lies between E and $E + \delta E$ and the external parameter takes the value x). The above equation can also be written

$$\sigma(E, x) = -\frac{\Omega(E, x)}{\delta E}\,\bar{X}\,dx, \tag{5.35}$$

where

$$\bar{X}(E, x) = -\overline{\frac{\partial E_r}{\partial x}} \tag{5.36}$$

is the mean generalized force conjugate to the external parameter x (see Sect. 4.4).

Consider the total number of microstates between E and $E + \delta E$. When the external parameter changes from x to $x + dx$, the number of states in this energy range changes by $(\partial\Omega/\partial x)\, dx$. This change is due to the difference between the number of states which *enter* the range because their energy is changed from a value less than E to one greater than E and the number which *leave* because their energy is changed from a value less than $E + \delta E$ to one greater than $E + \delta E$. In symbols,

$$\frac{\partial\Omega(E, x)}{\partial x}\, dx = \sigma(E) - \sigma(E + \delta E) \simeq -\frac{\partial\sigma}{\partial E}\,\delta E, \tag{5.37}$$

which yields

$$\frac{\partial\Omega}{\partial x} = \frac{\partial(\Omega\bar{X})}{\partial E}, \tag{5.38}$$

where use has been made of Eq. (5.35). Dividing both sides by Ω gives

$$\frac{\partial\ln\Omega}{\partial x} = \frac{\partial\ln\Omega}{\partial E}\,\bar{X} + \frac{\partial\bar{X}}{\partial E}. \tag{5.39}$$

However, according to the usual estimate $\Omega \propto E^f$, the first term on the right-hand side is of order $(f/\bar{E})\,\bar{X}$, whereas the second term is only of order $\bar{X}/\bar{E}$. Clearly, for a macroscopic system with many degrees of freedom, the second term is utterly negligible, so we have

$$\frac{\partial\ln\Omega}{\partial x} = \frac{\partial\ln\Omega}{\partial E}\,\bar{X} = \beta\,\bar{X}. \tag{5.40}$$

When there are several external parameters $x_1, \cdots, x_n$, so that $\Omega \equiv \Omega(E, x_1, \cdots, x_n)$, the above derivation is valid for each parameter taken in isolation. Thus,

$$\frac{\partial\ln\Omega}{\partial x_\alpha} = \beta\,\bar{X}_\alpha, \tag{5.41}$$

where $\bar{X}_\alpha$ is the mean generalized force conjugate to the parameter x_α.

5.5 General interaction between macrosystems

Consider two systems, A and A', which can interact by exchanging heat energy *and* doing work on one another. Let the system A have energy E and adjustable external parameters $x_1, \cdots, x_n$. Likewise, let the system A' have energy E' and adjustable external parameters $x_1', \cdots, x_n'$. The combined system $A^{(0)} = A + A'$ is assumed to be isolated. It follows from the first law of thermodynamics that

$$E + E' = E^{(0)} = \text{constant}. \tag{5.42}$$

Thus, the energy E' of system A' is determined once the energy E of system A is given, and *vice versa*. In fact, E' could be regarded as a function of E. Furthermore, if the two systems can interact mechanically then, in general, the parameters x' are some function of the parameters x. As a simple example, if the two systems are separated by a movable partition in an enclosure of fixed volume $V^{(0)}$, then

$$V + V' = V^{(0)} = \text{constant}, \tag{5.43}$$

where V and V' are the volumes of systems A and A', respectively.

The total number of microstates accessible to $A^{(0)}$ is clearly a function of E and the parameters x_α (where α runs from 1 to n), so $\Omega^{(0)} \equiv \Omega^{(0)}(E, x_1, \cdots, x_n)$. We have already demonstrated (in Sect. 5.2) that $\Omega^{(0)}$ exhibits a very pronounced maximum at one particular value of the energy $E = \tilde{E}$ when E is varied but the external parameters are held constant. This behaviour comes about because of the very strong,

$$\Omega \propto E^f, \tag{5.44}$$

increase in the number of accessible microstates of A (or A') with energy. However, according to Sect. 3.8, the number of accessible microstates exhibits a similar strong increase with the volume, which is a typical external parameter, so that

$$\Omega \propto V^f. \tag{5.45}$$

It follows that the variation of $\Omega^{(0)}$ with a typical parameter x_α, when all the other parameters and the energy are held constant, also exhibits a very sharp maximum at some particular value $x_\alpha = \tilde{x}_\alpha$. The equilibrium situation corresponds to the configuration of maximum probability, in which virtually all systems $A^{(0)}$ in the ensemble have values of E and x_α very close to $\tilde{E}$ and $\tilde{x}_\alpha$. The mean values of these quantities are thus given by $\bar{E} = \tilde{E}$ and $\bar{x}_\alpha = \tilde{x}_\alpha$.

Consider a quasi-static process in which the system A is brought from an equilibrium state described by $\bar{E}$ and $\bar{x}_\alpha$ to an infinitesimally different equilibrium state described by $\bar{E} + d\bar{E}$ and $\bar{x}_\alpha + d\bar{x}_\alpha$. Let us calculate the resultant change in the number of microstates accessible to A. Since $\Omega \equiv \Omega(E, x_1, \cdots, x_n)$, the change in $\ln\Omega$ follows from standard mathematics:

$$d\ln\Omega = \frac{\partial\ln\Omega}{\partial E}\,d\bar{E} + \sum_{\alpha=1}^{n}\frac{\partial\ln\Omega}{\partial x_\alpha}\,d\bar{x}_\alpha. \tag{5.46}$$

However, we have previously demonstrated that

$$\beta = \frac{\partial\ln\Omega}{\partial E}, \qquad \beta\,\bar{X}_\alpha = \frac{\partial\ln\Omega}{\partial x_\alpha} \tag{5.47}$$

[from Eqs. (5.30) and (5.41)], so Eq. (5.46) can be written

$$d\ln\Omega = \beta\left(d\bar{E} + \sum_\alpha \bar{X}_\alpha\,d\bar{x}_\alpha\right). \tag{5.48}$$

Note that the temperature parameter β and the mean conjugate forces $\bar{X}_\alpha$ are only well-defined for *equilibrium* states. This is why we are only considering quasi-static changes in which the two systems are always arbitrarily close to equilibrium.

Let us rewrite Eq. (5.48) in terms of the thermodynamic temperature T, using the relation $\beta \equiv 1/k\,T$. We obtain

$$dS = \left(d\bar{E} + \sum_\alpha \bar{X}_\alpha\,d\bar{x}_\alpha\right)\Big/\,T, \tag{5.49}$$

where

$$S = k\ln\Omega. \tag{5.50}$$

Equation (5.49) is a differential relation which enables us to calculate the quantity S as a function of the mean energy $\bar{E}$ and the mean external parameters $\bar{x}_\alpha$, assuming that we can calculate the temperature T and mean conjugate forces $\bar{X}_\alpha$ for each equilibrium state. The function $S(\bar{E},\bar{x}_\alpha)$ is termed the *entropy* of system A. The word entropy is derived from the Greek *en* + *trepien*, which means "in change." The reason for this etymology will become apparent presently. It can be seen from Eq. (5.50) that the entropy is merely a parameterization of the number of accessible microstates. Hence, according to statistical mechanics, $S(\bar{E},\bar{x}_\alpha)$ is essentially a measure of the relative *probability* of a state characterized by values of the mean energy and mean external parameters $\bar{E}$ and $\bar{x}_\alpha$, respectively.

According to Eq. (4.16), the net amount of work performed during a quasi-static change is given by

$$đW = \sum_\alpha \bar{X}_\alpha\, d\bar{x}_\alpha. \tag{5.51}$$

It follows from Eq. (5.49) that

$$dS = \frac{d\bar{E} + đW}{T} = \frac{đQ}{T}. \tag{5.52}$$

Thus, the thermodynamic temperature T is the *integrating factor* for the first law of thermodynamics,

$$đQ = d\bar{E} + đW, \tag{5.53}$$

which converts the *inexact* differential $đQ$ into the *exact* differential dS (see Sect. 4.5). It follows that the entropy difference between any two macrostates i and f can be written

$$S_f - S_i = \int_i^f dS = \int_i^f \frac{đQ}{T}, \tag{5.54}$$

where the integral is evaluated for any process through which the system is brought *quasi-statically* via a sequence of near-equilibrium configurations from its initial to its final macrostate. The process has to be quasi-static because the temperature T, which appears in the integrand, is only well-defined for an equilibrium state. Since the left-hand side of the above equation only depends on the initial and final states, it follows that the integral on the right-hand side is independent of the particular sequence of quasi-static changes used to get from i to f. Thus, $\int_i^f đQ/T$ is independent of the process (provided that it is quasi-static).

All of the concepts which we have encountered up to now in this course, such as temperature, heat, energy, volume, pressure, *etc*., have been fairly familiar to us from other branches of Physics. However, entropy, which turns out to be of crucial importance in thermodynamics, is something quite new. Let us consider the following questions. What does the entropy of a system actually signify? What use is the concept of entropy?

5.6 Entropy

Consider an isolated system whose energy is known to lie in a narrow range. Let Ω be the number of accessible microstates. According to the principle of equal *a priori* probabilities, the system is equally likely to be found in any one of these states when it is in thermal equilibrium. The accessible states are just that set of microstates which are consistent with the macroscopic constraints imposed on the system. These constraints can usually be quantified by specifying the values of some parameters $y_1, \cdots, y_n$ which characterize the macrostate. Note that these parameters are not necessarily external: *e.g.*, we could specify either the volume (an external parameter) or the mean pressure (the mean force conjugate to the volume). The number of accessible states is clearly a function of the chosen parameters, so we can write $\Omega \equiv \Omega(y_1, \cdots, y_n)$ for the number of microstates consistent with a macrostate in which the general parameter y_α lies in the range y_α to $y_\alpha + dy_\alpha$.

Suppose that we start from a system in thermal equilibrium. According to statistical mechanics, each of the Ω_i, say, accessible states are equally likely. Let us now remove, or relax, some of the constraints imposed on the system. Clearly, all of the microstates formally accessible to the system are still accessible, but many additional states will, in general, become accessible. Thus, removing or relaxing constraints can only have the effect of *increasing*, or possibly leaving unchanged, the number of microstates accessible to the system. If the final number of accessible states is Ω_f, then we can write

$$\Omega_f \geq \Omega_i. \tag{5.55}$$

Immediately after the constraints are relaxed, the systems in the ensemble are not in any of the microstates from which they were previously excluded. So the systems only occupy a fraction

$$P_i = \frac{\Omega_i}{\Omega_f} \tag{5.56}$$

of the Ω_f states now accessible to them. This is clearly not a equilibrium situation. Indeed, if $\Omega_f \gg \Omega_i$ then the configuration in which the systems are only distributed over the original Ω_i states is an extremely unlikely one. In fact, its probability of occurrence is given by Eq. (5.56). According to the H theorem (see Sect. 3.4), the ensemble will evolve in time until a more probable final state is reached in which the systems are evenly distributed over the Ω_f available states.

As a simple example, consider a system consisting of a box divided into two regions of equal volume. Suppose that, initially, one region is filled with gas and the other is empty. The constraint imposed on the system is, thus, that the coordinates of all of the molecules must lie within the filled region. In other words, the volume accessible to the system is $V = V_i$, where V_i is half the volume of the box. The constraints imposed on the system can be relaxed by removing the partition and allowing gas to flow into both regions. The volume accessible to the gas is now $V = V_f = 2\,V_i$. Immediately after the partition is removed, the system is in an extremely improbable state. We know, from Sect. 3.8, that at constant energy the variation of the number of accessible states of an ideal gas with the volume is

$$\Omega \propto V^N, \tag{5.57}$$

where N is the number of particles. Thus, the probability of observing the state immediately after the partition is removed in an ensemble of equilibrium systems with volume $V = V_f$ is

$$P_i = \frac{\Omega_i}{\Omega_f} = \left(\frac{V_i}{V_f}\right)^N = \left(\frac{1}{2}\right)^N. \tag{5.58}$$

If the box contains of order 1 mole of molecules then $N \sim 10^{24}$ and this probability is *fantastically* small:

$$P_i \sim \exp\left(-10^{24}\right). \tag{5.59}$$

Clearly, the system will evolve towards a more probable state.

This discussion can also be phrased in terms of the parameters $y_1, \cdots, y_n$ of the system. Suppose that a constraint is removed. For instance, one of the parameters, y, say, which originally had the value $y = y_i$, is now allowed to vary. According to statistical mechanics, all states accessible to the system are equally likely. So, the probability $P(y)$ of finding the system in equilibrium with the parameter in the range y to $y + \delta y$ is just proportional to the number of microstates in this interval: *i.e.*,

$$P(y) \propto \Omega(y). \tag{5.60}$$

Usually, $\Omega(y)$ has a very pronounced maximum at some particular value $\tilde{y}$ (see Sect. 5.2). This means that practically all systems in the final equilibrium ensemble have values of y close to $\tilde{y}$. Thus, if $y_i \neq \tilde{y}$ initially then the parameter y will change until it attains a final value close to $\tilde{y}$, where Ω is maximum. This discussion can be summed up in a single phrase:

> If some of the constraints of an isolated system are removed then the parameters of the system tend to readjust themselves in such a way that
>
> $$\Omega(y_1, \cdots, y_n) \rightarrow \text{maximum}. \tag{5.61}$$

Suppose that the final equilibrium state has been reached, so that the systems in the ensemble are uniformly distributed over the Ω_f accessible final states. If the original constraints are reimposed then the systems in the ensemble still occupy these Ω_f states with equal probability. Thus, if $\Omega_f > \Omega_i$, simply restoring the constraints does not restore the initial situation. Once the systems are randomly distributed over the Ω_f states they cannot be expected to spontaneously move out of some of these states and occupy a more restricted class of states merely in response to the reimposition of a constraint. The initial condition can also not be restored by removing further constraints. This could only lead to even more states becoming accessible to the system.

Suppose that some process occurs in which an isolated system goes from some initial configuration to some final configuration. If the final configuration is such that the imposition or removal of constraints cannot *by itself* restore the initial condition then the process is deemed *irreversible*. On the other hand, if it is such that the imposition or removal of constraints *can* restore the initial condition then the process is deemed *reversible*. From what we have already said, an irreversible process is clearly one in which the removal of constraints leads to a situation where $\Omega_{\rm f} > \Omega_{\rm i}$. A reversible process corresponds to the special case where the removal of constraints does not change the number of accessible states, so that $\Omega_{\rm f} = \Omega_{\rm i}$. In this situation, the systems remain distributed with equal probability over these states irrespective of whether the constraints are imposed or not.

Our *microscopic* definition of irreversibility is in accordance with the *macroscopic* definition discussed in Sect. 3.6. Recall that on a macroscopic level an irreversible process is one which "looks unphysical" when viewed in reverse. On a microscopic level it is clearly plausible that a system should spontaneously evolve from an improbable to a probable configuration in response to the relaxation of some constraint. However, it is quite clearly implausible that a system should ever spontaneously evolve from a probable to an improbable configuration. Let us consider our example again. If a gas is initially restricted to one half of a box, via a partition, then the flow of gas from one side of the box to the other when the partition is removed is an irreversible process. This process is irreversible on a microscopic level because the initial configuration cannot be recovered by simply replacing the partition. It is irreversible on a macroscopic level because it is obviously unphysical for the molecules of a gas to spontaneously distribute themselves in such a manner that they only occupy half of the available volume.

It is actually possible to *quantify* irreversibility. In other words, in addition to stating that a given process is irreversible, we can also give some indication of how irreversible it is. The parameter which measures irreversibility is just the number of accessible states Ω. Thus, if Ω for an isolated system spontaneously increases then the process is irreversible, the degree of irreversibility being proportional to the amount of the increase. If Ω stays the same then the process is reversible. Of course, it is unphysical for Ω to ever spontaneously decrease. In symbols, we can write

$$\Omega_{\rm f} - \Omega_{\rm i} \equiv \Delta\Omega \geq 0, \tag{5.62}$$

for any physical process operating on an isolated system. In practice, Ω itself is a rather unwieldy parameter with which to measure irreversibility. For instance, in the previous example, where an ideal gas doubles in volume (at constant energy) due to the removal of a partition, the fractional increase in Ω is

$$\frac{\Omega_{\rm f}}{\Omega_{\rm i}} \simeq 10^{\,2\,\nu\times 10^{23}}, \tag{5.63}$$

where ν is the number of moles. This is an extremely large number! It is far more convenient to measure irreversibility in terms of $\ln\Omega$. If Eq. (5.62) is true then it is certainly also true that

$$\ln\Omega_f - \ln\Omega_i \equiv \Delta\ln\Omega \geq 0 \tag{5.64}$$

for any physical process operating on an isolated system. The increase in $\ln\Omega$ when an ideal gas doubles in volume (at constant energy) is

$$\ln\Omega_f - \ln\Omega_i = \nu\, N_A\, \ln 2, \tag{5.65}$$

where $N_A = 6\times 10^{23}$. This is a far more manageable number! Since we usually deal with particles by the mole in laboratory physics, it makes sense to premultiply our measure of irreversibility by a number of order $1/N_A$. For historical reasons, the number which is generally used for this purpose is the Boltzmann constant k, which can be written

$$k = \frac{R}{N_A} \quad \text{joules/kelvin}, \tag{5.66}$$

where

$$R = 8.3143 \quad \text{joules/kelvin/mole} \tag{5.67}$$

is the ideal gas constant which appears in the well-known equation of state for an ideal gas, $P\,V = \nu\,R\,T$. Thus, the final form for our measure of irreversibility is

$$S = k\, \ln\Omega. \tag{5.68}$$

This quantity is termed "entropy", and is measured in joules per degree kelvin. The increase in entropy when an ideal gas doubles in volume (at constant energy) is

$$S_f - S_i = \nu\, R\, \ln 2, \tag{5.69}$$

which is order unity for laboratory scale systems (*i.e.*, those containing about one mole of particles). The essential irreversibility of macroscopic phenomena can be summed up as follows:

$$S_f - S_i \equiv \Delta S \geq 0, \tag{5.70}$$

for a process acting on an isolated system [this is equivalent to Eqs. (5.61), (5.62), and (5.64)]. Thus, the *entropy of an isolated system tends to increase* *with time and can never decrease*. This proposition is known as the *second law of thermodynamics*.

One way of thinking of the number of accessible states Ω is that it is a measure of the *disorder* associated with a macrostate. For a system exhibiting a high degree of order we would expect a strong correlation between the motions of the individual particles. For instance, in a fluid there might be a strong tendency for the particles to move in one particular direction, giving rise to an ordered flow of the system in that direction. On the other hand, for a system exhibiting a low degree of order we expect far less correlation between the motions of individual particles. It follows that, all other things being equal, an ordered system is more constrained than a disordered system, since the former is excluded from microstates in which there is not a strong correlation between individual particle motions, whereas the latter is not. Another way of saying this is that an ordered system has less accessible microstates than a corresponding disordered system. Thus, entropy is effectively a measure of the *disorder* in a system (the disorder increases with S). With this interpretation, the second law of thermodynamics reduces to the statement that isolated systems tend to become more disordered with time, and can never become more ordered.

Note that the second law of thermodynamics only applies to *isolated* systems. The entropy of a non-isolated system *can* decrease. For instance, if a gas expands (at constant energy) to twice its initial volume after the removal of a partition, we can subsequently recompress the gas to its original volume. The energy of the gas will increase because of the work done on it during compression, but if we absorb some heat from the gas then we can restore it to its initial state. Clearly, in restoring the gas to its original state, we have restored its original entropy. This appears to violate the second law of thermodynamics because the entropy should have increased in what is obviously an irreversible process (just try to make a gas spontaneously occupy half of its original volume!). However, if we consider a new system consisting of the gas plus the compression and heat absorption machinery, then it is still true that the entropy of this system (which is assumed to be isolated) must increase in time. Thus, the entropy of the gas is only kept the same at the expense of increasing the entropy of the rest of the system, and the total entropy is increased. If we consider the system of everything in the

Universe, which is certainly an isolated system since there is nothing outside it with which it could interact, then the second law of thermodynamics becomes:

> The disorder of the Universe tends to increase with time and can never decrease.

An irreversible process is clearly one which *increases* the disorder of the Universe, whereas a reversible process neither increases nor decreases disorder. This definition is in accordance with our previous definition of an irreversible process as one which "does not look right" when viewed backwards. One easy way of viewing macroscopic events in reverse is to film them, and then play the film backwards through a projector. There is a famous passage in the novel "Slaughterhouse 5," by Kurt Vonnegut, in which the hero, Billy Pilgrim, views a propaganda film of an American World War II bombing raid on a German city in reverse. This is what the film appeared to show:

> "American planes, full of holes and wounded men and corpses took off backwards from an airfield in England. Over France, a few German fighter planes flew at them backwards, sucked bullets and shell fragments from some of the planes and crewmen. They did the same for wrecked American bombers on the ground, and those planes flew up backwards and joined the formation.
>
> The formation flew backwards over a German city that was in flames. The bombers opened their bomb bay doors, exerted a miraculous magnetism which shrunk the fires, gathered them into cylindrical steel containers, and lifted the containers into the bellies of the planes. The containers were stored neatly in racks. The Germans had miraculous devices of their own, which were long steel tubes. They used them to suck more fragments from the crewmen and planes. But there were still a few wounded Americans, though, and some of the bombers were in bad repair. Over France, though, German fighters came up again, made everything and everybody as good as new."

Vonnegut's point, I suppose, is that the morality of actions is inverted when you view them in reverse.

What is there about this passage which strikes us as surreal and fantastic? What is there that immediately tells us that the events shown in the film could never happen in reality? It is not so much that the planes appear to fly backwards and the bombs appear to fall upwards. After all, given a little ingenuity and a sufficiently good pilot, it is probably possible to fly a plane backwards. Likewise, if we were to throw a bomb up in the air with just the right velocity we could, in principle, fix it so that the velocity of the bomb matched that of a passing bomber when their paths intersected. Certainly, if you had never seen a plane before it would not be obvious which way around it was supposed to fly. However, certain events are depicted in the film, "miraculous" events in Vonnegut's words, which would immediately strike us as the wrong way around even if we had never seen them before. For instance, the film might show thousands of white hot bits of shrapnel approach each other from all directions at great velocity, compressing an explosive gas in the process, which slows them down such that when they meet they fit together exactly to form a metal cylinder enclosing the gases and moving upwards at great velocity. What strikes us as completely implausible about this event is the spontaneous transition from the disordered motion of the gases and metal fragments to the ordered upward motion of the bomb.

5.7 Properties of entropy

Entropy, as we have defined it, has some dependence on the resolution δE to which the energy of macrostates is measured. Recall that $\Omega(E)$ is the number of accessible microstates with energy in the range E to $E + \delta E$. Suppose that we choose a new resolution $\delta^* E$ and define a new density of states $\Omega^*(E)$ which is the number of states with energy in the range E to $E + \delta^* E$. It can easily be seen that

$$\Omega^*(E) = \frac{\delta^* E}{\delta E}\,\Omega(E). \tag{5.71}$$

It follows that the new entropy $S^* = k \ln \Omega^*$ is related to the previous entropy $S = k \ln \Omega$ via

$$S^* = S + k \ln \frac{\delta^* E}{\delta E}. \tag{5.72}$$

Now, our usual estimate that $\Omega \sim E^f$ gives $S \sim k f$, where f is the number of degrees of freedom. It follows that even if $\delta^* E$ were to differ from δE by of order f (*i.e.*, twenty four orders of magnitude), which is virtually inconceivable, the second term on the right-hand side of the above equation is still only of order $k \ln f$, which is utterly negligible compared to $k f$. It follows that

$$S^* = S \tag{5.73}$$

to an excellent approximation, so our definition of entropy is completely insensitive to the resolution to which we measure energy (or any other macroscopic parameter).

Note that, like the temperature, the entropy of a macrostate is only well-defined if the macrostate is in equilibrium. The crucial point is that it only makes sense to talk about the number of accessible states if the systems in the ensemble are given sufficient time to thoroughly explore all of the possible microstates consistent with the known macroscopic constraints. In other words, we can only be sure that a given microstate is inaccessible when the systems in the ensemble have had ample opportunity to move into it, and yet have not done so. Note that for an equilibrium state, the entropy is just as well-defined as more familiar quantities such as the temperature and the mean pressure.

Consider, again, two systems A and A' which are in thermal contact but can do no work on one another (see Sect. 5.2). Let E and E' be the energies of the two systems, and $\Omega(E)$ and $\Omega'(E')$ the respective densities of states. Furthermore, let $E^{(0)}$ be the conserved energy of the system as a whole and $\Omega^{(0)}$ the corresponding density of states. We have from Eq. (5.2) that

$$\Omega^{(0)}(E) = \Omega(E)\,\Omega'(E'), \tag{5.74}$$

where $E' = E^{(0)} - E$. In other words, the number of states accessible to the whole system is the product of the numbers of states accessible to each subsystem, since every microstate of A can be combined with every microstate of A' to form a distinct microstate of the whole system. We know, from Sect. 5.2, that in equilibrium the mean energy of A takes the value $\bar{E} = \tilde{E}$ for which $\Omega^{(0)}(E)$ is maximum, and the *temperatures* of A and A' are equal. The distribution of E around the mean value is of order $\Delta^* E = \tilde{E}/\sqrt{f}$, where f is the number of degrees of freedom. It follows that the total number of accessible microstates is approximately the number of states which lie within $\Delta^* E$ of $\tilde{E}$. Thus,

$$\Omega^{(0)}_{\text{tot}} \simeq \frac{\Omega^{(0)}(\tilde{E})}{\delta E}\,\Delta^* E. \tag{5.75}$$

The entropy of the whole system is given by

$$S^{(0)} = k \ln \Omega^{(0)}_{\text{tot}} = k \ln \Omega^{(0)}(\tilde{E}) + k \ln \frac{\Delta^* E}{\delta E}. \tag{5.76}$$

According to our usual estimate, $\Omega \sim E^f$, the first term on the right-hand side is of order kf whereas the second term is of order $k \ln(\tilde{E}/\sqrt{f}\,\delta E)$. Any reasonable choice for the energy subdivision δE should be greater than $\tilde{E}/f$, otherwise there would be less than one microstate per subdivision. It follows that the second term is less than or of order $k \ln f$, which is utterly negligible compared to kf. Thus,

$$S^{(0)} = k \ln \Omega^{(0)}(\tilde{E}) = k \ln[\Omega(\tilde{E})\,\Omega(\tilde{E}')] = k \ln \Omega(\tilde{E}) + k \ln \Omega'(\tilde{E}') \tag{5.77}$$

to an excellent approximation, giving

$$S^{(0)} = S(\tilde{E}) + S'(\tilde{E}'). \tag{5.78}$$

It can be seen that the probability distribution for $\Omega^{(0)}(E)$ is so strongly peaked around its maximum value that, for the purpose of calculating the entropy, the total number of states is equal to the maximum number of states [*i.e.*, $\Omega^{(0)}_{\text{tot}} \sim \Omega^{(0)}(\tilde{E})$]. One consequence of this is that the entropy has the simple additive property shown in Eq. (5.78). Thus, the total entropy of two thermally interacting systems in equilibrium is the sum of the entropies of each system in isolation.

5.8 Uses of entropy

We have defined a new function called entropy, denoted S, which parameterizes the amount of disorder in a macroscopic system. The entropy of an equilibrium macrostate is related to the number of accessible microstates Ω via

$$S = k \ln \Omega. \tag{5.79}$$

On a macroscopic level, the increase in entropy due to a quasi-static change in which an infinitesimal amount of heat $đQ$ is absorbed by the system is given by

$$dS = \frac{đQ}{T}, \tag{5.80}$$

where T is the absolute temperature of the system. The second law of thermodynamics states that the entropy of an isolated system can never spontaneously decrease. Let us now briefly examine some consequences of these results.

Consider two bodies, A and A', which are in thermal contact but can do no work on one another. We know what is supposed to happen here. Heat flows from the hotter to the colder of the two bodies until their temperatures are the same. Consider a quasi-static exchange of heat between the two bodies. According to the first law of thermodynamics, if an infinitesimal amount of heat $đQ$ is absorbed by A then infinitesimal heat $đQ' = -đQ$ is absorbed by A'. The increase in the entropy of system A is $dS = đQ/T$ and the corresponding increase in the entropy of A' is $dS' = đQ'/T'$. Here, T and T' are the temperatures of the two systems, respectively. Note that $đQ$ is assumed to the sufficiently small that the heat transfer does not substantially modify the temperatures of either system. The change in entropy of the whole system is

$$dS^{(0)} = dS + dS' = \left(\frac{1}{T} - \frac{1}{T'}\right) đQ. \tag{5.81}$$

This change must be positive or zero, according to the second law of thermodynamics, so $dS^{(0)} \geq 0$. It follows that $đQ$ is positive (*i.e.*, heat flows from A' to A) when $T' > T$, and *vice versa*. The spontaneous flow of heat only ceases when $T = T'$. Thus, the direction of spontaneous heat flow is a consequence of the second law of thermodynamics. Note that the spontaneous flow of heat between bodies at different temperatures is always an irreversible process which increases the entropy, or disorder, of the Universe.

Consider, now, the slightly more complicated situation in which the two systems can exchange heat and also do work on one another via a movable partition. Suppose that the total volume is invariant, so that

$$V^{(0)} = V + V' = \text{constant}, \tag{5.82}$$

where V and V' are the volumes of A and A', respectively. Consider a quasi-static change in which system A absorbs an infinitesimal amount of heat $đQ$ and its volume simultaneously increases by an infinitesimal amount dV. The infinitesimal amount of work done by system A is $đW = \bar{p}\,dV$ (see Sect. 4.4), where $\bar{p}$ is the mean pressure of A. According to the first law of thermodynamics,

$$đQ = dE + đW = dE + \bar{p}\,dV, \tag{5.83}$$

where dE is the change in the internal energy of A. Since $dS = đQ/T$, the increase in entropy of system A is written

$$dS = \frac{dE + \bar{p}\,dV}{T}. \tag{5.84}$$

Likewise, the increase in entropy of system A' is given by

$$dS' = \frac{dE' + \bar{p}'\,dV'}{T'}. \tag{5.85}$$

According to Eq. (5.84),

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V, \tag{5.86}$$

$$\frac{\bar{p}}{T} = \left(\frac{\partial S}{\partial V}\right)_E, \tag{5.87}$$

where the subscripts are to remind us what is held constant in the partial derivatives. We can write a similar pair of equations for the system A'.

The overall system is assumed to be isolated, so conservation of energy gives $dE + dE' = 0$. Furthermore, Eq. (5.82) implies that $dV + dV' = 0$. It follows that the total change in entropy is given by

$$dS^{(0)} = dS + dS' = \left(\frac{1}{T} - \frac{1}{T'}\right) dE + \left(\frac{\bar{p}}{T} - \frac{\bar{p}'}{T'}\right) dV. \tag{5.88}$$

The equilibrium state is the most probable state (see Sect. 5.2). According to statistical mechanics, this is equivalent to the state with the largest number of accessible microstates. Finally, Eq. (5.79) implies that this is the maximum entropy state. The system can never spontaneously leave a maximum entropy state, since this would imply a spontaneous reduction in entropy, which is forbidden by the second law of thermodynamics. A maximum or minimum entropy state must satisfy $dS^{(0)} = 0$ for arbitrary small variations of the energy and external parameters. It follows from Eq. (5.88) that

$$T = T', \tag{5.89}$$

$$\bar{p} = \bar{p}', \tag{5.90}$$

for such a state. This corresponds to a *maximum* entropy state (*i.e.*, an equilibrium state) provided

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_V < 0, \tag{5.91}$$

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_E < 0, \tag{5.92}$$

with a similar pair of inequalities for system A'. The usual estimate $\Omega \propto E^f V^f$, giving $S = k f \ln E + k f \ln V + \cdots$, ensures that the above inequalities are satisfied in conventional macroscopic systems. In the maximum entropy state the systems A and A' have equal temperatures (*i.e.*, they are in thermal equilibrium) and equal pressures (*i.e.*, they are in mechanical equilibrium). The second law of thermodynamics implies that the two interacting systems will evolve towards this state, and will then remain in it indefinitely (if left undisturbed).

5.9 Entropy and quantum mechanics

The entropy of a system is defined in terms of the number Ω of accessible microstates consistent with an overall energy in the range E to $E + \delta E$ via

$$S = k \ln \Omega. \tag{5.93}$$

We have already demonstrated that this definition is utterly insensitive to the resolution δE to which the macroscopic energy is measured (see Sect. 5.7). In classical mechanics, if a system possesses f degrees of freedom then phase-space is conventionally subdivided into cells of arbitrarily chosen volume $h_0^{\,f}$ (see Sect. 3.2).

The number of accessible microstates is equivalent to the number of these cells in the volume of phase-space consistent with an overall energy of the system lying in the range E to $E + \delta E$. Thus,

$$\Omega = \frac{1}{h_0^{\,f}} \int \cdots \int dq_1 \cdots dq_f \, dp_1 \cdots dp_f, \tag{5.94}$$

giving

$$S = k \ln \left(\int \cdots \int dq_1 \cdots dq_f \, dp_1 \cdots dp_f \right) - k f \ln h_0. \tag{5.95}$$

Thus, in classical mechanics the *entropy is undetermined to an arbitrary additive constant* which depends on the size of the cells in phase-space. In fact, S increases as the cell size decreases. The second law of thermodynamics is only concerned with *changes* in entropy, and is, therefore, unaffected by an additive constant. Likewise, macroscopic thermodynamical quantities, such as the temperature and pressure, which can be expressed as partial derivatives of the entropy with respect to various macroscopic parameters [see Eqs. (5.86) and (5.87)] are unaffected by such a constant. So, in classical mechanics the entropy is rather like a gravitational potential: it is undetermined to an additive constant, but this does not affect any physical laws.

The non-unique value of the entropy comes about because there is no limit to the precision to which the state of a classical system can be specified. In other words, the cell size h_0 can be made arbitrarily small, which corresponds to specifying the particle coordinates and momenta to arbitrary accuracy. However, in quantum mechanics the uncertainty principle sets a definite limit to how accurately the particle coordinates and momenta can be specified. In general,

$$\delta q_i \, \delta p_i \geq h, \tag{5.96}$$

where p_i is the momentum conjugate to the generalized coordinate q_i, and δq_i, δp_i are the uncertainties in these quantities, respectively. In fact, in quantum mechanics the number of accessible quantum states with the overall energy in the range E to $E + \delta E$ is completely determined. This implies that, in reality, the entropy of a system has a unique and unambiguous value. Quantum mechanics can often be "mocked up" in classical mechanics by setting the cell size in phase-space equal to Planck's constant, so that $h_0 = h$. This automatically enforces the most restrictive form of the uncertainty principle, $\delta q_i\,\delta p_i = \hbar$. In many systems, the substitution $h_0 \to \hbar$ in Eq. (5.95) gives the same, unique value for S as that obtained from a full quantum mechanical calculation.

Consider a simple quantum mechanical system consisting of N non-interacting spinless particles of mass m confined in a cubic box of dimension L. The energy levels of the ith particle are given by

$$e_i = \frac{\hbar^2 \pi^2}{2\,m\,L^2}\left(n_{i1}^{\,2} + n_{i2}^{\,2} + n_{i3}^{\,2}\right), \tag{5.97}$$

where n_{i1}, n_{i2}, and n_{i3} are three (positive) quantum numbers. The overall energy of the system is the sum of the energies of the individual particles, so that for a general state r

$$E_r = \sum_{i=1}^{N} e_i. \tag{5.98}$$

The overall state of the system is completely specified by $3N$ quantum numbers, so the number of degrees of freedom is $f = 3\,N$. The classical limit corresponds to the situation where all of the quantum numbers are much greater than unity. In this limit, the number of accessible states varies with energy according to our usual estimate $\Omega \propto E^f$. The lowest possible energy state of the system, the so-called ground-state, corresponds to the situation where all quantum numbers take their lowest possible value, unity. Thus, the ground-state energy E_0 is given by

$$E_0 = \frac{f\,\hbar^2 \pi^2}{2\,m\,L^2}. \tag{5.99}$$

There is only one accessible microstate at the ground-state energy (*i.e.*, that where all quantum numbers are unity), so by our usual definition of entropy

$$S(E_0) = k \ln 1 = 0. \tag{5.100}$$

In other words, there is no disorder in the system when all the particles are in their ground-states.

Clearly, as the energy approaches the ground-state energy, the number of accessible states becomes far less than the usual classical estimate E^f. This is true for all quantum mechanical systems. In general, the number of microstates varies roughly like

$$\Omega(E) \sim 1 + C\,(E - E_0)^f, \tag{5.101}$$

where C is a positive constant. According to Eq. (5.31), the temperature varies approximately like

$$T \sim \frac{E - E_0}{k\,f}, \tag{5.102}$$

provided $\Omega \gg 1$. Thus, as the absolute temperature of a system approaches zero, the internal energy approaches a limiting value E_0 (the quantum mechanical ground-state energy), and the entropy approaches the limiting value *zero*. This proposition is known as *the third law of thermodynamics*.

At low temperatures, great care must be taken to ensure that equilibrium thermodynamical arguments are applicable, since the rate of attaining equilibrium may be very slow. Another difficulty arises when dealing with a system in which the atoms possess nuclear spins. Typically, when such a system is brought to a very low temperature the entropy associated with the degrees of freedom not involving nuclear spins becomes negligible. Nevertheless, the number of microstates Ω_s corresponding to the possible nuclear spin orientations may be very large. Indeed, it may be just as large as the number of states at room temperature. The reason for this is that nuclear magnetic moments are extremely small, and, therefore, have extremely weak mutual interactions. Thus, it only takes a tiny amount of heat energy in the system to completely randomize the spin orientations. Typically, a temperature as small as 10^{-3} degrees kelvin above absolute zero is sufficient to randomize the spins.

Suppose that the system consists of N atoms of spin $1/2$. Each spin can have two possible orientations. If there is enough residual heat energy in the system to randomize the spins then each orientation is equally likely. If follows that there are $\Omega_s = 2^N$ accessible spin states. The entropy associated with these states is $S_0 = k \ln \Omega_s = \nu\, R\, \ln 2$. Below some critical temperature, T_0, the interaction between the nuclear spins becomes significant, and the system settles down in some unique quantum mechanical ground-state (*e.g.*, with all spins aligned). In this situation, $S \rightarrow 0$, in accordance with the third law of thermodynamics. However, for temperatures which are small, but not small enough to "freeze out" the nuclear spin degrees of freedom, the entropy approaches a limiting value S_0 which depends only on the kinds of atomic nuclei in the system. This limiting value is independent of the spatial arrangement of the atoms, or the interactions between them. Thus, for most practical purposes the third law of thermodynamics can be written

$$\text{as } T \rightarrow 0_+, \quad S \rightarrow S_0, \tag{5.103}$$

where 0_+ denotes a temperature which is very close to absolute zero, but still much larger than T_0. This modification of the third law is useful because it can be applied at temperatures which are not prohibitively low.

5.10 The laws of thermodynamics

We have now come to the end of our investigation of the fundamental postulates of classical and statistical thermodynamics. The remainder of this course is devoted to the application of the ideas we have just discussed to various situations of interest in Physics. Before we proceed, however, it is useful to summarize the results of our investigations. Our summary takes the form of a number of general statements regarding macroscopic variables which are usually referred to as the *laws of thermodynamics*:

> **Zeroth Law:** If two systems are separately in thermal equilibrium with a third system then they must be in equilibrium with one another (see Sect. 5.3).
>
> **First Law:** The change in internal energy of a system in going from one macrostate to another is the difference between the net heat absorbed by the system from its surroundings and the net work done by the system on its surroundings (see Sect. 4.1).
>
> **Second Law:** The entropy of an isolated system can never spontaneously decrease (see Sect. 5.6).
>
> **Third Law:** In the limit as the absolute temperature tends to zero the entropy also tends to zero (see Sect. 5.9).

6 Classical thermodynamics

6.1 Introduction

We have learned that macroscopic quantities such as energy, temperature, and pressure are, in fact, statistical in nature: *i.e.*, in equilibrium they exhibit random fluctuations about some mean value. If we were to plot out the probability distribution for the energy, say, of a system in thermal equilibrium with its surroundings we would obtain a Gaussian with a very small fractional width. In fact, we expect

$$\frac{\Delta^* E}{\overline{E}} \sim \frac{1}{\sqrt{f}}, \tag{6.1}$$

where the number of degrees of freedom f is about 10^{24} for laboratory scale systems. This means that the statistical fluctuations of macroscopic quantities about their mean values are typically only about 1 in 10^{12}.

Since the statistical fluctuations of equilibrium quantities are so small, we can neglect them to an excellent approximation, and replace macroscopic quantities, such as energy, temperature, and pressure, by their *mean* values. So, $p \rightarrow \bar{p}$, and $T \rightarrow \overline{T}$, *etc.* In the following discussion, we shall drop the overbars altogether, so that p should be understood to represent the mean pressure $\bar{p}$, *etc.* This prescription, which is the essence of classical thermodynamics, is equivalent to replacing all statistically varying quantities by their most probable values.

Although there are formally four laws of thermodynamics (*i.e.*, the zeroth to the third), the zeroth law is really a consequence of the second law, and the third law is actually only important at temperatures close to absolute zero. So, for most purposes, the two laws which really matter are the first law and the second law. For an infinitesimal process, the first law is written

$$đQ = dE + đW, \tag{6.2}$$

where dE is the change in internal energy of the system, $đQ$ is the heat *absorbed* by the system, and $đW$ is the work done *by* the system on its surroundings. Note that this is just a convention. We could equally well write the first law in terms of the heat *emitted* by the system or the work done *on* the system. It does not really matter, as long as we are consistent in our definitions.

The second law of thermodynamics implies that

$$đQ = T\,dS, \tag{6.3}$$

for a *quasi-static* process, where T is the thermodynamic temperature, and dS is the change in entropy of the system. Furthermore, for systems in which the only external parameter is the volume (*i.e.*, gases), the work done on the environment is

$$đW = p\,dV, \tag{6.4}$$

where p is the pressure, and dV is the change in volume. Thus, it follows from the first and second laws of thermodynamics that

$$T\,dS = dE + p\,dV. \tag{6.5}$$

6.2 The equation of state of an ideal gas

Let us start our discussion by considering the simplest possible macroscopic system: *i.e.*, an ideal gas. All of the thermodynamic properties of an ideal gas are summed up in its equation of state, which determines the relationship between its pressure, volume, and temperature. Unfortunately, classical thermodynamics is unable to tell us what this equation of state is from first principles. In fact, classical thermodynamics cannot tell us anything from first principles. We always have to provide some information to begin with before classical thermodynamics can generate any new results. This initial information may come from statistical physics (*i.e.*, from our knowledge of the microscopic structure of the system under consideration), but, more usually, it is entirely empirical in nature (*i.e.*, it is the result of experiments). Of course, the ideal gas law was first discovered empirically by Robert Boyle, but, nowadays, we can justify it from statistical arguments. Recall (from Sect. 3.8), that the number of accessible states of a monotonic ideal gas varies like

$$\Omega \propto V^N \chi(E), \tag{6.6}$$

where N is the number of atoms, and $\chi(E)$ depends only on the energy of the gas (and is independent of the volume). We obtained this result by integrating over the volume of accessible phase-space. Since the energy of an ideal gas is independent of the particle coordinates (because there are no interatomic forces), the integrals over the coordinates just reduced to N simultaneous volume integrals, giving the V^N factor in the above expression. The integrals over the particle momenta were more complicated, but were clearly completely independent of V, giving the $\chi(E)$ factor in the above expression. Now, we have a statistical rule which tells us that

$$X_\alpha = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial x_\alpha} \tag{6.7}$$

[see Eq. (5.41)], where X_α is the mean force conjugate to the external parameter x_α (*i.e.*, $đW = \sum_\alpha X_\alpha dx_\alpha$), and $\beta = 1/kT$. For an ideal gas, the only external parameter is the volume, and its conjugate force is the pressure (since $đW = p\,dV$). So, we can write

$$p = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial V}. \tag{6.8}$$

If we simply apply this rule to Eq. (6.6), we obtain

$$p = \frac{N\,k\,T}{V}. \tag{6.9}$$

However, $N = \nu\,N_A$, where ν is the number of moles, and N_A is Avagadro's number. Also, $k\,N_A = R$, where R is the ideal gas constant. This allows us to write the equation of state in its usual form

$$p\,V = \nu\,R\,T. \tag{6.10}$$

The above derivation of the ideal gas equation of state is rather elegant. It is certainly far easier to obtain the equation of state in this manner than to treat the atoms which make up the gas as little billiard balls which continually bounce of the walls of a container. The latter derivation is difficult to perform correctly because it is necessary to average over all possible directions of atomic motion. It is clear, from the above derivation, that the crucial element needed to obtain the ideal gas equation of state is the absence of interatomic forces. This automatically gives rise to a variation of the number of accessible states with E and V of the form (6.6), which, in turn, implies the ideal gas law. So, the ideal gas law should also apply to polyatomic gases with no interatomic forces. Polyatomic gases are more complicated that monatomic gases because the molecules can rotate and vibrate, giving rise to extra degrees of freedom, in addition to the translational degrees of freedom of a monatomic gas. In other words, $\chi(E)$, in Eq. (6.6), becomes a lot more complicated in polyatomic gases. However, as long as there are no interatomic forces, the volume dependence of Ω is still V^N, and the ideal gas law should still hold true. In fact, we shall discover that the extra degrees of freedom of polyatomic gases manifest themselves by increasing the specific heat capacity.

There is one other conclusion we can draw from Eq. (6.6). The statistical definition of temperature is [Eq. (5.31)]

$$\frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E}. \tag{6.11}$$

It follows that

$$\frac{1}{kT} = \frac{\partial \ln \chi}{\partial E}. \tag{6.12}$$

We can see that since χ is a function of the energy, but *not* the volume, then the temperature must be a function of the energy, but not the volume. We can turn this around and write

$$E = E(T). \tag{6.13}$$

In other words, the internal energy of an ideal gas depends only on the temperature of the gas, and is independent of the volume. This is pretty obvious, since if there are no interatomic forces then increasing the volume, which effectively increases the mean separation between molecules, is not going to affect the molecular energies in any way. Hence, the energy of the whole gas is unaffected.

The volume independence of the internal energy can also be obtained directly from the ideal gas equation of state. The internal energy of a gas can be considered as a general function of the temperature and volume, so

$$E = E(T, V). \tag{6.14}$$

It follows from mathematics that

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV, \tag{6.15}$$

where the subscript V reminds us that the first partial derivative is taken at constant volume, and the subscript T reminds us that the second partial derivative is taken at constant temperature. Thermodynamics tells us that for a quasi-static change of parameters

$$T\,dS = dE + p\,dV. \tag{6.16}$$

The ideal gas law can be used to express the pressure in term of the volume and the temperature in the above expression. Thus,

$$dS = \frac{1}{T}\,dE + \frac{\nu\,R}{V}\,dV. \tag{6.17}$$

Using Eq. (6.15), this becomes

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu\,R}{V}\right] dV. \tag{6.18}$$

However, dS is the exact differential of a well-defined state function, S. This means that we can consider the entropy to be a function of temperature and volume. Thus, $S = S(T, V)$, and mathematics immediately tells us that

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV. \tag{6.19}$$

The above expression is true for all small values of dT and dV, so a comparison with Eq. (6.18) gives

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V, \tag{6.20}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu\,R}{V}. \tag{6.21}$$

One well-known property of partial differentials is the equality of second derivatives, irrespective of the order of differentiation, so

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}. \tag{6.22}$$

This implies that

$$\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial S}{\partial V}\right)_T. \tag{6.23}$$

The above expression can be combined with Eqs. (6.20) and (6.21) to give

$$\frac{1}{T}\left(\frac{\partial^2 E}{\partial V \partial T}\right) = \left[-\frac{1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial^2 E}{\partial T \partial V}\right)\right]. \tag{6.24}$$

Since second derivatives are equivalent, irrespective of the order of differentiation, the above relation reduces to

$$\left(\frac{\partial E}{\partial V}\right)_T = 0, \tag{6.25}$$

which implies that the internal energy is independent of the volume for any gas obeying the ideal equation of state. This result was confirmed experimentally by James Joule in the middle of the nineteenth century.

6.3 Heat capacity or specific heat

Suppose that a body absorbs an amount of heat ΔQ and its temperature consequently rises by ΔT. The usual definition of the heat capacity, or *specific heat*, of the body is

$$C = \frac{\Delta Q}{\Delta T}. \tag{6.26}$$

If the body consists of ν moles of some substance then the *molar specific heat* (*i.e.*, the specific heat of one mole of this substance) is defined

$$c = \frac{1}{\nu}\frac{\Delta Q}{\Delta T}. \tag{6.27}$$

In writing the above expressions, we have tacitly assumed that the specific heat of a body is independent of its temperature. In general, this is not true. We can overcome this problem by only allowing the body in question to absorb a very small amount of heat, so that its temperature only rises slightly, and its specific heat remains approximately constant. In the limit as the amount of absorbed heat becomes infinitesimal, we obtain

$$c = \frac{1}{\nu}\frac{đQ}{dT}. \tag{6.28}$$

In classical thermodynamics, it is usual to define two specific heats. Firstly, the molar specific heat at constant volume, denoted

$$c_V = \frac{1}{\nu}\left(\frac{đQ}{dT}\right)_V, \tag{6.29}$$

and, secondly, the molar specific heat at constant pressure, denoted

$$c_p = \frac{1}{\nu}\left(\frac{đQ}{dT}\right)_p. \tag{6.30}$$

Consider the molar specific heat at constant volume of an ideal gas. Since $dV = 0$, no work is done by the gas, and the first law of thermodynamics reduces to

$$đQ = dE. \tag{6.31}$$

It follows from Eq. (6.29) that

$$c_V = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V. \tag{6.32}$$

Now, for an ideal gas the internal energy is volume independent. Thus, the above expression implies that the specific heat at constant volume is also volume independent. Since E is a function only of T, we can write

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT. \tag{6.33}$$

The previous two expressions can be combined to give

$$dE = \nu\, c_V\, dT \tag{6.34}$$

for an *ideal* gas.

Let us now consider the molar specific heat at constant pressure of an ideal gas. In general, if the pressure is kept constant then the volume changes, and so the gas does work on its environment. According to the first law of thermodynamics,

$$đQ = dE + p\, dV = \nu\, c_V\, dT + p\, dV. \tag{6.35}$$

The equation of state of an ideal gas tells us that if the volume changes by dV, the temperature changes by dT, and the pressure remains constant, then

$$p\,dV = \nu R\,dT. \tag{6.36}$$

The previous two equations can be combined to give

$$đQ = \nu\,c_V\,dT + \nu R\,dT. \tag{6.37}$$

Now, by definition

$$c_p = \frac{1}{\nu}\left(\frac{đQ}{dT}\right)_p, \tag{6.38}$$

so we obtain

$$c_p = c_V + R \tag{6.39}$$

for an ideal gas. This is a very famous result. Note that at constant volume all of the heat absorbed by the gas goes into increasing its internal energy, and, hence, its temperature, whereas at constant pressure some of the absorbed heat is used to do work on the environment as the volume increases. This means that, in the latter case, less heat is available to increase the temperature of the gas. Thus, we expect the specific heat at constant pressure to exceed that at constant volume, as indicated by the above formula.

The ratio of the two specific heats c_p/c_V is conventionally denoted γ. We have

$$\gamma \equiv \frac{c_p}{c_V} = 1 + \frac{R}{c_V} \tag{6.40}$$

for an ideal gas. In fact, γ is very easy to measure because the speed of sound in an ideal gas is written

$$c_s = \sqrt{\frac{\gamma\,p}{\rho}}, \tag{6.41}$$

where ρ is the density. Table 2 lists some experimental measurements of c_V and γ for common gases. The extent of the agreement between γ calculated from Eq. (6.40) and the experimental γ is quite remarkable.

Gas	Symbol	c_V (experiment)	γ (experiment)	γ (theory)
Helium	He	12.5	1.666	1.666
Argon	Ar	12.5	1.666	1.666
Nitrogen	N_2	20.6	1.405	1.407
Oxygen	O_2	21.1	1.396	1.397
Carbon Dioxide	CO_2	28.2	1.302	1.298
Ethane	C_2H_6	39.3	1.220	1.214

Table 2: *Specific heats of common gases in joules/mole/deg. (at 15°C and 1 atm.) From Reif.*

6.4 Calculation of specific heats

Now that we know the relationship between the specific heats at constant volume and constant pressure for an ideal gas, it would be nice if we could calculate either one of these quantities from first principles. Classical thermodynamics cannot help us here. However, it is quite easy to calculate the specific heat at constant volume using our knowledge of statistical physics. Recall, that the variation of the number of accessible states of an ideal gas with energy and volume is written

$$\Omega(E, V) \propto V^N \chi(E). \tag{6.42}$$

For the specific case of a *monatomic* ideal gas, we worked out a more exact expression for Ω in Sect. 3.8: *i.e.*,

$$\Omega(E, V) = B\, V^N E^{3N/2}, \tag{6.43}$$

where B is a constant independent of the energy and volume. It follows that

$$\ln \Omega = \ln B + N \ln V + \frac{3N}{2} \ln E. \tag{6.44}$$

The temperature is given by

$$\frac{1}{k\,T} = \frac{\partial \ln \Omega}{\partial E} = \frac{3N}{2} \frac{1}{E}, \tag{6.45}$$

so

$$E = \frac{3}{2} N\, k\, T. \tag{6.46}$$

Since, $N = \nu\, N_A$, and $N_A\, k = R$, we can rewrite the above expression as

$$E = \frac{3}{2}\nu\, R\, T, \tag{6.47}$$

where $R = 8.3143$ joules/mole/deg. is the ideal gas constant. The above formula tells us exactly how the internal energy of a monatomic ideal gas depends on its temperature.

The molar specific heat at constant volume of a monatomic ideal gas is clearly

$$c_V = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}R. \tag{6.48}$$

This has the numerical value

$$c_V = 12.47 \text{ joules/mole/deg.} \tag{6.49}$$

Furthermore, we have

$$c_p = c_V + R = \frac{5}{2}R, \tag{6.50}$$

and

$$\gamma \equiv \frac{c_p}{c_V} = \frac{5}{3} = 1.667. \tag{6.51}$$

We can see from the previous table that these predictions are borne out pretty well for the monatomic gases Helium and Argon. Note that the specific heats of polyatomic gases are larger than those of monatomic gases. This is because polyatomic molecules can rotate around their centres of mass, as well as translate, so polyatomic gases can store energy in the rotational, as well as the translational, energy states of their constituent particles. We shall analyze this effect in greater detail later on in this course.

6.5 Isothermal and adiabatic expansion

Suppose that the temperature of an ideal gas is held constant by keeping the gas in thermal contact with a heat reservoir. If the gas is allowed to expand quasi-statically under these so called *isothermal* conditions then the ideal equation of state tells us that

$$p\, V = \text{constant.} \tag{6.52}$$

This is usually called the *isothermal gas law*.

Suppose, now, that the gas is thermally isolated from its surroundings. If the gas is allowed to expand quasi-statically under these so called *adiabatic* conditions then it does work on its environment, and, hence, its internal energy is reduced, and its temperature changes. Let us work out the relationship between the pressure and volume of the gas during adiabatic expansion.

According to the first law of thermodynamics,

$$đQ = \nu\, c_V\, dT + p\, dV = 0, \tag{6.53}$$

in an adiabatic process (in which no heat is absorbed). The ideal gas equation of state can be differentiated, yielding

$$p\, dV + V\, dp = \nu\, R\, dT. \tag{6.54}$$

The temperature increment dT can be eliminated between the above two expressions to give

$$0 = \frac{c_V}{R}(p\, dV + V\, dp) + p\, dV = \left(\frac{c_V}{R} + 1\right) p\, dV + \frac{c_V}{R} V\, dp, \tag{6.55}$$

which reduces to

$$(c_V + R)\, p\, dV + c_V\, V\, dp = 0. \tag{6.56}$$

Dividing through by $c_V\, p\, V$ yields

$$\gamma\, \frac{dV}{V} + \frac{dp}{p} = 0, \tag{6.57}$$

where

$$\gamma \equiv \frac{c_p}{c_V} = \frac{c_V + R}{c_V}. \tag{6.58}$$

It turns out that c_V is a very slowly varying function of temperature in most gases. So, it is always a fairly good approximation to treat the ratio of specific heats γ as a constant, at least over a limited temperature range. If γ is constant then we can integrate Eq. (6.57) to give

$$\gamma \ln V + \ln p = \text{constant}, \tag{6.59}$$

or

$$p\,V^{\gamma} = \text{constant}. \tag{6.60}$$

This is the famous *adiabatic gas law*. It is very easy to obtain similar relationships between V and T and p and T during adiabatic expansion or contraction. Since $p = \nu\,R\,T/V$, the above formula also implies that

$$T\,V^{\gamma-1} = \text{constant}, \tag{6.61}$$

and

$$p^{\,1-\gamma}\,T^{\gamma} = \text{constant}. \tag{6.62}$$

Equations (6.60)–(6.62) are all completely equivalent.

6.6 Hydrostatic equilibrium of the atmosphere

The gas which we are most familiar with in everyday life is, of course, the Earth's atmosphere. In fact, we can use the isothermal and adiabatic gas laws to explain most of the observable features of the atmosphere.

Let us, first of all, consider the hydrostatic equilibrium of the atmosphere. Consider a thin vertical slice of the atmosphere of cross-sectional area A which starts at height z above ground level and extends to height $z + dz$. The upwards force exerted on this slice from the gas below is $p(z)\,A$, where $p(z)$ is the pressure at height z. Likewise, the downward force exerted by the gas above the slice is $p(z+dz)\,A$. The net upward force is clearly $[p(z)-p(z+dz)]A$. In equilibrium, this upward force must be balanced by the downward force due to the weight of the slice: this is $\rho\,A\,dz\,g$, where ρ is the density of the gas, and g is the acceleration due to gravity. In follows that the force balance condition can be written

$$[p(z) - p(z + dz)]A = \rho\,A\,dz\,g, \tag{6.63}$$

which reduces to

$$\frac{dp}{dz} = -\rho\,g. \tag{6.64}$$

This is called the *equation of hydrostatic equilibrium* for the atmosphere.

We can write the density of a gas in the following form,

$$\rho = \frac{\nu\,\mu}{V}, \tag{6.65}$$

where μ is the *molecular weight* of the gas, and is equal to the mass of one mole of gas particles. For instance, the molecular weight of Nitrogen gas is 28 grams. The above formula for the density of a gas combined with the ideal gas law $p\,V = \nu\,R\,T$ yields

$$\rho = \frac{p\,\mu}{R\,T}. \tag{6.66}$$

It follows that the equation of hydrostatic equilibrium can be rewritten

$$\frac{dp}{p} = -\frac{\mu\,g}{R\,T}\,dz. \tag{6.67}$$

6.7 The isothermal atmosphere

As a first approximation, let us assume that the temperature of the atmosphere is uniform. In such an *isothermal atmosphere*, we can directly integrate the previous equation to give

$$p = p_0 \exp\left(-\frac{z}{z_0}\right). \tag{6.68}$$

Here, p_0 is the pressure at ground level ($z = 0$), which is generally about 1 bar, or 1 atmosphere (10^5 N m^{-2} in SI units). The quantity

$$z_0 = \frac{R\,T}{\mu\,g} \tag{6.69}$$

is called the *isothermal scale-height* of the atmosphere. At ground level, the temperature is on average about 15° centigrade, which is 288° kelvin on the absolute scale. The mean molecular weight of air at sea level is 29 (*i.e.*, the molecular weight of a gas made up of 78% Nitrogen, 21% Oxygen, and 1% Argon). The acceleration due to gravity is 9.81 m s^{-2} at ground level. Also, the ideal gas constant is 8.314 joules/mole/degree. Putting all of this information together, the isothermal scale-height of the atmosphere comes out to be about 8.4 kilometers.

We have discovered that in an isothermal atmosphere the pressure decreases exponentially with increasing height. Since the temperature is assumed to be constant, and $\rho \propto p/T$ [see Eq. (6.66)], it follows that the density also decreases exponentially with the same scale-height as the pressure. According to Eq. (6.68), the pressure, or density, decreases by a factor 10 every $\ln 10\, z_0$, or 19.3 kilometers, we move vertically upwards. Clearly, the effective height of the atmosphere is pretty small compared to the Earth's radius, which is about $6,400$ kilometers. In other words, the atmosphere constitutes a very thin layer covering the surface of the Earth. Incidentally, this justifies our neglect of the decrease of g with increasing altitude.

One of the highest points in the United States of America is the peak of Mount Elbert in Colorado. This peak lies $14,432$ feet, or about 4.4 kilometers, above sea level. At this altitude, our formula says that the air pressure should be about 0.6 atmospheres. Surprisingly enough, after a few days acclimatization, people can survive quite comfortably at this sort of pressure. In the highest inhabited regions of the Andes and Tibet, the air pressure falls to about 0.5 atmospheres. Humans can just about survive at such pressures. However, people cannot survive for any extended period in air pressures below half an atmosphere. This sets an upper limit on the altitude of permanent human habitation, which is about $19,000$ feet, or 5.8 kilometers, above sea level. Incidentally, this is also the maximum altitude at which a pilot can fly an unpressurized aircraft without requiring additional Oxygen.

The highest point in the world is, of course, the peak of Mount Everest in Nepal. This peak lies at an altitude of $29,028$ feet, or 8.85 kilometers, above sea level, where we expect the air pressure to be a mere 0.35 atmospheres. This explains why Mount Everest was only conquered after lightweight portable oxygen cylinders were invented. Admittedly, some climbers have subsequently ascended Mount Everest without the aid of additional oxygen, but this is a very foolhardy venture, because above $19,000$ feet the climbers are slowly dying.

Commercial airliners fly at a cruising altitude of $32,000$ feet. At this altitude, we expect the air pressure to be only 0.3 atmospheres, which explains why airline cabins are pressurized. In fact, the cabins are only pressurized to 0.85 atmospheres (which accounts for the "popping" of passangers ears during air travel). The reason for this partial pressurization is quite simple. At $32,000$ feet, the pressure difference between the air in the cabin and that outside is about half an atmosphere. Clearly, the walls of the cabin must be strong enough to support this pressure difference, which means that they must be of a certain thickness, and, hence, the aircraft must be of a certain weight. If the cabin were fully pressurized then the pressure difference at cruising altitude would increase by about 30%, which means that the cabin walls would have to be much thicker, and, hence, the aircraft would have to be substantially heavier. So, a fully pressurized aircraft would be more comfortable to fly in (because your ears would not "pop"), but it would also be far less economical to operate.

6.8 The adiabatic atmosphere

Of course, we know that the atmosphere is not isothermal. In fact, air temperature falls quite noticeably with increasing altitude. In ski resorts, you are told to expect the temperature to drop by about 1 degree per 100 meters you go upwards. Many people cannot understand why the atmosphere gets colder the higher up you go. They reason that as higher altitudes are closer to the Sun they ought to be hotter. In fact, the explanation is quite simple. It depends on three important properties of air. The first important property is that air is transparent to most, but by no means all, of the electromagnetic spectrum. In particular, most infrared radiation, which carries heat energy, passes straight through the lower atmosphere and heats the ground. In other words, the lower atmosphere is heated from below, not from above. The second important property of air is that it is constantly in motion. In fact, the lower 20 kilometers of the atmosphere (the so called *troposphere*) are fairly thoroughly mixed. You might think that this would imply that the atmosphere is isothermal. However, this is not the case because of the final important properly of air: *i.e.*, it is a very poor conductor of heat. This, of course, is why woolly sweaters work: they trap a layer of air close to the body, and because air is such a poor conductor of heat you stay warm.

Imagine a packet of air which is being swirled around in the atmosphere. We would expect it to always remain at the same pressure as its surroundings, otherwise it would be mechanically unstable. It is also plausible that the packet moves around too quickly to effectively exchange heat with its surroundings, since air is very a poor heat conductor, and heat flow is consequently quite a slow process. So, to a first approximation, the air in the packet is *adiabatic*. In a *steady-state* atmosphere, we expect that as the packet moves upwards, expands due to the reduced pressure, and cools adiabatically, its temperature always remains the same as that of its immediate surroundings. This means that we can use the adiabatic gas law to characterize the cooling of the atmosphere with increasing altitude. In this particular case, the most useful manifestation of the adiabatic law is

$$p^{1-\gamma}\,T^{\gamma} = \text{constant}, \tag{6.70}$$

giving

$$\frac{dp}{p} = \frac{\gamma}{\gamma-1}\frac{dT}{T}. \tag{6.71}$$

Combining the above relation with the equation of hydrostatic equilibrium, (6.67), we obtain

$$\frac{\gamma}{\gamma-1}\frac{dT}{T} = -\frac{\mu\,g}{R\,T}\,dz, \tag{6.72}$$

or

$$\frac{dT}{dz} = -\frac{\gamma-1}{\gamma}\frac{\mu\,g}{R}. \tag{6.73}$$

Now, the ratio of specific heats for air (which is effectively a diatomic gas) is about 1.4 (see Tab. 2). Hence, we can calculate, from the above expression, that the temperature of the atmosphere decreases with increasing height at a constant rate of 9.8° centigrade per kilometer. This value is called the *adiabatic lapse rate* of the atmosphere. Our calculation accords well with the "1 degree colder per 100 meters higher" rule of thumb used in ski resorts. The basic reason why air is colder at higher altitudes is that it expands as its pressure decreases with height. It, therefore, does work on its environment, without absorbing any heat (because of its low thermal conductivity), so its internal energy, and, hence, its temperature decreases.

According to the adiabatic lapse rate calculated above, the air temperature at the cruising altitude of airliners ($32,000$ feet) should be about -80° centigrade (assuming a sea level temperature of 15° centigrade). In fact, this is somewhat of an underestimate. A more realistic value is about -60° centigrade. The explanation for this discrepancy is the presence of water vapour in the atmosphere. As air rises, expands, and cools, water vapour condenses out releasing latent heat which prevents the temperature from falling as rapidly with height as the adiabatic lapse rate would indicate. In fact, in the Tropics, where the humidity is very high, the lapse rate of the atmosphere (*i.e.*, the rate of decrease of temperature with altitude) is significantly less than the adiabatic value. The adiabatic lapse rate is only observed when the humidity is low. This is the case in deserts, in the Arctic (where water vapour is frozen out of the atmosphere), and, of course, in ski resorts.

Suppose that the lapse rate of the atmosphere differs from the adiabatic value. Let us ignore the complication of water vapour and assume that the atmosphere is dry. Consider a packet of air which moves slightly upwards from its equilibrium height. The temperature of the packet will decrease with altitude according to the adiabatic lapse rate, because its expansion is adiabatic. We assume that the packet always maintains pressure balance with its surroundings. It follows that since $\rho\,T \propto p$, according to the ideal gas law, then

$$(\rho\,T)_{\rm packet} = (\rho\,T)_{\rm atmosphere}. \tag{6.74}$$

If the atmospheric lapse rate is less than the adiabatic value then $T_{\rm atmosphere} > T_{\rm packet}$ implying that $\rho_{\rm packet} > \rho_{\rm atmosphere}$. So, the packet will be denser than its immediate surroundings, and will, therefore, tend to fall back to its original height. Clearly, an atmosphere whose lapse rate is less than the adiabatic value is *stable*. On the other hand, if the atmospheric lapse rate exceeds the adiabatic value then, after rising a little way, the packet will be less dense than its immediate surroundings, and will, therefore, continue to rise due to buoyancy effects. Clearly, an atmosphere whose lapse rate is greater than the adiabatic value is *unstable*. This effect is of great importance in Meteorology. The normal stable state of the atmosphere is for the lapse rate to be slightly less than the adiabatic value. Occasionally, however, the lapse rate exceeds the adiabatic value, and this is always associated with extremely disturbed weather patterns.

Let us consider the temperature, pressure, and density profiles in an adiabatic atmosphere. We can directly integrate Eq. (6.73) to give

$$T = T_0 \left(1 - \frac{\gamma - 1}{\gamma} \frac{z}{z_0}\right), \tag{6.75}$$

where T_0 is the ground level temperature, and

$$z_0 = \frac{R\,T_0}{\mu\,g} \tag{6.76}$$

is the isothermal scale-height calculated using this temperature. The pressure profile is easily calculated from the adiabatic gas law $p^{\,1-\gamma}\,T^{\gamma} =$ constant, or $p \propto T^{\gamma/(\gamma-1)}$. It follows that

$$p = p_0 \left(1 - \frac{\gamma - 1}{\gamma} \frac{z}{z_0}\right)^{\gamma/(\gamma-1)}. \tag{6.77}$$

Consider the limit $\gamma \to 1$. In this limit, Eq. (6.75) yields T independent of height (*i.e.*, the atmosphere becomes isothermal). We can evaluate Eq. (6.77) in the limit as $\gamma \to 1$ using the mathematical identity

$$\mathrm{lt}_{\,m\to 0}\,(1 + m\,x)^{1/m} \equiv \exp(x). \tag{6.78}$$

We obtain

$$p = p_0 \exp\left(-\frac{z}{z_0}\right), \tag{6.79}$$

which, not surprisingly, is the predicted pressure variation in an isothermal atmosphere. In reality, the ratio of specific heats of the atmosphere is not unity, it is about 1.4 (*i.e.*, the ratio for diatomic gases), which implies that in the real atmosphere

$$p = p_0 \left(1 - \frac{z}{3.5\,z_0}\right)^{3.5}. \tag{6.80}$$

In fact, this formula gives very similar results to the exponential formula, Eq. (6.79), for heights below one scale-height (*i.e.*, $z < z_0$). For heights above one scale-height, the exponential formula tends to predict too low a pressure. So, in an adiabatic atmosphere, the pressure falls off less quickly with altitude than in an isothermal atmosphere, but this effect is only really noticeable at pressures significantly below one atmosphere. In fact, the isothermal formula is a pretty good approximation below altitudes of about 10 kilometers. Since $\rho \propto p/T$, the variation of density with height goes like

$$\rho = \rho_0 \left(1 - \frac{\gamma - 1}{\gamma} \frac{z}{z_0}\right)^{1/(\gamma-1)}, \tag{6.81}$$

where ρ_0 is the density at ground level. Thus, the density falls off more rapidly with altitude than the temperature, but less rapidly than the pressure.

Note that an adiabatic atmosphere has a sharp upper boundary. Above height $z_1 = [\gamma/(\gamma - 1)]\, z_0$ the temperature, pressure, and density are all zero: *i.e.*, there is no atmosphere. For real air, with $\gamma = 1.4$, $z_1 \simeq 3.5\, z_0 \simeq 29.4$ kilometers. This behaviour is quite different to that of an isothermal atmosphere, which has a diffuse upper boundary. In reality, there is no sharp upper boundary to the atmosphere. The adiabatic gas law does not apply above about 20 kilometers (*i.e.*, in the *stratosphere*) because at these altitudes the air is no longer strongly mixed. Thus, in the stratosphere the pressure falls off exponentially with increasing height.

In conclusion, we have demonstrated that the temperature of the lower atmosphere should fall off approximately *linearly* with increasing height above ground level, whilst the pressure should fall off far more rapidly than this, and the density should fall off at some intermediate rate. We have also shown that the lapse rate of the temperature should be about 10° centigrade per kilometer in dry air, but somewhat less than this in wet air. In fact, all off these predictions are, more or less, correct. It is amazing that such accurate predictions can be obtained from the two simple laws, $p\, V =$ constant for an isothermal gas, and $p\, V^{\gamma} =$ constant for an adiabatic gas.

6.9 Heat engines

Thermodynamics was invented, almost by accident, in 1825 by a young French engineer called Sadi Carnot who was investigating the theoretical limitations on the efficiency of steam engines. Although we are not particularly interested in steam engines, nowadays, it is still highly instructive to review some of Carnot's arguments. We know, by observation, that it is possible to do mechanical work w

upon a device M, and then to extract an equivalent amount of heat q, which goes to increase the internal energy of some heat reservoir. (Here, we use small letters w and q to denote intrinsically *positive* amounts of work and heat, respectively.) An example of this is Joule's classic experiment by which he verified the first law of thermodynamics: a paddle wheel is spun in a liquid by a falling weight, and the work done by the weight on the wheel is converted into heat, and absorbed by the liquid. Carnot's question was this: is it possible to reverse this process and build a device, called a *heat engine,* which extracts heat energy from a reservoir and converts it into useful macroscopic work? For instance, is it possible to extract heat from the ocean and use it to run an electric generator?

There are a few caveats to Carnot's question. First of all, the work should not be done at the expense of the heat engine itself, otherwise the conversion of heat into work could not continue indefinitely. We can ensure that this is the case if the heat engine performs some sort of cycle, by which it periodically returns to the same macrostate, but, in the meantime, has extracted heat from the reservoir and done an equivalent amount of useful work. Furthermore, a cyclic process seems reasonable because we know that both steam engines and internal combustion engines perform continuous cycles. The second caveat is that the work done by the heat engine should be such as to change a single parameter of some external device (*e.g.*, by lifting a weight) without doing it at the expense of affecting the other degrees of freedom, or the entropy, of that device. For instance, if we are extracting heat from the ocean to generate electricity, we want to spin the shaft of the electrical generator without increasing the generator's entropy; *i.e.*, causing the generator to heat up or fall to bits.

Let us examine the feasibility of a heat engine using the laws of thermodynamics. Suppose that a heat engine M performs a single cycle. Since M has returned to its initial macrostate, its internal energy is unchanged, and the first law of thermodynamics tell us that the work done by the engine w must equal the heat extracted from the reservoir q, so

$$w = q. \tag{6.82}$$

The above condition is certainly a *necessary* condition for a feasible heat engine, but is it also a *sufficient* condition? In other words, does every device which satisfies this condition actually work? Let us think a little more carefully about what we are actually expecting a heat engine to do. We want to construct a device which will extract energy from a heat reservoir, where it is randomly distributed over very many degrees of freedom, and convert it into energy distributed over a single degree of freedom associated with some parameter of an external device. Once we have expressed the problem in these terms, it is fairly obvious that what we are really asking for is a spontaneous transition from a probable to an improbable state, which we know is forbidden by the second law of thermodynamics. So, unfortunately, we cannot run an electric generator off heat extracted from the ocean, because it is like asking all of the molecules in the ocean, which are jiggling about every which way, to all suddenly jig in the same direction, so as to exert a force on some lever, say, which can then be converted into a torque on the generator shaft. We know from our investigation of statistical thermodynamics that such a process is possible, in principle, but is *fantastically improbable*.

The improbability of the scenario just outlined is summed up in the second law of thermodynamics. This says that the total entropy of an isolated system can never spontaneously decrease, so

$$\Delta S \geq 0. \tag{6.83}$$

For the case of a heat engine, the isolated system consists of the engine, the reservoir from which it extracts heat, and the outside device upon which it does work. The engine itself returns periodically to the same state, so its entropy is clearly unchanged after each cycle. We have already specified that there is no change in the entropy of the external device upon which the work is done. On the other hand, the entropy change per cycle of the heat reservoir, which is at absolute temperature T_1, say, is given by

$$\Delta S_{\text{reservoir}} = \oint \frac{đQ}{T_1} = -\frac{q}{T_1}, \tag{6.84}$$

where $đQ$ is the infinitesimal heat absorbed by the reservoir, and the integral is taken over a whole cycle of the heat engine. The integral can be converted into the expression $-q/T_1$ because the amount of heat extracted by the engine is assumed to be too small to modify the temperature of the reservoir (this is the definition of a heat reservoir), so that T_1 is a constant during the cycle. The second law of thermodynamics clearly reduces to

$$\frac{-q}{T_1} \geq 0 \tag{6.85}$$

or, making use of the first law of thermodynamics,

$$\frac{q}{T_1} = \frac{w}{T_1} \leq 0. \tag{6.86}$$

Since we wish the work w done by the engine to be positive, the above relation clearly cannot be satisfied, which proves that an engine which converts heat directly into work is thermodynamically impossible.

A perpetual motion device, which continuously executes a cycle without extracting heat from, or doing work on, its surroundings, is just about possible according to Eq. (6.86). In fact, such a device corresponds to the equality sign in Eq. (6.83), which means that it must be completely *reversible*. In reality, there is no such thing as a completely reversible engine. All engines, even the most efficient, have frictional losses which make them, at least, slightly irreversible. Thus, the equality sign in Eq. (6.83) corresponds to an asymptotic limit which reality can closely approach, but never quite attain. It follows that a perpetual motion device is thermodynamically impossible. Nevertheless, the U.S. patent office receives about 100 patent applications a year regarding perpetual motion devices. The British patent office, being slightly less open-minded that its American counterpart, refuses to entertain such applications on the basis that perpetual motion devices are forbidden by the second law of thermodynamics.

According to Eq. (6.86), there is no thermodynamic objection to a heat engine which runs backwards, and converts work directly into heat. This is not surprising, since we know that this is essentially what frictional forces do. Clearly, we have, here, another example of a natural process which is fundamentally irreversible according to the second law of thermodynamics. In fact, the statement

> It is impossible to construct a perfect heat engine which converts heat directly into work

is called Kelvin's formulation of the second law.

We have demonstrated that a *perfect heat engine*, which converts heat directly into work, is impossible. But, there must be some way of obtaining useful work from heat energy, otherwise steam engines would not operate. Well, the reason that our previous scheme did not work was that it decreased the entropy of a heat reservoir, at some temperature T_1, by extracting an amount of heat q per cycle, without any compensating increase in the entropy of anything else, so the second law of thermodynamics was violated. How can we remedy this situation? We still want the heat engine itself to perform periodic cycles (so, by definition, its entropy cannot increase over a cycle), and we also do not want to increase the entropy of the external device upon which the work is done. Our only other option is to increase the entropy of some other body. In Carnot's analysis, this other body is a second heat reservoir at temperature T_2. We can increase the entropy of the second reservoir by dumping some of the heat we extracted from the first reservoir into it. Suppose that the heat per cycle we extract from the first reservoir is q_1, and the heat per cycle we reject into the second reservoir is q_2. Let the work done on the external device be w per cycle. The first law of thermodynamics tells us that

$$q_1 = w + q_2. \tag{6.87}$$

Note that $q_2 < q_1$ if positive (*i.e.*, useful) work is done on the external device. The total entropy change per cycle is due to the heat extracted from the first reservoir and the heat dumped into the second, and has to be positive (or zero) according to the second law of thermodynamics. So,

$$\Delta S = \frac{-q_1}{T_1} + \frac{q_2}{T_2} \geq 0. \tag{6.88}$$

We can combine the previous two equations to give

$$\frac{-q_1}{T_1} + \frac{q_1 - w}{T_2} \geq 0, \tag{6.89}$$

or

$$\frac{w}{T_2} \leq q_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{6.90}$$

It is clear that the engine is only going to perform useful work (*i.e.*, w is only going to be positive) if $T_2 < T_1$. So, the second reservoir has to be *colder* than the first if the heat dumped into the former is to increase the entropy of the Universe more than the heat extracted from the latter decreases it. It is useful to define the efficiency η of a heat engine. This is the ratio of the work done per cycle on the external device to the heat energy absorbed per cycle from the first reservoir. The efficiency of a perfect heat engine is unity, but we have already shown that such an engine is impossible. What is the efficiency of a realizable engine? It is clear from the previous equation that

$$\eta \equiv \frac{w}{q_1} \leq 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}. \tag{6.91}$$

Note that the efficiency is always less than unity. A real engine must always reject some energy into the second heat reservoir in order to satisfy the second law of thermodynamics, so less energy is available to do external work, and the efficiency of the engine is reduced. The equality sign in the above expression corresponds to a completely reversible heat engine (*i.e.*, one which is quasi-static). It is clear that real engines, which are always irreversible to some extent, are less efficient than reversible engines. Furthermore, all reversible engines which operate between the two temperatures T_1 and T_2 must have the *same* efficiency,

$$\eta = \frac{T_1 - T_2}{T_1}, \tag{6.92}$$

irrespective of the way in which they operate.

Let us consider how we might construct one of these reversible heat engines. Suppose that we have some gas in a cylinder equipped with a frictionless piston. The gas is not necessarily a perfect gas. Suppose that we also have two heat reservoirs at temperatures T_1 and T_2 (where $T_1 > T_2$). These reservoirs might take the form of large water baths. Let us start off with the gas in thermal contact with the first reservoir. We now pull the piston out very slowly so that heat energy flows reversibly into the gas from the reservoir. Let us now thermally isolate the gas and slowly pull out the piston some more. During this adiabatic process the temperature of the gas falls (since there is no longer any heat flowing into it to compensate for the work it does on the piston). Let us continue this process until the temperature of the gas falls to T_2. We now place the gas in thermal contact with the second reservoir and slowly push the piston in. During this isothermal

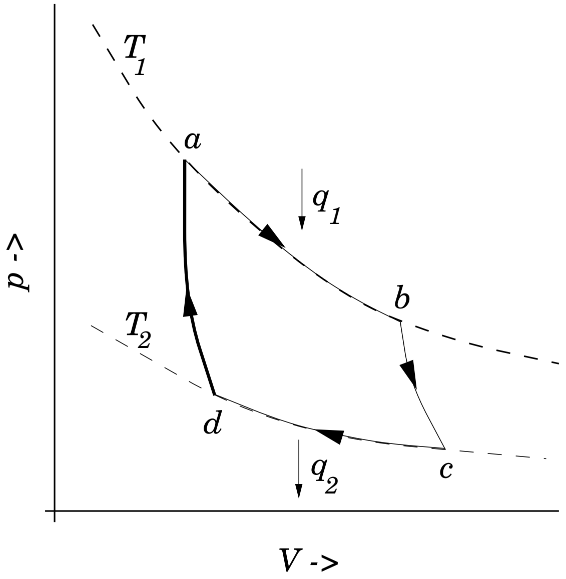

Figure 1: *An ideal gas Carnot engine.*

process heat flows out of the gas into the reservoir. We next thermally isolate the gas a second time and slowly compress it some more. In this process the temperature of the gas increases. We stop the compression when the temperature reaches T_1. If we carry out each step properly we can return the gas to its initial state and then repeat the cycle *ad infinitum*. We now have a set of reversible processes by which a quantity of heat is extracted from the first reservoir and a quantity of heat is dumped into the second. We can best evaluate the work done by the system during each cycle by plotting out the locus of the gas in a p-V diagram. The locus takes the form of a closed curve—see Fig. 1. The net work done per cycle is the "area" contained inside this curve, since $đW = p\,dV$ [if p is plotted vertically and V horizontally, then $p\,dV$ is clearly an element of area under the curve $p(V)$]. The engine we have just described is called a *Carnot engine*, and is the simplest conceivable device capable of converting heat energy into useful work.

For the specific case of an ideal gas, we can actually calculate the work done per cycle, and, thereby, verify Eq. (6.92). Consider the isothermal expansion phase of the gas. For an ideal gas, the internal energy is a function of the temperature alone. The temperature does not change during isothermal expansion, so the internal energy remains constant, and the net heat absorbed by the gas must equal the work it does on the piston. Thus,

$$q_1 = \int_a^b p\,dV, \tag{6.93}$$

where the expansion takes the gas from state a to state b. Since $p\,V = \nu\,R\,T$, for an ideal gas, we have

$$q_1 = \int_a^b \nu\,R\,T_1 \frac{dV}{V} = \nu\,R\,T_1\,\ln\frac{V_b}{V_a}. \tag{6.94}$$

Likewise, during the isothermal compression phase, in which the gas goes from state c to state d, the net heat rejected to the second reservoir is

$$q_2 = \nu\,R\,T_2\,\ln\frac{V_c}{V_d}. \tag{6.95}$$

Now, during adiabatic expansion or compression

$$T\,V^{\gamma-1} = \text{constant}. \tag{6.96}$$

It follows that during the adiabatic expansion phase, which takes the gas from state b to state c,

$$T_1\,V_b^{\gamma-1} = T_2\,V_c^{\gamma-1}. \tag{6.97}$$

Likewise, during the adiabatic compression phase, which takes the gas from state d to state a,

$$T_1\,V_a^{\gamma-1} = T_2\,V_d^{\gamma-1}. \tag{6.98}$$

If we take the ratio of the previous two equations we obtain

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}. \tag{6.99}$$

Hence, the work done by the engine, which we can calculate using the first law of thermodynamics,

$$w = q_1 - q_2, \tag{6.100}$$

is

$$w = \nu\,R\,(T_1 - T_2)\,\ln\frac{V_b}{V_a}. \tag{6.101}$$

Thus, the efficiency of the engine is

$$\eta = \frac{w}{q_1} = \frac{T_1 - T_2}{T_1} \tag{6.102}$$

which, not surprisingly, is exactly the same as Eq. (6.92).

The engine described above is very idealized. Of course, real engines are far more complicated than this. Nevertheless, the maximum efficiency of an ideal heat engine places severe constraints on real engines. Conventional power stations have many different "front ends" (*e.g.*, coal fired furnaces, oil fired furnaces, nuclear reactors), but their "back ends" are all very similar, and consist of a steam driven turbine connected to an electric generator. The "front end" heats water extracted from a local river and turns it into steam, which is then used to drive the turbine, and, hence, to generate electricity. Finally, the steam is sent through a heat exchanger so that it can heat up the incoming river water, which means that the incoming water does not have to be heated so much by the "front end." At this stage, some heat is rejected to the environment, usually as clouds of steam escaping from the top of cooling towers. We can see that a power station possesses many of the same features as our idealized heat engine. There is a cycle which operates between two temperatures. The upper temperature is the temperature to which the steam is heated by the "front end," and the lower temperature is the temperature of the environment into which heat is rejected. Suppose that the steam is only heated to 100° C (or 373° K), and the temperature of the environment is 15° C (or 288° K). It follows from Eq. (6.91) that the *maximum* possible efficiency of the steam cycle is

$$\eta = \frac{373 - 288}{373} \simeq 0.23. \tag{6.103}$$

So, at least 77% of the heat energy generated by the "front end" goes straight up the cooling towers! Not be surprisingly, commercial power stations do not operate with 100° C steam. The only way in which the thermodynamic efficiency of the steam cycle can be raised to an acceptable level is to use very hot steam (clearly, we cannot refrigerate the environment). Using 400° C steam, which is not uncommon, the maximum efficiency becomes

$$\eta = \frac{673 - 288}{673} \simeq 0.57, \tag{6.104}$$

which is more reasonable. In fact, the steam cycles of modern power stations are so well designed that they come surprisingly close to their maximum thermodynamic efficiencies.

6.10 Refrigerators

Let us now move on to consider refrigerators. An idealized refrigerator is an engine which extracts heat from a cold heat reservoir (temperature T_2, say) and rejects it to a somewhat hotter heat reservoir, which is usually the environment (temperature T_1, say). To make this machine work we always have to do some external work on the engine. For instance, the refrigerator in your home contains a small electric pump which does work on the freon (or whatever) in the cooling circuit. We can see that, in fact, a refrigerator is just a heat engine run in reverse. Hence, we can immediately carry over most of our heat engine analysis. Let q_2 be the heat absorbed per cycle from the colder reservoir, q_1 the heat rejected per cycle into the hotter reservoir, and w the external work done per cycle on the engine. The first law of thermodynamics tells us that

$$w + q_2 = q_1. \tag{6.105}$$

The second law says that

$$\frac{q_1}{T_1} + \frac{-q_2}{T_2} \geq 0. \tag{6.106}$$

We can combine these two laws to give

$$\frac{w}{T_1} \geq q_2 \left(\frac{1}{T_2} - \frac{1}{T_1} \right). \tag{6.107}$$

The most sensible way of defining the efficiency of a refrigerator is as the ratio of the heat extracted per cycle from the cold reservoir to the work done per cycle on the engine. With this definition

$$\eta = \frac{T_2}{T_1 - T_2}. \tag{6.108}$$

We can see that this efficiency is, in general, greater than unity. In other words, for one joule of work done on the engine, or pump, more than one joule of energy is extracted from whatever it is we are cooling. Clearly, refrigerators are intrinsically very efficient devices. Domestic refrigerators cool stuff down to about 4° C (277° K) and reject heat to the environment at about 15° C (288° K). The maximum theoretical efficiency of such devices is

$$\eta = \frac{277}{288 - 277} = 25.2. \tag{6.109}$$

So, for every joule of electricity we put into a refrigerator we can extract up to 25 joules of heat from its contents.

7 Applications of statistical thermodynamics

7.1 Introduction

In our study of classical thermodynamics, we concentrated on the application of statistical physics to *macroscopic* systems. Somewhat paradoxically, statistical arguments did not figure very prominently in this investigation. In fact, the only statistical statement we made was that it was *extremely unlikely* that a macroscopic system could violate the second law of thermodynamics. The resolution of this paradox is, of course, that macroscopic systems contain a very large number of particles, and their statistical fluctuations are, therefore, negligible. Let us now apply statistical physics to *microscopic* systems, such as atoms and molecules. In this study, the underlying statistical nature of thermodynamics will become far more apparent.

7.2 Boltzmann distributions

We have gained some understanding of the macroscopic properties of the air around us. For instance, we know something about its internal energy and specific heat capacity. How can we obtain some information about the statistical properties of the molecules which make up air? Consider a specific molecule: it constantly collides with its immediate neighbour molecules, and occasionally bounces off the walls of the room. These interactions "inform" it about the macroscopic state of the air, such as its temperature, pressure, and volume. The statistical distribution of the molecule over its own particular microstates must be consistent with this macrostate. In other words, if we have a large group of such molecules with similar statistical distributions, then they must be equivalent to air with the appropriate macroscopic properties. So, it ought to be possible to calculate the probability distribution of the molecule over its microstates from a knowledge of these macroscopic properties.

We can think of the interaction of a molecule with the air in a classroom as analogous to the interaction of a small system A in thermal contact with a heat reservoir A'. The air acts like a heat reservoir because its energy fluctuations due to any interactions with the molecule are far too small to affect any of its macroscopic parameters. Let us determine the probability P_r of finding system A in one particular microstate r of energy E_r when it is thermal equilibrium with the heat reservoir A'.

As usual, we assume fairly weak interaction between A and A', so that the energies of these two systems are additive. The energy of A is not known at this stage. In fact, only the *total* energy of the combined system $A^{(0)} = A + A'$ is known. Suppose that the total energy lies in the range $E^{(0)}$ to $E^{(0)} + \delta E$. The overall energy is constant in time, since $A^{(0)}$ is assumed to be an isolated system, so

$$E_r + E' = E^{(0)}, \tag{7.1}$$

where E' denotes the energy of the reservoir A'. Let $\Omega'(E')$ be the number of microstates accessible to the reservoir when its energy lies in the range E' to $E' + \delta E$. Clearly, if system A has an energy E_r then the reservoir A' must have an energy close to $E' = E^{(0)} - E_r$. Hence, since A is in *one* definite state (*i.e.*, state r), and the total number of states accessible to A' is $\Omega'(E^{(0)} - E_r)$, it follows that the total number of states accessible to the combined system is simply $\Omega'(E^{(0)} - E_r)$. The principle of equal *a priori* probabilities tells us the the probability of occurrence of a particular situation is proportional to the number of accessible microstates. Thus,

$$P_r = C'\,\Omega'(E^{(0)} - E_r), \tag{7.2}$$

where C' is a constant of proportionality which is independent of r. This constant can be determined by the normalization condition

$$\sum_r P_r = 1, \tag{7.3}$$

where the sum is over all possible states of system A, irrespective of their energy.

Let us now make use of the fact that system A is far smaller than system A'. It follows that $E_r \ll E^{(0)}$, so the slowly varying logarithm of P_r can be Taylor expanded about $E' = E^{(0)}$. Thus,

$$\ln P_r = \ln C' + \ln \Omega'(E^{(0)}) - \left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 E_r + \cdots. \tag{7.4}$$

Note that we must expand $\ln P_r$, rather than P_r itself, because the latter function varies so rapidly with energy that the radius of convergence of its Taylor series is far too small for the series to be of any practical use. The higher order terms in Eq. (7.4) can be safely neglected, because $E_r \ll E^{(0)}$. Now the derivative

$$\left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 \equiv \beta \tag{7.5}$$

is evaluated at the fixed energy $E' = E^{(0)}$, and is, thus, a constant independent of the energy E_r of A. In fact, we know, from Sect. 5, that this derivative is just the temperature parameter $\beta = (k\,T)^{-1}$ characterizing the heat reservoir A'. Hence, Eq. (7.4) becomes

$$\ln P_r = \ln C' + \ln \Omega'(E^{(0)}) - \beta\, E_r, \tag{7.6}$$

giving

$$P_r = C \exp(-\beta\, E_r), \tag{7.7}$$

where C is a constant independent of r. The parameter C is determined by the normalization condition, which gives

$$C^{-1} = \sum_r \exp(-\beta\, E_r), \tag{7.8}$$

so that the distribution becomes

$$P_r = \frac{\exp(-\beta\, E_r)}{\sum_r \exp(-\beta\, E_r)}. \tag{7.9}$$

This is known as the *Boltzmann probability distribution*, and is undoubtably the most famous result in statistical physics.

The Boltzmann distribution often causes confusion. People who are used to the principle of equal *a priori* probabilities, which says that all microstates are equally probable, are understandably surprised when they come across the Boltzmann distribution which says that high energy microstates are markedly less probable then low energy states. However, there is no need for any confusion. The principle of equal *a priori* probabilities applies to the *whole* system, whereas the Boltzmann distribution only applies to a small part of the system. The two results are perfectly consistent. If the small system is in a microstate with a comparatively high energy E_r then the rest of the system (*i.e.*, the reservoir) has a slightly lower energy E' than usual (since the overall energy is fixed). The number of accessible microstates of the reservoir is a very strongly increasing function of its energy. It follows that when the small system has a high energy then significantly less states than usual are accessible to the reservoir, and so the number of microstates accessible to the overall system is reduced, and, hence, the configuration is comparatively unlikely. The strong increase in the number of accessible microstates of the reservoir with increasing E' gives rise to the strong (*i.e.*, exponential) decrease in the likelihood of a state r of the small system with increasing E_r. The exponential factor $\exp(-\beta\, E_r)$ is called the *Boltzmann factor*.

The Boltzmann distribution gives the probability of finding the small system A in *one* particular state r of energy E_r. The probability $P(E)$ that A has an energy in the small range between E and $E + \delta E$ is just the sum of all the probabilities of the states which lie in this range. However, since each of these states has approximately the same Boltzmann factor this sum can be written

$$P(E) = C\,\Omega(E)\,\exp(-\beta E), \tag{7.10}$$

where $\Omega(E)$ is the number of microstates of A whose energies lie in the appropriate range. Suppose that system A is itself a large system, but still very much smaller than system A'. For a large system, we expect $\Omega(E)$ to be a very rapidly increasing function of energy, so the probability $P(E)$ is the product of a rapidly increasing function of E and another rapidly decreasing function (*i.e.*, the Boltzmann factor). This gives a sharp maximum of $P(E)$ at some particular value of the energy. The larger system A, the sharper this maximum becomes. Eventually, the maximum becomes so sharp that the energy of system A is almost bound to lie at the most probable energy. As usual, the most probable energy is evaluated by looking for the maximum of $\ln P$, so

$$\frac{\partial \ln P}{\partial E} = \frac{\partial \ln \Omega}{\partial E} - \beta = 0, \tag{7.11}$$

giving

$$\frac{\partial \ln \Omega}{\partial E} = \beta. \tag{7.12}$$

Of course, this corresponds to the situation in which the temperature of A is the same as that of the reservoir. This is a result which we have seen before (see Sect. 5). Note, however, that the Boltzmann distribution is applicable no matter how *small* system A is, so it is a far more general result than any we have previously obtained.

7.3 Paramagnetism

The simplest microscopic system which we can analyze using the Boltzmann distribution is one which has only two possible states (there would clearly be little point in analyzing a system with only one possible state). Most elements, and some compounds, are *paramagnetic*: *i.e.*, their constituent atoms, or molecules, possess a permanent magnetic moment due to the presence of one or more unpaired electrons. Consider a substance whose constituent particles contain only one unpaired electron. Such particles have spin 1/2, and consequently possess an intrinsic magnetic moment μ. According to quantum mechanics, the magnetic moment of a spin 1/2 particle can point either parallel or antiparallel to an external magnetic field $\mathbf{B}$. Let us determine the mean magnetic moment $\overline{\mu}_B$ (in the direction of $\mathbf{B}$) of the constituent particles of the substance when its absolute temperature is T. We assume, for the sake of simplicity, that each atom (or molecule) only interacts weakly with its neighbouring atoms. This enables us to focus attention on a single atom, and treat the remaining atoms as a heat bath at temperature T.

Our atom can be in one of two possible states: the $(+)$ state in which its spin points up (*i.e.*, parallel to $\mathbf{B}$), and the $(-)$ state in which its spin points down (*i.e.*, antiparallel to $\mathbf{B}$). In the $(+)$ state, the atomic magnetic moment is parallel to the magnetic field, so that $\mu_B = \mu$. The magnetic energy of the atom is $\epsilon_+ = -\mu\,B$. In the $(-)$ state, the atomic magnetic moment is antiparallel to the magnetic field, so that $\mu_B = -\mu$. The magnetic energy of the atom is $\epsilon_- = \mu\,B$.

According to the Boltzmann distribution, the probability of finding the atom in the $(+)$ state is

$$P_+ = C \exp(-\beta\,\epsilon_+) = C \exp(\beta\,\mu\,B), \tag{7.13}$$

where C is a constant, and $\beta = (k\,T)^{-1}$. Likewise, the probability of finding the atom in the $(-)$ state is

$$P_- = C\exp(-\beta\,\epsilon_-) = C\exp(-\beta\,\mu\,B). \tag{7.14}$$

Clearly, the most probable state is the state with the lowest energy [*i.e.*, the $(+)$ state]. Thus, the mean magnetic moment points in the direction of the magnetic field (*i.e.*, the atom is more likely to point parallel to the field than antiparallel).

It is clear that the critical parameter in a paramagnetic system is

$$y \equiv \beta\,\mu\,B = \frac{\mu\,B}{k\,T}. \tag{7.15}$$

This parameter measures the ratio of the typical magnetic energy of the atom to its typical thermal energy. If the thermal energy greatly exceeds the magnetic energy then $y \ll 1$, and the probability that the atomic moment points parallel to the magnetic field is about the same as the probability that it points antiparallel. In this situation, we expect the mean atomic moment to be small, so that $\overline{\mu}_B \simeq 0$. On the other hand, if the magnetic energy greatly exceeds the thermal energy then $y \gg 1$, and the atomic moment is far more likely to point parallel to the magnetic field than antiparallel. In this situation, we expect $\overline{\mu}_B \simeq \mu$.

Let us calculate the mean atomic moment $\overline{\mu}_B$. The usual definition of a mean value gives

$$\overline{\mu}_B = \frac{P_+\,\mu + P_-\,(-\mu)}{P_+ + P_-} = \mu\,\frac{\exp(\beta\,\mu\,B) - \exp(-\beta\,\mu\,B)}{\exp(\beta\,\mu\,B) + \exp(-\beta\,\mu\,B)}. \tag{7.16}$$

This can also be written

$$\overline{\mu}_B = \mu\tanh\frac{\mu\,B}{k\,T}, \tag{7.17}$$

where the hyperbolic tangent is defined

$$\tanh y \equiv \frac{\exp(y) - \exp(-y)}{\exp(y) + \exp(-y)}. \tag{7.18}$$

For small arguments, $y \ll 1$,

$$\tanh y \simeq y - \frac{y^3}{3} + \cdots, \tag{7.19}$$

whereas for large arguments, $y \gg 1$,

$$\tanh y \simeq 1. \tag{7.20}$$

It follows that at comparatively high temperatures, $k\,T \gg \mu\,B$,

$$\overline{\mu}_B \simeq \frac{\mu^2 B}{k\,T}, \tag{7.21}$$

whereas at comparatively low temperatures, $k\,T \ll \mu\,B$,

$$\overline{\mu}_B \simeq \mu. \tag{7.22}$$

Suppose that the substance contains N_0 atoms (or molecules) per unit volume. The *magnetization* is defined as the mean magnetic moment per unit volume, and is given by

$$\overline{M}_0 = N_0\,\overline{\mu}_B. \tag{7.23}$$

At high temperatures, $k\,T \gg \mu\,B$, the mean magnetic moment, and, hence, the magnetization, is proportional to the applied magnetic field, so we can write

$$\overline{M}_0 \simeq \chi\,B, \tag{7.24}$$

where χ is a constant of proportionality known as the *magnetic susceptibility*. It is clear that the magnetic susceptibility of a spin 1/2 paramagnetic substance takes the form

$$\chi = \frac{N_0\,\mu^2}{k\,T}. \tag{7.25}$$

The fact that $\chi \propto T^{-1}$ is known as *Curie's law*, because it was discovered experimentally by Pierre Curie at the end of the nineteenth century. At low temperatures, $k\,T \ll \mu\,B$,

$$\overline{M}_0 \rightarrow N_0\,\mu, \tag{7.26}$$

so the magnetization becomes independent of the applied field. This corresponds to the maximum possible magnetization, where all atomic moments are lined up parallel to the field. The breakdown of the $\overline{M}_0 \propto B$ law at low temperatures (or high magnetic fields) is known as *saturation*.

The above analysis is only valid for paramagnetic substances made up of spin one-half ($J = 1/2$) atoms or molecules. However, the analysis can easily be

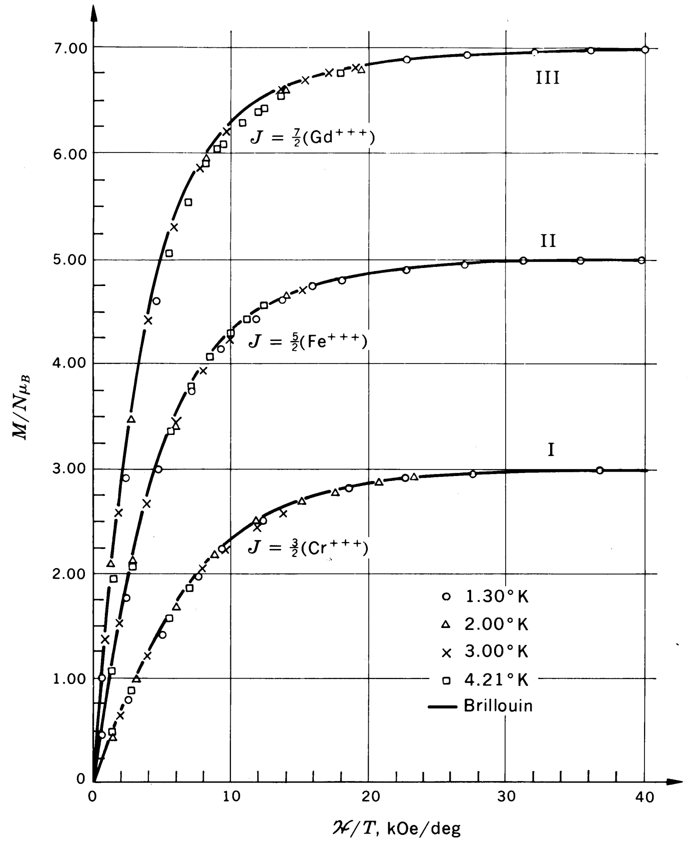

Figure 2: *The magnetization (vertical axis) versus* B/T *(horizontal axis) curves for (I) chromium potassium alum* ($J = 3/2$)*, (II) iron ammonium alum* ($J = 5/2$)*, and (III) gadolinium sulphate* ($J = 7/2$)*. The solid lines are the theoretical predictions whereas the data points are experimental measurements. From W.E. Henry, Phys. Rev.* **88***, 561 (1952).*

generalized to take account of substances whose constituent particles possess higher spin (*i.e.*, $J > 1/2$). Figure 2 compares the experimental and theoretical magnetization versus field-strength curves for three different substances made up of spin 3/2, spin 5/2, and spin 7/2 particles, showing the excellent agreement between the two sets of curves. Note that, in all cases, the magnetization is proportional to the magnetic field-strength at small field-strengths, but saturates at some constant value as the field-strength increases.

The previous analysis completely neglects any interaction between the spins of neighbouring atoms or molecules. It turns out that this is a fairly good approximation for paramagnetic substances. However, for *ferromagnetic* substances, in which the spins of neighbouring atoms interact very strongly, this approximation breaks down completely. Thus, the above analysis *does not* apply to ferromagnetic substances.

7.4 Mean values

Consider a system in contact with a heat reservoir. The systems in the representative ensemble are distributed over their accessible states in accordance with the Boltzmann distribution. Thus, the probability of occurrence of some state r with energy E_r is given by

$$P_r = \frac{\exp(-\beta\, E_r)}{\sum_r \exp(-\beta\, E_r)}. \tag{7.27}$$

The mean energy is written

$$\overline{E} = \frac{\sum_r \exp(-\beta\, E_r)\, E_r}{\sum_r \exp(-\beta\, E_r)}, \tag{7.28}$$

where the sum is taken over all states of the system, irrespective of their energy. Note that

$$\sum_r \exp(-\beta\, E_r)\, E_r = -\sum_r \frac{\partial}{\partial\beta} \exp(-\beta\, E_r) = -\frac{\partial Z}{\partial\beta}, \tag{7.29}$$

where

$$Z = \sum_r \exp(-\beta\, E_r). \tag{7.30}$$

It follows that

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}. \tag{7.31}$$

The quantity Z, which is defined as the sum of the Boltzmann factor over all states, irrespective of their energy, is called the *partition function*. We have just demonstrated that it is fairly easy to work out the mean energy of a system using its partition function. In fact, as we shall discover, it is easy to calculate virtually any piece of statistical information using the partition function.

Let us evaluate the variance of the energy. We know that

$$\overline{(\Delta E)^2} = \overline{E^2} - \overline{E}^2 \tag{7.32}$$

(see Sect. 2). Now, according to the Boltzmann distribution,

$$\overline{E^2} = \frac{\sum_r \exp(-\beta\, E_r)\, {E_r}^2}{\sum_r \exp(-\beta\, E_r)}. \tag{7.33}$$

However,

$$\sum_r \exp(-\beta\, E_r)\, {E_r}^2 = -\frac{\partial}{\partial \beta}\left[\sum_r \exp(-\beta\, E_r)\, E_r\right] = \left(-\frac{\partial}{\partial \beta}\right)^2 \left[\sum_r \exp(-\beta E_r)\right]. \tag{7.34}$$

Hence,

$$\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}. \tag{7.35}$$

We can also write

$$\overline{E^2} = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = -\frac{\partial \overline{E}}{\partial \beta} + \overline{E}^2, \tag{7.36}$$

where use has been made of Eq. (7.31). It follows from Eq. (7.32) that

$$\overline{(\Delta E)^2} = -\frac{\partial \overline{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}. \tag{7.37}$$

Thus, the variance of the energy can be worked out from the partition function almost as easily as the mean energy. Since, by definition, a variance can never be negative, it follows that $\partial \overline{E}/\partial \beta \leq 0$, or, equivalently, $\partial \overline{E}/\partial T \geq 0$. Hence, the mean energy of a system governed by the Boltzmann distribution always increases with temperature.

Suppose that the system is characterized by a single external parameter x (such as its volume). The generalization to the case where there are several external parameters is obvious. Consider a quasi-static change of the external parameter from x to $x + dx$. In this process, the energy of the system in state r changes by

$$\delta E_r = \frac{\partial E_r}{\partial x}\,dx. \tag{7.38}$$

The macroscopic work $đW$ done by the system due to this parameter change is

$$đW = \frac{\sum_r \exp(-\beta\,E_r)(-\partial E_r/\partial x\;\,dx)}{\sum_r \exp(-\beta\,E_r)}. \tag{7.39}$$

In other words, the work done is minus the average change in internal energy of the system, where the average is calculated using the Boltzmann distribution. We can write

$$\sum_r \exp(-\beta\,E_r)\,\frac{\partial E_r}{\partial x} = -\frac{1}{\beta}\frac{\partial}{\partial x}\left[\sum_r \exp(-\beta\,E_r)\right] = -\frac{1}{\beta}\frac{\partial Z}{\partial x}, \tag{7.40}$$

which gives

$$đW = \frac{1}{\beta Z}\frac{\partial Z}{\partial x}\,dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}\,dx. \tag{7.41}$$

We also have the following general expression for the work done by the system

$$đW = \overline{X}\,dx, \tag{7.42}$$

where

$$\overline{X} = -\overline{\frac{\partial E_r}{\partial x}} \tag{7.43}$$

is the mean generalized force conjugate to x (see Sect. 4). It follows that

$$\overline{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}. \tag{7.44}$$

Suppose that the external parameter is the volume, so $x = V$. It follows that

$$đW = \overline{p}\,dV = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}\,dV \tag{7.45}$$

and

$$\overline{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}. \tag{7.46}$$

Since the partition function is a function of β and V (the energies E_r depend on V), it is clear that the above equation relates the mean pressure $\overline{p}$ to T (via $\beta = 1/k\,T$) and V. In other words, the above expression is the *equation of state*. Hence, we can work out the pressure, and even the equation of state, using the partition function.

7.5 Partition functions

It is clear that all important macroscopic quantities associated with a system can be expressed in terms of its partition function Z. Let us investigate how the partition function is related to thermodynamical quantities. Recall that Z is a function of both β and x (where x is the single external parameter). Hence, $Z = Z(\beta, x)$, and we can write

$$d\ln Z = \frac{\partial \ln Z}{\partial x}\,dx + \frac{\partial \ln Z}{\partial \beta}\,d\beta. \tag{7.47}$$

Consider a quasi-static change by which x and β change so slowly that the system stays close to equilibrium, and, thus, remains distributed according to the Boltzmann distribution. If follows from Eqs. (7.31) and (7.41) that

$$d\ln Z = \beta\,đW - \overline{E}\,d\beta. \tag{7.48}$$

The last term can be rewritten

$$d\ln Z = \beta\,đW - d(\overline{E}\,\beta) + \beta\,d\overline{E}, \tag{7.49}$$

giving

$$d(\ln Z + \beta\,\overline{E}) = \beta(đW + d\overline{E}) \equiv \beta\,đQ. \tag{7.50}$$

The above equation shows that although the heat absorbed by the system $đQ$ is not an exact differential, it becomes one when multiplied by the temperature parameter β. This is essentially the second law of thermodynamics. In fact, we know that

$$dS = \frac{đQ}{T}. \tag{7.51}$$

Hence,

$$S \equiv k\,(\ln Z + \beta\,\overline{E}). \tag{7.52}$$

This expression enables us to calculate the entropy of a system from its partition function.

Suppose that we are dealing with a system $A^{(0)}$ consisting of two systems A and A' which only interact weakly with one another. Let each state of A be denoted by an index r and have a corresponding energy E_r. Likewise, let each state of A' be denoted by an index s and have a corresponding energy E_s'. A state of the combined system $A^{(0)}$ is then denoted by two indices r and s. Since A and A' only interact weakly their energies are additive, and the energy of state rs is

$$E_{rs}^{(0)} = E_r + E_s'. \tag{7.53}$$

By definition, the partition function of $A^{(0)}$ takes the form

$$\begin{aligned} Z^{(0)} &= \sum_{r,s} \exp[-\beta\,E_{rs}^{(0)}] \\ &= \sum_{r,s} \exp(-\beta\,[E_r + E_s']) \\ &= \sum_{r,s} \exp(-\beta\,E_r)\exp(-\beta\,E_s') \\ &= \left[\sum_r \exp(-\beta\,E_r)\right]\left[\sum_s \exp(-\beta\,E_s')\right]. \end{aligned} \tag{7.54}$$

Hence,

$$Z^{(0)} = Z\,Z', \tag{7.55}$$

giving

$$\ln Z^{(0)} = \ln Z + \ln Z', \tag{7.56}$$

where Z and Z' are the partition functions of A and A', respectively. It follows from Eq. (7.31) that the mean energies of $A^{(0)}$, A, and A' are related by

$$\overline{E}^{(0)} = \overline{E} + \overline{E}'. \tag{7.57}$$

It also follows from Eq. (7.52) that the respective entropies of these systems are related via

$$S^{(0)} = S + S'. \tag{7.58}$$

Hence, the partition function tells us that the extensive thermodynamic functions of two weakly interacting systems are simply additive.

It is clear that we can perform statistical thermodynamical calculations using the partition function Z instead of the more direct approach in which we use the density of states Ω. The former approach is advantageous because the partition function is an *unrestricted* sum of Boltzmann factors over all accessible states, irrespective of their energy, whereas the density of states is a *restricted* sum over all states whose energies lie in some narrow range. In general, it is far easier to perform an unrestricted sum than a restricted sum. Thus, it is generally easier to derive statistical thermodynamical results using Z rather than Ω, although Ω has a far more direct physical significance than Z.

7.6 Ideal monatomic gases

Let us now practice calculating thermodynamic relations using the partition function by considering an example with which we are already quite familiar: *i.e.*, an ideal monatomic gas. Consider a gas consisting of N identical monatomic molecules of mass m enclosed in a container of volume V. Let us denote the position and momentum vectors of the ith molecule by $\mathbf{r}_i$ and $\mathbf{p}_i$, respectively. Since the gas is ideal, there are no interatomic forces, and the total energy is simply the sum of the individual kinetic energies of the molecules:

$$E = \sum_{i=1}^{N} \frac{{p_i}^2}{2\,m}, \tag{7.59}$$

where ${p_i}^2 = \mathbf{p}_i \cdot \mathbf{p}_i$.

Let us treat the problem classically. In this approach, we divide up phase-space into cells of equal volume ${h_0}^f$. Here, f is the number of degrees of freedom, and h_0 is a small constant with dimensions of angular momentum which parameterizes the precision to which the positions and momenta of molecules are determined (see Sect. 3.2). Each cell in phase-space corresponds to a different state. The partition function is the sum of the Boltzmann factor $\exp(-\beta\, E_r)$ over all possible states, where E_r is the energy of state r. Classically, we can approximate the summation over cells in phase-space as an integration over all phase-space. Thus,

$$Z = \int\cdots\int \exp(-\beta\, E)\,\frac{d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\, d^3\mathbf{p}_1\cdots d^3\mathbf{p}_N}{{h_0}^{3N}}, \tag{7.60}$$

where $3N$ is the number of degrees of freedom of a monatomic gas containing N molecules. Making use of Eq. (7.59), the above expression reduces to

$$Z = \frac{V^N}{{h_0}^{3N}}\int\cdots\int \exp[-(\beta/2m)\, {p_1}^2]\, d^3\mathbf{p}_1\cdots \exp[-(\beta/2m)\, p_N^2]\, d^3\mathbf{p}_N. \tag{7.61}$$

Note that the integral over the coordinates of a given molecule simply yields the volume of the container, V, since the energy E is independent of the locations of the molecules in an ideal gas. There are N such integrals, so we obtain the factor V^N in the above expression. Note, also, that each of the integrals over the molecular momenta in Eq. (7.61) are identical: they differ only by irrelevant dummy variables of integration. It follows that the partition function Z of the gas is made up of the product of N identical factors: *i.e.*,

$$Z = \zeta^N, \tag{7.62}$$

where

$$\zeta = \frac{V}{{h_0}^3}\int \exp[-(\beta/2m)\, p^2]\, d^3\mathbf{p} \tag{7.63}$$

is the partition function for a single molecule. Of course, this result is obvious, since we have already shown that the partition function for a system made up of a number of weakly interacting subsystems is just the product of the partition functions of the subsystems (see Sect. 7.5).

The integral in Eq. (7.63) is easily evaluated:

$$\int \exp[-(\beta/2m)\, p^2]\, d^3\mathbf{p} = \int_{-\infty}^{\infty}\exp[-(\beta/2m)\, {p_x}^2]\, dp_x \int_{-\infty}^{\infty}\exp[-(\beta/2m)\, {p_y}^2]\, dp_y$$
$$\times\int_{-\infty}^{\infty}\exp[-(\beta/2m)\, {p_z}^2]\, dp_z$$

$$= \left(\sqrt{\frac{2\,\pi\,m}{\beta}}\right)^3, \tag{7.64}$$

where use has been made of Eq. (2.79). Thus,

$$\zeta = V\left(\frac{2\,\pi\,m}{h_0^{\,2}\,\beta}\right)^{3/2}, \tag{7.65}$$

and

$$\ln Z = N\ln\zeta = N\left[\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\,\pi\,m}{h_0^{\,2}}\right)\right]. \tag{7.66}$$

The expression for the mean pressure (7.46) yields

$$\overline{p} = \frac{1}{\beta}\frac{\partial\ln Z}{\partial V} = \frac{1}{\beta}\frac{N}{V}, \tag{7.67}$$

which reduces to the ideal gas equation of state

$$\overline{p}\,V = N\,k\,T = \nu\,R\,T, \tag{7.68}$$

where use has been made of $N = \nu\,N_A$ and $R = N_A\,k$. According to Eq. (7.31), the mean energy of the gas is given by

$$\overline{E} = -\frac{\partial\ln Z}{\partial\beta} = \frac{3}{2}\frac{N}{\beta} = \nu\,\frac{3}{2}\,R\,T. \tag{7.69}$$

Note that the internal energy is a function of temperature alone, with no dependence on volume. The molar heat capacity at constant volume of the gas is given by

$$c_V = \frac{1}{\nu}\left(\frac{\partial\overline{E}}{\partial T}\right)_V = \frac{3}{2}\,R, \tag{7.70}$$

so the mean energy can be written

$$\overline{E} = \nu\,c_V\,T. \tag{7.71}$$

We have seen all of the above results before. Let us now use the partition function to calculate a new result. The entropy of the gas can be calculated quite simply from the expression

$$S = k\,(\ln Z + \beta\,\overline{E}). \tag{7.72}$$

Thus,

$$S = \nu R \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln\left(\frac{2\pi m}{h_0^2}\right) + \frac{3}{2} \right], \tag{7.73}$$

or

$$S = \nu R \left[\ln V + \frac{3}{2} \ln T + \sigma \right], \tag{7.74}$$

where

$$\sigma = \frac{3}{2} \ln\left(\frac{2\pi m k}{h_0^2}\right) + \frac{3}{2}. \tag{7.75}$$

The above expression for the entropy of an ideal gas is certainly new. Unfortunately, it is also quite obviously incorrect!

7.7 Gibb's paradox

What has gone wrong? First of all, let us be clear why Eq. (7.74) is incorrect.

We can see that $S \rightarrow -\infty$ as $T \rightarrow 0$, which contradicts the third law of thermodynamics. However, this is not a problem. Equation (7.74) was derived using classical physics, which breaks down at low temperatures. Thus, we would not expect this equation to give a sensible answer close to the absolute zero of temperature.

Equation (7.74) is wrong because it implies that the entropy does not behave properly as an extensive quantity. Thermodynamic quantities can be divided into two groups, *extensive* and *intensive*. Extensive quantities increase by a factor α when the size of the system under consideration is increased by the same factor. Intensive quantities stay the same. Energy and volume are typical extensive quantities. Pressure and temperature are typical intensive quantities. Entropy is very definitely an extensive quantity. We have shown [see Eq. (7.58)] that the entropies of two weakly interacting systems are additive. Thus, if we double the size of a system we expect the entropy to double as well. Suppose that we have a system of volume V containing ν moles of ideal gas at temperature T. Doubling the size of the system is like joining two identical systems together to form a new system of volume $2\,V$ containing $2\,\nu$ moles of gas at temperature T. Let

$$S = \nu\,R\left[\ln V + \frac{3}{2}\ln T + \sigma\right] \tag{7.76}$$

denote the entropy of the original system, and let

$$S' = 2\,\nu\,R\left[\ln 2\,V + \frac{3}{2}\ln T + \sigma\right] \tag{7.77}$$

denote the entropy of the double-sized system. Clearly, if entropy is an extensive quantity (which it is!) then we should have

$$S' = 2\,S. \tag{7.78}$$

But, in fact, we find that

$$S' - 2\,S = 2\,\nu\,R\,\ln 2. \tag{7.79}$$

So, the entropy of the double-sized system is *more* than double the entropy of the original system.

Where does this extra entropy come from? Well, let us consider a little more carefully how we might go about doubling the size of our system. Suppose that we put another identical system adjacent to it, and separate the two systems by a partition. Let us now suddenly remove the partition. If entropy is a properly extensive quantity then the entropy of the overall system should be the same before and after the partition is removed. It is certainly the case that the energy (another extensive quantity) of the overall system stays the same. However, according to Eq. (7.79), the overall entropy of the system *increases* by $2\,\nu\,R\,\ln 2$ after the partition is removed. Suppose, now, that the second system is identical to the first system in all respects except that its molecules are in some way slightly different to the molecules in the first system, so that the two sets of molecules are *distinguishable*. In this case, we would certainly expect an overall increase in entropy when the partition is removed. Before the partition is removed, it separates type 1 molecules from type 2 molecules. After the partition is removed, molecules of both types become jumbled together. This is clearly an irreversible process. We cannot imagine the molecules spontaneously sorting themselves out again. The increase in entropy associated with this jumbling is called *entropy of mixing*, and is easily calculated. We know that the number of accessible states of an ideal gas varies with volume like $\Omega \propto V^N$. The volume accessible to type 1 molecules clearly doubles after the partition is removed, as does the volume accessible to type 2 molecules. Using the fundamental formula $S = k \ln \Omega$, the increase in entropy due to mixing is given by

$$S = 2\,k \ln \frac{\Omega_f}{\Omega_i} = 2\,N\,k \ln \frac{V_f}{V_i} = 2\,\nu\,R\,\ln 2. \tag{7.80}$$

It is clear that the additional entropy $2\,\nu\,R\,\ln 2$, which appears when we double the size of an ideal gas system by joining together two identical systems, is entropy of mixing of the molecules contained in the original systems. But, if the molecules in these two systems are *indistinguishable*, why should there be any entropy of mixing? Well, clearly, there is no entropy of mixing in this case. At this point, we can begin to understand what has gone wrong in our calculation. We have calculated the partition function assuming that all of the molecules in our system have the same mass and temperature, but we have never explicitly taken into account the fact that we consider the molecules to be indistinguishable. In other words, we have been treating the molecules in our ideal gas as if each carried a little license plate, or a social security number, so that we could always tell one from another. In quantum mechanics, which is what we really should be using to study microscopic phenomena, the essential indistinguishability of atoms and molecules is hard-wired into the theory at a very low level. Our problem is that we have been taking the classical approach a little too seriously. It is plainly silly to pretend that we can distinguish molecules in a statistical problem, where we do not closely follow the motions of individual particles. A paradox arises if we try to treat molecules as if they were distinguishable. This is called *Gibb's paradox*, after the American physicist Josiah Gibbs who first discussed it. The resolution of Gibb's paradox is quite simple: treat all molecules of the same species as if they were *indistinguishable*.

In our previous calculation of the ideal gas partition function, we inadvertently treated each of the N molecules in the gas as distinguishable. Because of this, we overcounted the number of states of the system. Since the $N!$ possible permutations of the molecules amongst themselves do not lead to physically different situations, and, therefore, cannot be counted as separate states, the number of actual states of the system is a factor N! less than what we initially thought. We can easily correct our partition function by simply dividing by this factor, so that

$$Z = \frac{\zeta^N}{N!}. \tag{7.81}$$

This gives

$$\ln Z = N \ln \zeta - \ln N!, \tag{7.82}$$

or

$$\ln Z = N \ln \zeta - N \ln N + N, \tag{7.83}$$

using Stirling's approximation. Note that our new version of $\ln Z$ differs from our previous version by an additive term involving the number of particles in the system. This explains why our calculations of the mean pressure and mean energy, which depend on partial derivatives of $\ln Z$ with respect to the volume and the temperature parameter β, respectively, came out all right. However, our expression for the entropy S is modified by this additive term. The new expression is

$$S = \nu R \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2 \pi m k}{h_0^{\,2}} \right) + \frac{3}{2} \right] + k \left(-N \ln N + N \right). \tag{7.84}$$

This gives

$$S = \nu R \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_0 \right] \tag{7.85}$$

where

$$\sigma_0 = \frac{3}{2} \ln \left(\frac{2 \pi m k}{h_0^{\,2}} \right) + \frac{5}{2}. \tag{7.86}$$

It is clear that the entropy behaves properly as an extensive quantity in the above expression: *i.e.*, it is multiplied by a factor α when ν, V, and N are multiplied by the same factor.

7.8 The equipartition theorem

The internal energy of a monatomic ideal gas containing N particles is $(3/2)\, N\, k\, T$. This means that each particle possess, on average, $(3/2)\, k\, T$ units of energy. Monatomic particles have only three translational degrees of freedom, corresponding to their motion in three dimensions. They possess no internal rotational or vibrational degrees of freedom. Thus, the mean energy per degree of freedom in a monatomic ideal gas is $(1/2)\,k\,T$. In fact, this is a special case of a rather general result. Let us now try to prove this.

Suppose that the energy of a system is determined by some f generalized coordinates q_k and corresponding f generalized momenta p_k, so that

$$E = E(q_1, \cdots, q_f, p_1, \cdots, p_f). \tag{7.87}$$

Suppose further that:

1. The total energy splits additively into the form

   $$E = \epsilon_i(p_i) + E'(q_1, \cdots, p_f), \tag{7.88}$$

   where ϵ_i involves only one variable p_i, and the remaining part E' does not depend on p_i.

2. The function ϵ_i is quadratic in p_i, so that

   $$\epsilon_i(p_i) = b\,{p_i}^2, \tag{7.89}$$

   where b is a constant.

The most common situation in which the above assumptions are valid is where p_i is a momentum. This is because the kinetic energy is usually a quadratic function of each momentum component, whereas the potential energy does not involve the momenta at all. However, if a coordinate q_i were to satisfy assumptions 1 and 2 then the theorem we are about to establish would hold just as well.

What is the mean value of ϵ_i in thermal equilibrium if conditions 1 and 2 are satisfied? If the system is in equilibrium at absolute temperature $T \equiv (k\,\beta)^{-1}$ then it is distributed according to the Boltzmann distribution. In the classical approximation, the mean value of ϵ_i is expressed in terms of integrals over all phase-space:

$$\overline{\epsilon_i} = \frac{\int_{-\infty}^{\infty} \exp[-\beta E(q_1, \cdots, p_f)]\,\epsilon_i\,dq_1 \cdots dp_f}{\int_{-\infty}^{\infty} \exp[-\beta E(q_1, \cdots, p_f)]\,dq_1 \cdots dp_f}. \tag{7.90}$$

Condition 1 gives

$$\begin{aligned}\overline{\epsilon}_i &= \frac{\int_{-\infty}^{\infty}\exp[-\beta\,(\epsilon_i+E')]\,\epsilon_i\,dq_1\cdots dp_f}{\int_{-\infty}^{\infty}\exp[-\beta\,(\epsilon_i+E')]\,dq_1\cdots dp_f}\\ &= \frac{\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,\epsilon_i\,dp_i\int_{-\infty}^{\infty}\exp(-\beta\,E')\,dq_1\cdots dp_f}{\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,dp_i\int_{-\infty}^{\infty}\exp(-\beta\,E')\,dq_1\cdots dp_f},\end{aligned} \tag{7.91}$$

where use has been made of the multiplicative property of the exponential function, and where the last integrals in both the numerator and denominator extend over all variables q_k and p_k except p_i. These integrals are equal and, thus, cancel. Hence,

$$\overline{\epsilon}_i = \frac{\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,\epsilon_i\,dp_i}{\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,dp_i}. \tag{7.92}$$

This expression can be simplified further since

$$\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,\epsilon_i\,dp_i \equiv -\frac{\partial}{\partial\beta}\left[\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,dp_i\right], \tag{7.93}$$

so

$$\overline{\epsilon}_i = -\frac{\partial}{\partial\beta}\ln\left[\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,dp_i\right]. \tag{7.94}$$

According to condition 2,

$$\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,dp_i = \int_{-\infty}^{\infty}\exp(-\beta\,b\,{p_i}^2)\,dp_i = \frac{1}{\sqrt{\beta}}\int_{-\infty}^{\infty}\exp(-b\,y^2)\,dy, \tag{7.95}$$

where $y = \sqrt{\beta}\,p_i$. Thus,

$$\ln\int_{-\infty}^{\infty}\exp(-\beta\,\epsilon_i)\,dp_i = -\frac{1}{2}\ln\beta + \ln\int_{-\infty}^{\infty}\exp(-b\,y^2)\,dy. \tag{7.96}$$

Note that the integral on the right-hand side does not depend on β at all. It follows from Eq. (7.94) that

$$\overline{\epsilon}_i = -\frac{\partial}{\partial\beta}\left(-\frac{1}{2}\ln\beta\right) = \frac{1}{2\,\beta}, \tag{7.97}$$

giving

$$\overline{\epsilon}_i = \frac{1}{2}\,k\,T. \tag{7.98}$$

This is the famous *equipartition theorem* of classical physics. It states that the mean value of every independent quadratic term in the energy is equal to $(1/2)\,k\,T$. If all terms in the energy are quadratic then the mean energy is spread equally over all degrees of freedom (hence the name “equipartition”).

7.9 Harmonic oscillators

Our proof of the equipartition theorem depends crucially on the classical approximation. To see how quantum effects modify this result, let us examine a particularly simple system which we know how to analyze using both classical and quantum physics: *i.e.*, a simple harmonic oscillator. Consider a one-dimensional harmonic oscillator in equilibrium with a heat reservoir at temperature T. The energy of the oscillator is given by

$$E = \frac{p^2}{2\,m} + \frac{1}{2}\kappa\,x^2, \tag{7.99}$$

where the first term on the right-hand side is the kinetic energy, involving the momentum p and mass m, and the second term is the potential energy, involving the displacement x and the force constant κ. Each of these terms is quadratic in the respective variable. So, in the classical approximation the equipartition theorem yields:

$$\frac{\overline{p^2}}{2\,m} = \frac{1}{2}\,k\,T, \tag{7.100}$$

$$\frac{1}{2}\kappa\,\overline{x^2} = \frac{1}{2}\,k\,T. \tag{7.101}$$

That is, the mean kinetic energy of the oscillator is equal to the mean potential energy which equals $(1/2)\,k\,T$. It follows that the mean total energy is

$$\overline{E} = \frac{1}{2}\,k\,T + \frac{1}{2}\,k\,T = k\,T. \tag{7.102}$$

According to quantum mechanics, the energy levels of a harmonic oscillator are equally spaced and satisfy

$$E_n = (n + 1/2)\,\hbar\,\omega, \tag{7.103}$$

where n is a non-negative integer, and

$$\omega = \sqrt{\frac{\kappa}{m}}. \tag{7.104}$$

The partition function for such an oscillator is given by

$$Z = \sum_{n=0}^{\infty} \exp(-\beta\,E_n) = \exp[-(1/2)\,\beta\,\hbar\,\omega] \sum_{n=0}^{\infty} \exp(-n\,\beta\,\hbar\,\omega). \tag{7.105}$$

Now,

$$\sum_{n=0}^{\infty} \exp(-n\,\beta\,\hbar\,\omega) = 1 + \exp(-\beta\,\hbar\,\omega) + \exp(-2\,\beta\,\hbar\,\omega) + \cdots \tag{7.106}$$

is simply the sum of an infinite geometric series, and can be evaluated immediately,

$$\sum_{n=0}^{\infty} \exp(-n\,\beta\,\hbar\,\omega) = \frac{1}{1 - \exp(-\beta\,\hbar\,\omega)}. \tag{7.107}$$

Thus, the partition function takes the form

$$Z = \frac{\exp[-(1/2)\,\beta\,\hbar\,\omega]}{1 - \exp(-\beta\,\hbar\,\omega)}, \tag{7.108}$$

and

$$\ln Z = -\frac{1}{2}\,\beta\,\hbar\,\omega - \ln[1 - \exp(-\beta\,\hbar\,\omega)] \tag{7.109}$$

The mean energy of the oscillator is given by [see Eq. (7.31)]

$$\overline{E} = -\frac{\partial}{\partial\beta}\ln Z = -\left[-\frac{1}{2}\,\hbar\,\omega - \frac{\exp(-\beta\,\hbar\,\omega)\,\hbar\,\omega}{1 - \exp(-\beta\,\hbar\,\omega)}\right], \tag{7.110}$$

or

$$\overline{E} = \hbar\,\omega\left[\frac{1}{2} + \frac{1}{\exp(\beta\,\hbar\,\omega) - 1}\right]. \tag{7.111}$$

Consider the limit

$$\beta\,\hbar\,\omega = \frac{\hbar\,\omega}{k\,T} \ll 1, \tag{7.112}$$

in which the thermal energy $k\,T$ is large compared to the separation $\hbar\,\omega$ between the energy levels. In this limit,

$$\exp(\beta\,\hbar\,\omega) \simeq 1 + \beta\,\hbar\,\omega, \tag{7.113}$$

so

$$\overline{E} \simeq \hbar\,\omega \left[\frac{1}{2} + \frac{1}{\beta\,\hbar\,\omega}\right] \simeq \hbar\,\omega \left[\frac{1}{\beta\,\hbar\,\omega}\right], \tag{7.114}$$

giving

$$\overline{E} \simeq \frac{1}{\beta} = k\,T. \tag{7.115}$$

Thus, the classical result (7.102) holds whenever the thermal energy greatly exceeds the typical spacing between quantum energy levels.

Consider the limit

$$\beta\,\hbar\,\omega = \frac{\hbar\,\omega}{k\,T} \gg 1, \tag{7.116}$$

in which the thermal energy is small compared to the separation between the energy levels. In this limit,

$$\exp(\beta\,\hbar\,\omega) \gg 1, \tag{7.117}$$

and so

$$\overline{E} \simeq \hbar\,\omega\,[1/2 + \exp(-\beta\,\hbar\,\omega)] \simeq \frac{1}{2}\,\hbar\,\omega. \tag{7.118}$$

Thus, if the thermal energy is much less than the spacing between quantum states then the mean energy approaches that of the ground-state (the so-called *zero point* energy). Clearly, the equipartition theorem is only valid in the former limit, where $k\,T \gg \hbar\,\omega$, and the oscillator possess sufficient thermal energy to explore many of its possible quantum states.

7.10 Specific heats

We have discussed the internal energies and entropies of substances (mostly ideal gases) at some length. Unfortunately, these quantities cannot be directly measured. Instead, they must be inferred from other information. The thermodynamic property of substances which is the easiest to measure is, of course, the heat capacity, or specific heat. In fact, once the variation of the specific heat with temperature is known, both the internal energy and entropy can be easily reconstructed via

$$E(T,V) = \nu \int_0^T c_V(T,V)\,dT + E(0,V), \tag{7.119}$$

$$S(T,V) = \nu \int_0^T \frac{c_V(T,V)}{T}\,dT. \tag{7.120}$$

Here, use has been made of $dS = đQ/T$, and the third law of thermodynamics. Clearly, the optimum way of verifying the results of statistical thermodynamics is to compare the theoretically predicted heat capacities with the experimentally measured values.

Classical physics, in the guise of the equipartition theorem, says that each independent degree of freedom associated with a quadratic term in the energy possesses an average energy $(1/2)\,k\,T$ in thermal equilibrium at temperature T. Consider a substance made up of N molecules. Every molecular degree of freedom contributes $(1/2)\,N\,k\,T$, or $(1/2)\,\nu\,R\,T$, to the mean energy of the substance (with the tacit proviso that each degree of freedom is associated with a quadratic term in the energy). Thus, the contribution to the molar heat capacity at constant volume (we wish to avoid the complications associated with any external work done on the substance) is

$$\frac{1}{\nu}\left(\frac{\partial \overline{E}}{\partial T}\right)_V = \frac{1}{\nu}\frac{\partial[(1/2)\,\nu\,R\,T]}{\partial T} = \frac{1}{2}\,R, \tag{7.121}$$

per molecular degree of freedom. The total classical heat capacity is therefore

$$c_V = \frac{g}{2}\,R, \tag{7.122}$$

where g is the number of molecular degrees of freedom. Since large complicated molecules clearly have very many more degrees of freedom than small simple molecules, the above formula predicts that the molar heat capacities of substances made up of the former type of molecules should greatly exceed those of substances made up of the latter. In fact, the experimental heat capacities of substances containing complicated molecules are generally greater than those of substances containing simple molecules, but by nowhere near the large factor predicted by Eq. (7.122). This equation also implies that heat capacities are temperature independent. In fact, this is not the case for most substances. Experimental heat capacities generally increase with increasing temperature. These two experimental facts pose severe problems for classical physics. Incidentally, these problems were fully appreciated as far back as 1850. Stories that physicists at the end of the nineteenth century thought that classical physics explained absolutely everything are largely apocryphal.

The equipartition theorem (and the whole classical approximation) is only valid when the typical thermal energy $k\,T$ greatly exceeds the spacing between quantum energy levels. Suppose that the temperature is sufficiently low that this condition is not satisfied for one particular molecular degree of freedom. In fact, suppose that $k\,T$ is much less than the spacing between the energy levels. According to Sect. 7.9, in this situation the degree of freedom only contributes the ground-state energy, E_0, say, to the mean energy of the molecule. The ground-state energy can be a quite complicated function of the internal properties of the molecule, but is certainly not a function of the temperature, since this is a collective property of all molecules. It follows that the contribution to the molar heat capacity is

$$\frac{1}{\nu}\left(\frac{\partial[N E_0]}{\partial T}\right)_V = 0. \tag{7.123}$$

Thus, if $k\,T$ is much less than the spacing between the energy levels then the degree of freedom contributes nothing at all to the molar heat capacity. We say that this particular degree of freedom is *frozen out*. Clearly, at very low temperatures just about all degrees of freedom are frozen out. As the temperature is gradually increased, degrees of freedom successively “kick in,” and eventually contribute their full $(1/2)\,R$ to the molar heat capacity, as $k\,T$ approaches, and then greatly exceeds, the spacing between their quantum energy levels. We can use these simple ideas to explain the behaviours of most experimental heat capacities.

To make further progress, we need to estimate the typical spacing between the quantum energy levels associated with various degrees of freedom. We can

Radiation type	Frequency (Hz)	T_{rad} (°K)
Radio	$< 10^9$	< 0.05
Microwave	$10^9 - 10^{11}$	$0.05 - 5$
Infrared	$10^{11} - 10^{14}$	$5 - 5000$
Visible	5×10^{14}	2×10^4
Ultraviolet	$10^{15} - 10^{17}$	$5 \times 10^4 - 5 \times 10^6$
X-ray	$10^{17} - 10^{20}$	$5 \times 10^6 - 5 \times 10^9$
γ-ray	$> 10^{20}$	$> 5 \times 10^9$

Table 3: *Effective "temperatures" of various types of electromagnetic radiation*

do this by observing the frequency of the electromagnetic radiation emitted and absorbed during transitions between these energy levels. If the typical spacing between energy levels is ΔE then transitions between the various levels are associated with photons of frequency ν, where $h\nu = \Delta E$. We can define an *effective temperature* of the radiation via $h\nu = k T_{rad}$. If $T \gg T_{rad}$ then $kT \gg \Delta E$, and the degree of freedom makes its full contribution to the heat capacity. On the other hand, if $T \ll T_{rad}$ then $kT \ll \Delta E$, and the degree of freedom is frozen out. Table 3 lists the "temperatures" of various different types of radiation. It is clear that degrees of freedom which give rise to emission or absorption of radio or microwave radiation contribute their full $(1/2)\,R$ to the molar heat capacity at room temperature. Degrees of freedom which give rise to emission or absorption in the visible, ultraviolet, X-ray, or γ-ray regions of the electromagnetic spectrum are frozen out at room temperature. Degrees of freedom which emit or absorb infrared radiation are on the border line.

7.11 Specific heats of gases

Let us now investigate the specific heats of gases. Consider, first of all, translational degrees of freedom. Every molecule in a gas is free to move in three dimensions. If one particular molecule has mass m and momentum $\mathbf{p} = m\,\mathbf{v}$ then its kinetic energy of translation is

$$K = \frac{1}{2\,m}({p_x}^2 + {p_y}^2 + {p_z}^2). \tag{7.124}$$

The kinetic energy of other molecules does not involve the momentum **p** of this particular molecule. Moreover, the potential energy of interaction between molecules depends only on their position coordinates, and, thus, certainly does not involve **p**. Any internal rotational, vibrational, electronic, or nuclear degrees of freedom of the molecule also do not involve **p**. Hence, the essential conditions of the equipartition theorem are satisfied (at least, in the classical approximation). Since Eq. (7.124) contains three independent quadratic terms, there are clearly three degrees of freedom associated with translation (one for each dimension of space), so the translational contribution to the molar heat capacity of gases is

$$(c_V)_{\rm translation} = \frac{3}{2}\,R. \tag{7.125}$$

Suppose that our gas is contained in a cubic enclosure of dimensions L. According to Schrödinger's equation, the quantized translational energy levels of an individual molecule are given by

$$E = \frac{\hbar^2\pi^2}{2\,m\,L^2}\left({n_1}^2 + {n_2}^2 + {n_3}^2\right), \tag{7.126}$$

where n_1, n_2, and n_3 are positive integer quantum numbers. Clearly, the spacing between the energy levels can be made arbitrarily small by increasing the size of the enclosure. This implies that translational degrees of freedom can be treated classically, so that Eq. (7.125) is always valid (except very close to absolute zero). We conclude that all gases possess a minimum molar heat capacity of $(3/2)\,R$ due to the translational degrees of freedom of their constituent molecules.

The electronic degrees of freedom of gas molecules (*i.e.*, the possible configurations of electrons orbiting the atomic nuclei) typically give rise to absorption and emission in the ultraviolet or visible regions of the spectrum. It follows from Tab. 3 that electronic degrees of freedom are frozen out at room temperature. Similarly, nuclear degrees of freedom (*i.e.*, the possible configurations of protons and neutrons in the atomic nuclei) are frozen out because they are associated with absorption and emission in the X-ray and γ-ray regions of the electromagnetic spectrum. In fact, the only additional degrees of freedom we need worry about for gases are rotational and vibrational degrees of freedom. These typically give rise to absorption lines in the infrared region of the spectrum.

The rotational kinetic energy of a molecule tumbling in space can be written

$$K = \frac{1}{2}\,I_x\,\omega_x^{\,2} + \frac{1}{2}\,I_y\,\omega_y^{\,2} + \frac{1}{2}\,I_z\,\omega_z^{\,2}, \tag{7.127}$$

where the x-, y-, and z-axes are the so called *principle axes of inertia* of the molecule (these are mutually perpendicular), ω_x, ω_y, and ω_z are the angular velocities of rotation about these axes, and I_x, I_y, and I_z are the moments of inertia of the molecule about these axes. No other degrees of freedom depend on the angular velocities of rotation. Since the kinetic energy of rotation is the sum of three quadratic terms, the rotational contribution to the molar heat capacity of gases is

$$(c_V)_{\rm rotation} = \frac{3}{2}\,R, \tag{7.128}$$

according to the equipartition theorem. Note that the typical magnitude of a molecular moment of inertia is $m\,d^2$, where m is the molecular mass, and d is the typical interatomic spacing in the molecule. A special case arises if the molecule is linear (*e.g.* if the molecule is diatomic). In this case, one of the principle axes lies along the line of centers of the atoms. The moment of inertia about this axis is of order $m\,a^2$, where a is a typical nuclear dimension (remember that nearly all of the mass of an atom resides in the nucleus). Since $a \sim 10^{-5}\,d$, it follows that the moment of inertia about the line of centres is minuscule compared to the moments of inertia about the other two principle axes. In quantum mechanics, angular momentum is quantized in units of $\hbar$. The energy levels of a rigid rotator are written

$$E = \frac{\hbar^2}{2\,I}\,J(J+1), \tag{7.129}$$

where I is the moment of inertia and J is an integer. Note the inverse dependence of the spacing between energy levels on the moment of inertia. It is clear that for the case of a linear molecule, the rotational degree of freedom associated with spinning along the line of centres of the atoms is frozen out at room temperature, given the very small moment of inertia along this axis, and, hence, the very widely spaced rotational energy levels.

Classically, the vibrational degrees of freedom of a molecule are studied by standard normal mode analysis of the molecular structure. Each normal mode behaves like an independent harmonic oscillator, and, therefore, contributes R to the molar specific heat of the gas [$(1/2)\,R$ from the kinetic energy of vibration and $(1/2)\,R$ from the potential energy of vibration]. A molecule containing n atoms has $n-1$ normal modes of vibration. For instance, a diatomic molecule has just one normal mode (corresponding to periodic stretching of the bond between the two atoms). Thus, the classical contribution to the specific heat from vibrational degrees of freedom is

$$(c_V)_{\rm vibration} = (n-1)\,R. \tag{7.130}$$

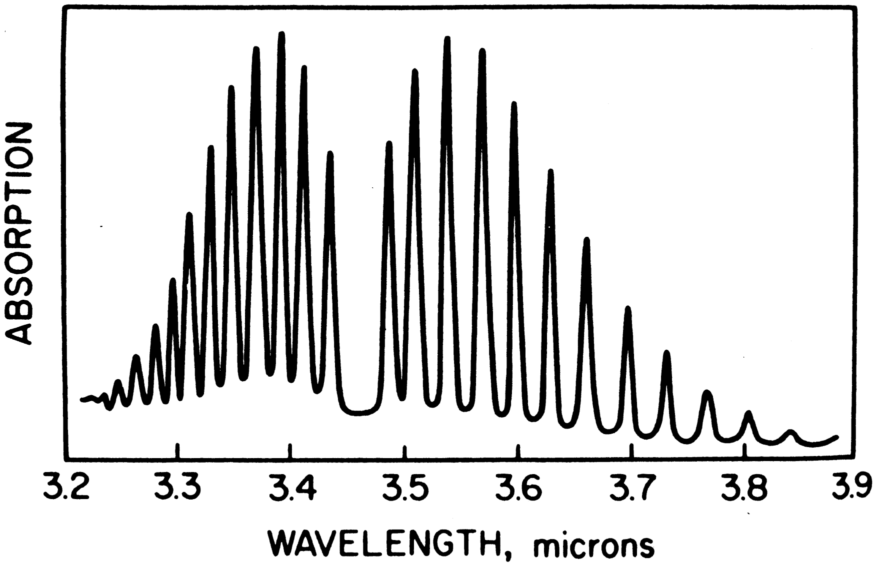

Figure 3: *The infrared vibration-absorption spectrum of H Cl.*

So, do any of the rotational and vibrational degrees of freedom actually make a contribution to the specific heats of gases at room temperature, once quantum effects are taken into consideration? We can answer this question by examining just one piece of data. Figure 3 shows the infrared absorption spectrum of Hydrogen Chloride. The absorption lines correspond to simultaneous transitions between different vibrational and rotational energy levels. Hence, this is usually called a *vibration-rotation spectrum*. The missing line at about 3.47 microns corresponds to a pure vibrational transition from the ground-state to the first excited state (pure vibrational transitions are *forbidden*: H Cl molecules always have to simultaneously change their rotational energy level if they are to couple effectively to electromagnetic radiation). The longer wavelength absorption lines correspond to vibrational transitions in which there is a simultaneous decrease in the rotational energy level. Likewise, the shorter wavelength absorption lines correspond to vibrational transitions in which there is a simultaneous increase in the rotational energy level. It is clear that the rotational energy levels are more closely spaced than the vibrational energy levels. The pure vibrational transition gives rise to absorption at about 3.47 microns, which corresponds to infrared radiation of frequency 8.5×10^{11} hertz with an associated radiation "temperature" of 4400 degrees kelvin. We conclude that the vibrational degrees of freedom of $H\,Cl$, or any other small molecule, are frozen out at room temperature. The rotational transitions split the vibrational lines by about 0.2 microns. This implies that pure rotational transitions would be associated with infrared radiation of frequency 5×10^{12} hertz and corresponding radiation "temperature" 260 degrees kelvin. We conclude that the rotational degrees of freedom of $H\,Cl$, or any other small molecule, are not frozen out at room temperature, and probably contribute the classical $(1/2)\,R$ to the molar specific heat. There is one proviso, however. Linear molecules (like $H\,Cl$) effectively only have two rotational degrees of freedom (instead of the usual three), because of the very small moment of inertia of such molecules along the line of centres of the atoms.

We are now in a position to make some predictions regarding the specific heats of various gases. Monatomic molecules only possess three translational degrees of freedom, so monatomic gases should have a molar heat capacity $(3/2)\,R = 12.47$ joules/degree/mole. The ratio of specific heats $\gamma = c_p/c_V = (c_V + R)/c_V$ should be $5/3 = 1.667$. It can be seen from Tab. 2 that both of these predictions are borne out pretty well for Helium and Argon. Diatomic molecules possess three translational degrees of freedom and two rotational degrees of freedom (all other degrees of freedom are frozen out at room temperature). Thus, diatomic gases should have a molar heat capacity $(5/2)\,R = 20.8$ joules/degree/mole. The ratio of specific heats should be $7/5 = 1.4$. It can be seen from Tab. 2 that these are pretty accurate predictions for Nitrogen and Oxygen. The freezing out of vibrational degrees of freedom becomes gradually less effective as molecules become heavier and more complex. This is partly because such molecules are generally less stable, so the force constant κ is reduced, and partly because the molecular mass is increased. Both these effect reduce the frequency of vibration of the molecular normal modes [see Eq. (7.104)], and, hence, the spacing between vibrational energy levels [see Eq. (7.103)]. This accounts for the obviously non-classical [*i.e.*, not a multiple of $(1/2)\,R$] specific heats of Carbon Dioxide and Ethane in Tab. 2. In both molecules, vibrational degrees of freedom contribute to the molar specific heat (but not the full R because the temperature is not high enough).

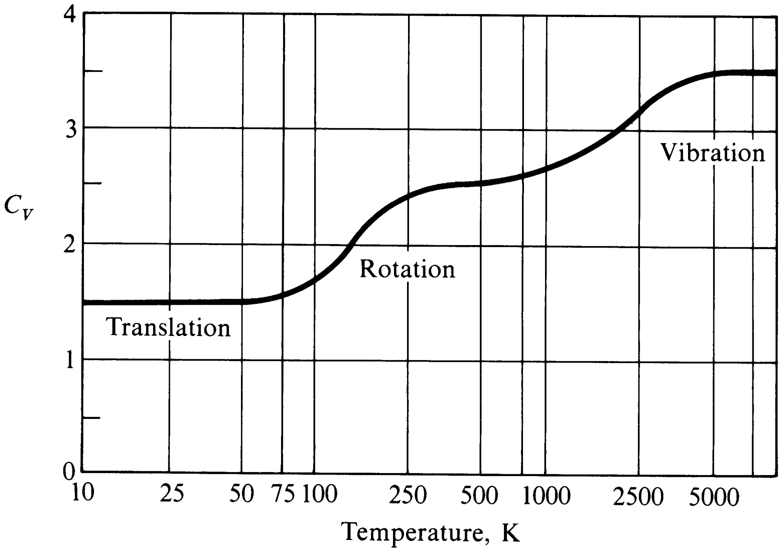

Figure 4: *The molar heat capacity at constant volume (in units of* R*) of gaseous* H_2 *versus temperature.*

Figure 4 shows the variation of the molar heat capacity at constant volume (in units of R) of gaseous hydrogen with temperature. The expected contribution from the translational degrees of freedom is $(3/2)\,R$ (there are three translational degrees of freedom per molecule). The expected contribution at high temperatures from the rotational degrees of freedom is R (there are effectively two rotational degrees of freedom per molecule). Finally, the expected contribution at high temperatures from the vibrational degrees of freedom is R (there is one vibrational degree of freedom per molecule). It can be seen that as the temperature rises the rotational, and then the vibrational, degrees of freedom eventually make their full classical contributions to the heat capacity.

7.12 Specific heats of solids

Consider a simple solid containing N atoms. Now, atoms in solids cannot translate (unlike those in gases), but are free to vibrate about their equilibrium positions. Such vibrations are called *lattice vibrations*, and can be thought of as sound waves propagating through the crystal lattice. Each atom is specified by three independent position coordinates, and three conjugate momentum coordinates. Let us only consider small amplitude vibrations. In this case, we can expand the potential energy of interaction between the atoms to give an expression which is quadratic in the atomic displacements from their equilibrium positions. It is always possible to perform a *normal mode analysis* of the oscillations. In effect, we can find $3\,N$ independent modes of oscillation of the solid. Each mode has its own particular oscillation frequency, and its own particular pattern of atomic displacements. Any general oscillation can be written as a linear combination of these *normal modes*. Let q_i be the (appropriately normalized) amplitude of the ith normal mode, and p_i the momentum conjugate to this coordinate. In *normal mode coordinates*, the total energy of the lattice vibrations takes the particularly simple form

$$E = \frac{1}{2}\sum_{i=1}^{3N}({p_i}^2 + {\omega_i}^2 {q_i}^2), \tag{7.131}$$

where ω_i is the (angular) oscillation frequency of the ith normal mode. It is clear that in normal mode coordinates, the linearized lattice vibrations are equivalent to $3\,N$ independent harmonic oscillators (of course, each oscillator corresponds to a different normal mode).

The typical value of ω_i is the (angular) frequency of a sound wave propagating through the lattice. Sound wave frequencies are far lower than the typical vibration frequencies of gaseous molecules. In the latter case, the mass involved in the vibration is simply that of the molecule, whereas in the former case the mass involved is that of very many atoms (since lattice vibrations are non-localized). The strength of interatomic bonds in gaseous molecules is similar to those in solids, so we can use the estimate $\omega \sim \sqrt{\kappa/m}$ (κ is the force constant which measures the strength of interatomic bonds, and m is the mass involved in the oscillation) as proof that the typical frequencies of lattice vibrations are very much less than the vibration frequencies of simple molecules. It follows from $\Delta E = \hbar\,\omega$ that the quantum energy levels of lattice vibrations are far more closely spaced than the vibrational energy levels of gaseous molecules. Thus, it is likely (and is, indeed, the case) that lattice vibrations are not frozen out at room temperature, but, instead, make their full classical contribution to the molar specific heat of the solid.

If the lattice vibrations behave classically then, according to the equipartition theorem, each normal mode of oscillation has an associated mean energy $k\,T$ in equilibrium at temperature T $[(1/2)\,k\,T$ resides in the kinetic energy of the oscillation, and $(1/2)\,k\,T$ resides in the potential energy$]$. Thus, the mean internal energy per mole of the solid is

$$\overline{E} = 3\,N\,k\,T = 3\,\nu\,R\,T. \tag{7.132}$$

It follows that the molar heat capacity at constant volume is

$$c_V = \frac{1}{\nu}\left(\frac{\partial\overline{E}}{\partial T}\right)_V = 3\,R \tag{7.133}$$

for solids. This gives a value of 24.9 joules/mole/degree. In fact, at room temperature most solids (in particular, metals) have heat capacities which lie remarkably close to this value. This fact was discovered experimentally by Dulong and Petite at the beginning of the nineteenth century, and was used to make some of the first crude estimates of the molecular weights of solids (if we know the molar heat capacity of a substance then we can easily work out how much of it corresponds to one mole, and by weighing this amount, and then dividing the result by Avogadro's number, we can obtain an estimate of the molecular weight). Table 4 lists the experimental molar heat capacities c_p at constant pressure for various solids. The heat capacity at constant volume is somewhat less than the constant pressure value, but not by much, because solids are fairly incompressible. It can be seen that *Dulong and Petite's law* (*i.e.*, that all solids have a molar heat capacities close to 24.9 joules/mole/degree) holds pretty well for metals. However, the law fails badly for diamond. This is not surprising. As is well-known, diamond is an extremely hard substance, so its intermolecular bonds must be very strong, suggesting that the force constant κ is large. Diamond is also a fairly low density

Solid	c_p	Solid	c_p
Copper	24.5	Aluminium	24.4
Silver	25.5	Tin (white)	26.4
Lead	26.4	Sulphur (rhombic)	22.4
Zinc	25.4	Carbon (diamond)	6.1

Table 4: *Values of* c_p *(joules/mole/degree) for some solids at* $T = 298^\circ$ *K. From Reif.*

substance, so the mass m involved in lattice vibrations is comparatively small. Both these facts suggest that the typical lattice vibration frequency of diamond ($\omega \sim \sqrt{\kappa/m}$) is high. In fact, the spacing between the different vibration energy levels (which scales like $\hbar\,\omega$) is sufficiently large in diamond for the vibrational degrees of freedom to be largely frozen out at room temperature. This accounts for the anomalously low heat capacity of diamond in Tab. 4.

Dulong and Petite's law is essentially a high temperature limit. The molar heat capacity cannot remain a constant as the temperature approaches absolute zero, since, by Eq. (7.120), this would imply $S \rightarrow \infty$, which violates the third law of thermodynamics. We can make a crude model of the behaviour of c_V at low temperatures by assuming that all the normal modes oscillate at the same frequency, ω, say. This approximation was first employed by Einstein in a paper published in 1907. According to Eq. (7.131), the solid acts like a set of 3N independent oscillators which, making use of Einstein's approximation, all vibrate at the same frequency. We can use the quantum mechanical result (7.111) for a single oscillator to write the mean energy of the solid in the form

$$\overline{E} = 3\,N\,\hbar\,\omega\left(\frac{1}{2} + \frac{1}{\exp(\beta\,\hbar\,\omega) - 1}\right). \tag{7.134}$$

The molar heat capacity is defined

$$c_V = \frac{1}{\nu}\left(\frac{\partial \overline{E}}{\partial T}\right)_V = \frac{1}{\nu}\left(\frac{\partial \overline{E}}{\partial \beta}\right)_V \frac{\partial \beta}{\partial T} = -\frac{1}{\nu\,k\,T^2}\left(\frac{\partial \overline{E}}{\partial \beta}\right)_V, \tag{7.135}$$

giving

$$c_V = -\frac{3\,N_A\,\hbar\,\omega}{k\,T^2}\left[-\frac{\exp(\beta\,\hbar\,\omega)\,\hbar\,\omega}{[\exp(\beta\,\hbar\,\omega) - 1]^2}\right], \tag{7.136}$$

which reduces to

$$c_V = 3\,R\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T)-1]^2}. \tag{7.137}$$

Here,

$$\theta_E = \frac{\hbar\,\omega}{k} \tag{7.138}$$

is called the *Einstein temperature*. If the temperature is sufficiently high that $T \gg \theta_E$ then $k\,T \gg \hbar\,\omega$, and the above expression reduces to $c_V = 3\,R$, after expansion of the exponential functions. Thus, the law of Dulong and Petite is recovered for temperatures significantly in excess of the Einstein temperature. On the other hand, if the temperature is sufficiently low that $T \ll \theta_E$ then the exponential factors in Eq. (7.137) become very much larger than unity, giving

$$c_V \sim 3\,R\left(\frac{\theta_E}{T}\right)^2 \exp(-\theta_E/T). \tag{7.139}$$

So, in this simple model the specific heat approaches zero exponentially as $T \rightarrow 0$.

In reality, the specific heats of solids do not approach zero quite as quickly as suggested by Einstein's model when $T \rightarrow 0$. The experimentally observed low temperature behaviour is more like $c_V \propto T^3$ (see Fig. 6). The reason for this discrepancy is the crude approximation that all normal modes have the same frequency. In fact, long wavelength modes have lower frequencies than short wavelength modes, so the former are much harder to freeze out than the latter (because the spacing between quantum energy levels, $\hbar\,\omega$, is smaller in the former case). The molar heat capacity does not decrease with temperature as rapidly as suggested by Einstein's model because these long wavelength modes are able to make a significant contribution to the heat capacity even at very low temperatures. A more realistic model of lattice vibrations was developed by the Dutch physicist Peter Debye in 1912. In the Debye model, the frequencies of the normal modes of vibration are estimated by treating the solid as an isotropic continuous medium. This approach is reasonable because the only modes which really matter at low temperatures are the long wavelength modes: *i.e.*, those whose wavelengths greatly exceed the interatomic spacing. It is plausible that these modes are not particularly sensitive to the discrete nature of the solid: *i.e.*, the fact that it is made up of atoms rather than being continuous.

Consider a sound wave propagating through an isotropic continuous medium. The disturbance varies with position vector **r** and time t like $\exp[-i\,(\mathbf{k}\cdot\mathbf{r}-\omega\,t)]$, where the wave-vector **k** and the frequency of oscillation ω satisfy the dispersion relation for sound waves in an isotropic medium:

$$\omega = k\,c_s. \tag{7.140}$$

Here, c_s is the speed of sound in the medium. Suppose, for the sake of argument, that the medium is periodic in the x-, y-, and z-directions with periodicity lengths L_x, L_y, and L_z, respectively. In order to maintain periodicity we need

$$k_x\,(x+L_x) = k_x\,x + 2\,\pi\,n_x, \tag{7.141}$$

where n_x is an integer. There are analogous constraints on k_y and k_z. It follows that in a periodic medium the components of the wave-vector are quantized, and can only take the values

$$k_x = \frac{2\pi}{L_x}\,n_x, \tag{7.142}$$

$$k_y = \frac{2\pi}{L_y}\,n_y, \tag{7.143}$$

$$k_z = \frac{2\pi}{L_z}\,n_z, \tag{7.144}$$

where n_x, n_y, and n_z are all integers. It is assumed that L_x, L_y, and L_z are macroscopic lengths, so the allowed values of the components of the wave-vector are very closely spaced. For given values of k_y and k_z, the number of allowed values of k_x which lie in the range k_x to $k_x + dk_x$ is given by

$$\Delta n_x = \frac{L_x}{2\pi}\,dk_x. \tag{7.145}$$

It follows that the number of allowed values of **k** (*i.e.*, the number of allowed modes) when k_x lies in the range k_x to k_x+dk_x, k_y lies in the range k_y to k_y+dk_y, and k_z lies in the range k_z to $k_z + dk_z$, is

$$\rho\,d^3\mathbf{k} = \left(\frac{L_x}{2\pi}\,dk_x\right)\left(\frac{L_y}{2\pi}\,dk_y\right)\left(\frac{L_z}{2\pi}\,dk_z\right) = \frac{V}{(2\pi)^3}\,dk_x\,dk_y\,dk_z, \tag{7.146}$$

where $V = L_x L_y L_z$ is the periodicity volume, and $d^3\mathbf{k} \equiv dk_x\, dk_y\, dk_z$. The quantity ρ is called the density of modes. Note that this density is independent of $\mathbf{k}$, and proportional to the periodicity volume. Thus, the density of modes *per unit volume* is a constant independent of the magnitude or shape of the periodicity volume. The density of modes per unit volume when the *magnitude* of $\mathbf{k}$ lies in the range k to $k+dk$ is given by multiplying the density of modes per unit volume by the "volume" in $\mathbf{k}$-space of the spherical shell lying between radii k and $k+dk$. Thus,

$$\rho_k\, dk = \frac{4\pi k^2\, dk}{(2\pi)^3} = \frac{k^2}{2\pi^2}\, dk. \tag{7.147}$$

Consider an isotropic continuous medium of volume V. According to the above relation, the number of normal modes whose frequencies lie between ω and $\omega + d\omega$ (which is equivalent to the number of modes whose k values lie in the range ω/c_s to $\omega/c_s + d\omega/c_s$) is

$$\sigma_c(\omega)\, d\omega = 3\,\frac{k^2\, V}{2\pi^2}\, dk = 3\,\frac{V}{2\pi^2\, {c_s}^3}\, \omega^2\, d\omega. \tag{7.148}$$

The factor of 3 comes from the three possible polarizations of sound waves in solids. For every allowed wavenumber (or frequency) there are two independent torsional modes, where the displacement is perpendicular to the direction of propagation, and one longitudinal mode, where the displacement is parallel to the direction of propagation. Torsion waves are vaguely analogous to electromagnetic waves (these also have two independent polarizations). The longitudinal mode is very similar to the compressional sound wave in gases. Of course, torsion waves can not propagate in gases because gases have no resistance to deformation without change of volume.

The Debye approach consists in approximating the actual density of normal modes $\sigma(\omega)$ by the density in a continuous medium $\sigma_c(\omega)$, not only at low frequencies (long wavelengths) where these should be nearly the same, but also at higher frequencies where they may differ substantially. Suppose that we are dealing with a solid consisting of N atoms. We know that there are only $3\,N$ independent normal modes. It follows that we must cut off the density of states above some critical frequency, ω_D say, otherwise we will have too many modes.

Thus, in the Debye approximation the density of normal modes takes the form

$$\begin{aligned} \sigma_D(\omega) &= \sigma_c(\omega) \quad \text{for } \omega < \omega_D \\ \sigma_D(\omega) &= 0 \quad\quad\;\; \text{for } \omega > \omega_D. \end{aligned} \tag{7.149}$$

Here, ω_D is the *Debye frequency*. This critical frequency is chosen such that the total number of normal modes is $3\,N$, so

$$\int_0^\infty \sigma_D(\omega)\,d\omega = \int_0^{\omega_D} \sigma_c(\omega)\,d\omega = 3\,N. \tag{7.150}$$

Substituting Eq. (7.148) into the previous formula yields

$$\frac{3V}{2\pi^2\,{c_s}^3}\int_0^{\omega_D} \omega^2\,d\omega = \frac{V}{2\pi^2\,{c_s}^3}\,\omega_D^3 = 3\,N. \tag{7.151}$$

This implies that

$$\omega_D = c_s\left(6\pi^2\,\frac{N}{V}\right)^{1/3}. \tag{7.152}$$

Thus, the Debye frequency depends only on the sound velocity in the solid and the number of atoms per unit volume. The wavelength corresponding to the Debye frequency is $2\pi\,c_s/\omega_D$, which is clearly on the order of the interatomic spacing $a \sim (V/N)^{1/3}$. It follows that the cut-off of normal modes whose frequencies exceed the Debye frequency is equivalent to a cut-off of normal modes whose wavelengths are less than the interatomic spacing. Of course, it makes physical sense that such modes should be absent.

Figure 5 compares the actual density of normal modes in diamond with the density predicted by Debye theory. Not surprisingly, there is not a particularly strong resemblance between these two curves, since Debye theory is highly idealized. Nevertheless, both curves exhibit sharp cut-offs at high frequencies, and coincide at low frequencies. Furthermore, the areas under both curves are the same. As we shall see, this is sufficient to allow Debye theory to correctly account for the temperature variation of the specific heat of solids at low temperatures.

We can use the quantum mechanical expression for the mean energy of a single oscillator, Eq. (7.111), to calculate the mean energy of lattice vibrations in the

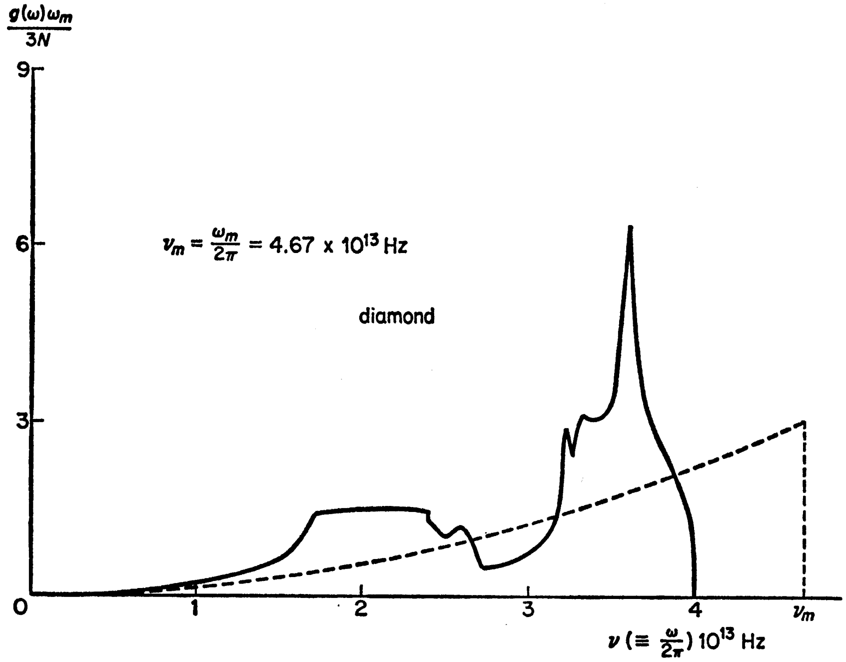

Figure 5: *The true density of normal modes in diamond compared with the density of normal modes predicted by Debye theory. From C.B. Walker, Phys. Rev.* **103**, *547 (1956).*

Debye approximation. We obtain

$$\overline{E} = \int_0^\infty \sigma_D(\omega)\,\hbar\,\omega\left(\frac{1}{2} + \frac{1}{\exp(\beta\,\hbar\,\omega) - 1}\right)d\omega. \tag{7.153}$$

According to Eq. (7.135), the molar heat capacity takes the form

$$c_V = \frac{1}{\nu\,k\,T^2}\int_0^\infty \sigma_D(\omega)\,\hbar\,\omega\left[\frac{\exp(\beta\,\hbar\,\omega)\,\hbar\,\omega}{[\exp(\beta\,\hbar\,\omega) - 1]^2}\right]d\omega. \tag{7.154}$$

Substituting in Eq. (7.149), we find that

$$c_V = \frac{k}{\nu}\int_0^{\omega_D}\frac{\exp(\beta\,\hbar\,\omega)\,(\beta\,\hbar\,\omega)^2}{[\exp(\beta\,\hbar\,\omega) - 1]^2}\,\frac{3\,V}{2\pi^2\,c_s^{\,3}}\,\omega^2\,d\omega, \tag{7.155}$$

giving

$$c_V = \frac{3\,V\,k}{2\pi^2\,\nu\,(c_s\,\beta\,\hbar)^3}\int_0^{\beta\,\hbar\,\omega_D}\frac{\exp x}{(\exp x - 1)^2}\,x^4\,dx, \tag{7.156}$$

in terms of the dimensionless variable $x = \beta\,\hbar\,\omega$. According to Eq. (7.152), the volume can be written

$$V = 6\,\pi^2\,N\left(\frac{c_s}{\omega_D}\right)^3, \tag{7.157}$$

so the heat capacity reduces to

$$c_V = 3R\, f_D(\beta\, \hbar\, \omega_D) = 3\, R\, f_D(\theta_D/T), \tag{7.158}$$

where the *Debye function* is defined

$$f_D(y) \equiv \frac{3}{y^3} \int_0^y \frac{\exp x}{(\exp x - 1)^2}\, x^4\, dx. \tag{7.159}$$

We have also defined the *Debye temperature* θ_D as

$$k\, \theta_D = \hbar\, \omega_D. \tag{7.160}$$

Consider the asymptotic limit in which $T \gg \theta_D$. For small y, we can approximate $\exp x$ as $1 + x$ in the integrand of Eq. (7.159), so that

$$f_D(y) \to \frac{3}{y^3} \int_0^y x^2\, dx = 1. \tag{7.161}$$

Thus, if the temperature greatly exceeds the Debye temperature we recover the law of Dulong and Petite that $c_V = 3\, R$. Consider, now, the asymptotic limit in which $T \ll \theta_D$. For large y,

$$\int_0^y \frac{\exp x}{(\exp x - 1)^2}\, x^4\, dx \simeq \int_0^\infty \frac{\exp x}{(\exp x - 1)^2}\, x^4\, dx = \frac{4\pi^4}{15}. \tag{7.162}$$

The latter integration is standard (if rather obscure), and can be looked up in any (large) reference book on integration. Thus, in the low temperature limit

$$f_D(y) \to \frac{4\pi^4}{5} \frac{1}{y^3}. \tag{7.163}$$

This yields

$$c_V \simeq \frac{12\pi^4}{5} R \left(\frac{T}{\theta_D}\right)^3 \tag{7.164}$$

in the limit $T \ll \theta_D$: *i.e.*, c_V varies with temperature like T^3.

The fact that c_V goes like T^3 at low temperatures is quite well verified experimentally, although it is sometimes necessary to go to temperatures as low as

Solid	θ_D from low temp.	θ_D from sound speed
Na Cl	308	320
K Cl	230	246
Ag	225	216
Zn	308	305

Table 5: *Comparison of Debye temperatures (in degrees kelvin) obtained from the low temperature behaviour of the heat capacity with those calculated from the sound speed. From C. Kittel, Introduction to solid-state physics, 2nd Ed. (John Wiley & Sons, New York NY, 1956).*

$0.02\,\theta_D$ to obtain this asymptotic behaviour. Theoretically, θ_D should be calculable from Eq. (7.152) in terms of the sound speed in the solid and the molar volume. Table 5 shows a comparison of Debye temperatures evaluated by this means with temperatures obtained empirically by fitting the law (7.164) to the low temperature variation of the heat capacity. It can be seen that there is fairly good agreement between the theoretical and empirical Debye temperatures. This suggests that the Debye theory affords a good, thought not perfect, representation of the behaviour of c_V in solids over the entire temperature range.

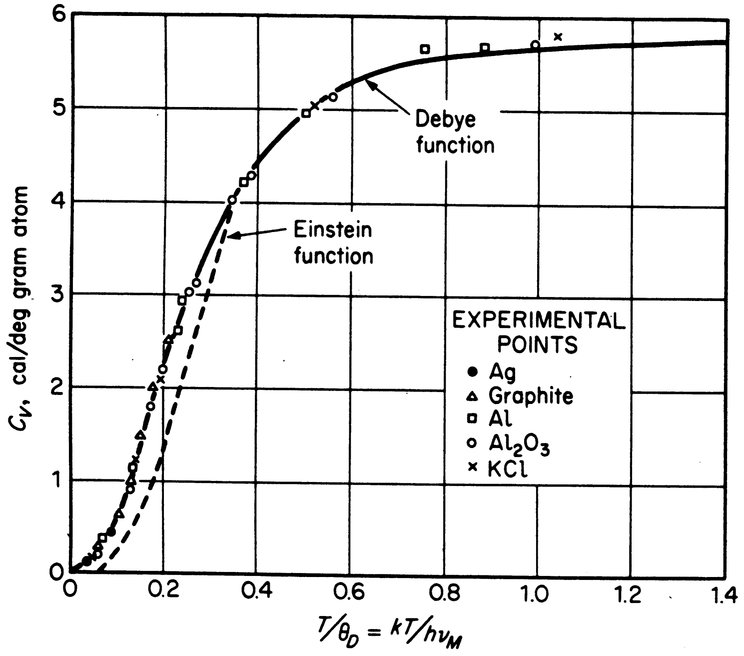

Figure 6: *The molar heat capacity of various solids.*

Finally, Fig. 6 shows the actual temperature variation of the molar heat capacities of various solids as well as that predicted by Debye's theory. The prediction of Einstein's theory is also show for the sake of comparison. Note that 24.9 joules/mole/degree is about 6 calories/gram-atom/degree (the latter are chemist's units).

7.13 The Maxwell distribution

Consider a molecule of mass m in a gas which is sufficiently dilute for the intermolecular forces to be negligible (*i.e.*, an ideal gas). The energy of the molecule is written

$$\epsilon = \frac{\mathbf{p}^2}{2\,m} + \epsilon^{\rm int}, \tag{7.165}$$

where $\mathbf{p}$ is its momentum vector, and $\epsilon^{\rm int}$ is its internal (*i.e.*, non-translational) energy. The latter energy is due to molecular rotation, vibration, *etc*. Translational degrees of freedom can be treated classically to an excellent approximation, whereas internal degrees of freedom usually require a quantum mechanical approach. Classically, the probability of finding the molecule in a given internal state with a position vector in the range $\mathbf{r}$ to $\mathbf{r} + d\mathbf{r}$, and a momentum vector in the range $\mathbf{p}$ to $\mathbf{p} + d\mathbf{p}$, is proportional to the number of cells (of "volume" h_0) contained in the corresponding region of phase-space, weighted by the Boltzmann factor. In fact, since classical phase-space is divided up into *uniform* cells, the number of cells is just proportional to the "volume" of the region under consideration. This "volume" is written $d^3\mathbf{r}\,d^3\mathbf{p}$. Thus, the probability of finding the molecule in a given internal state s is

$$P_s(\mathbf{r},\mathbf{p})\,d^3\mathbf{r}\,d^3\mathbf{p} \propto \exp(-\beta\,p^2/2\,m)\exp(-\beta\,\epsilon_s^{\rm int})\;d^3\mathbf{r}\,d^3\mathbf{p}, \tag{7.166}$$

where P_s is a probability density defined in the usual manner. The probability $P(\mathbf{r},\mathbf{p})\,d^3\mathbf{r}\,d^3\mathbf{p}$ of finding the molecule in *any* internal state with position and momentum vectors in the specified range is obtained by summing the above expression over all possible internal states. The sum over $\exp(-\beta\,\epsilon_s^{\rm int})$ just contributes a constant of proportionality (since the internal states do not depend on $\mathbf{r}$ or $\mathbf{p}$), so

$$P(\mathbf{r},\mathbf{p})\,d^3\mathbf{r}\,d^3\mathbf{p} \propto \exp(-\beta\,p^2/2m)\;d^3\mathbf{r}\,d^3\mathbf{p}. \tag{7.167}$$

Of course, we can multiply this probability by the total number of molecules N in order to obtain the mean number of molecules with position and momentum vectors in the specified range.

Suppose that we now want to determine $f(\mathbf{r}, \mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v}$: *i.e.*, the mean number of molecules with positions between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$, and velocities in the range $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$. Since $\mathbf{v} = \mathbf{p}/m$, it is easily seen that

$$f(\mathbf{r}, \mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = C \exp(-\beta\, m v^2/2)\, d^3\mathbf{r}\, d^3\mathbf{v}, \tag{7.168}$$

where C is a constant of proportionality. This constant can be determined by the condition

$$\int_{(\mathbf{r})}\int_{(\mathbf{v})} f(\mathbf{r}, \mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = N : \tag{7.169}$$

i.e., the sum over molecules with all possible positions and velocities gives the total number of molecules, N. The integral over the molecular position coordinates just gives the volume V of the gas, since the Boltzmann factor is independent of position. The integration over the velocity coordinates can be reduced to the product of three identical integrals (one for v_x, one for v_y, and one for v_z), so we have

$$C\, V \left[\int_{-\infty}^{\infty} \exp(-\beta\, m {v_z}^2/2)\, dv_z\right]^3 = N. \tag{7.170}$$

Now,

$$\int_{-\infty}^{\infty} \exp(-\beta\, m {v_z}^2/2)\, dv_z = \sqrt{\frac{2}{\beta\, m}} \int_{-\infty}^{\infty} \exp(-y^2)\, dy = \sqrt{\frac{2\pi}{\beta\, m}}, \tag{7.171}$$

so $C = (N/V)(\beta\, m/2\pi)^{3/2}$. Thus, the properly normalized distribution function for molecular velocities is written

$$f(\mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = n \left(\frac{m}{2\pi\, k\, T}\right)^{3/2} \exp(-m v^2/2\, k\, T)\, d^3\mathbf{r}\, d^3\mathbf{v}. \tag{7.172}$$

Here, $n = N/V$ is the number density of the molecules. We have omitted the variable $\mathbf{r}$ in the argument of f, since f clearly does not depend on position. In other words, the distribution of molecular velocities is uniform in space. This is hardly surprising, since there is nothing to distinguish one region of space from another in our calculation. The above distribution is called the *Maxwell velocity distribution*, because it was discovered by James Clark Maxwell in the middle of the nineteenth century. The average number of molecules *per unit volume* with velocities in the range $\mathbf{v}$ to $\mathbf{v} + d\mathbf{v}$ is obviously $f(\mathbf{v})\, d^3\mathbf{v}$.

Let us consider the distribution of a given component of velocity: the z-component, say. Suppose that $g(v_z)\, dv_z$ is the average number of molecules per unit volume with the z-component of velocity in the range v_z to $v_z + dv_z$, irrespective of the values of their other velocity components. It is fairly obvious that this distribution is obtained from the Maxwell distribution by summing (integrating actually) over all possible values of v_x and v_y, with v_z in the specified range. Thus,

$$g(v_z)\, dv_z = \int_{(v_x)}\int_{(v_y)} f(\mathbf{v})\, d^3\mathbf{v}. \tag{7.173}$$

This gives

$$\begin{aligned} g(v_z)\, dv_z &= n\left(\frac{m}{2\pi\, k\, T}\right)^{3/2}\int_{(v_x)}\int_{(v_y)} \exp[-(m/2\, k\, T)({v_x}^2 + {v_y}^2 + {v_z}^2)]\, dv_x\, dv_y\, dv_z \\ &= n\left(\frac{m}{2\pi\, k\, T}\right)^{3/2} \exp(-m\, {v_z}^2/2\, k\, T)\left[\int_{-\infty}^{\infty} \exp(-m\, {v_x}^2/2\, k\, T)\right]^2 \\ &= n\left(\frac{m}{2\pi\, k\, T}\right)^{3/2} \exp(-m\, {v_z}^2/2\, k\, T)\left(\sqrt{\frac{2\pi\, k\, T}{m}}\right)^2, \end{aligned} \tag{7.174}$$

or

$$g(v_z)\, dv_z = n\left(\frac{m}{2\pi\, k\, T}\right)^{1/2} \exp(-m\, {v_z}^2/2\, k\, T)\, dv_z. \tag{7.175}$$

Of course, this expression is properly normalized, so that

$$\int_{-\infty}^{\infty} g(v_z)\, dv_z = n. \tag{7.176}$$

It is clear that each component (since there is nothing special about the z-component) of the velocity is distributed with a Gaussian probability distribution (see Sect. 2), centred on a mean value

$$\overline{v_z} = 0, \tag{7.177}$$

with variance

$$\overline{v_z^{\,2}} = \frac{k\,T}{m}. \tag{7.178}$$

Equation (7.177) implies that each molecule is just as likely to be moving in the plus z-direction as in the minus z-direction. Equation (7.178) can be rearranged to give

$$\overline{\frac{1}{2}\,m\,v_z^{\,2}} = \frac{1}{2}\,k\,T, \tag{7.179}$$

in accordance with the equipartition theorem.

Note that Eq. (7.172) can be rewritten

$$\frac{f(\mathbf{v})\,d^3\mathbf{v}}{n} = \left[\frac{g(v_x)\,dv_x}{n}\right]\left[\frac{g(v_y)\,dv_y}{n}\right]\left[\frac{g(v_z)\,dv_z}{n}\right], \tag{7.180}$$

where $g(v_x)$ and $g(v_y)$ are defined in an analogous way to $g(v_z)$. Thus, the probability that the velocity lies in the range $\mathbf{v}$ to $\mathbf{v} + d\mathbf{v}$ is just equal to the product of the probabilities that the velocity components lie in their respective ranges. In other words, the individual velocity components act like statistically independent variables.

Suppose that we now want to calculate $F(v)\,dv$: *i.e.*, the average number of molecules per unit volume with a speed $v = |\mathbf{v}|$ in the range v to $v + dv$. It is obvious that we can obtain this quantity by adding up all molecules with speeds in this range, irrespective of the *direction* of their velocities. Thus,

$$F(v)\,dv = \int f(\mathbf{v})\,d^3\mathbf{v}, \tag{7.181}$$

where the integral extends over all velocities satisfying

$$v < |\mathbf{v}| < v + dv. \tag{7.182}$$

This inequality is satisfied by a spherical shell of radius v and thickness dv in velocity space. Since $f(\mathbf{v})$ only depends on $|v|$, so $f(\mathbf{v}) \equiv f(v)$, the above integral is just $f(v)$ multiplied by the volume of the spherical shell in velocity space. So,

$$F(v)\,dv = 4\pi f(v)\,v^2\,dv, \tag{7.183}$$

which gives

$$F(v)\,dv = 4\pi n \left(\frac{m}{2\pi k T}\right)^{3/2} v^2 \exp(-m v^2/2\,k T)\,dv. \tag{7.184}$$

This is the famous *Maxwell distribution of molecular speeds*. Of course, it is properly normalized, so that

$$\int_0^\infty F(v)\,dv = n. \tag{7.185}$$

Note that the Maxwell distribution exhibits a maximum at some non-zero value of v. The reason for this is quite simple. As v increases, the Boltzmann factor *decreases*, but the volume of phase-space available to the molecule (which is proportional to v^2) *increases*: the net result is a distribution with a non-zero maximum.

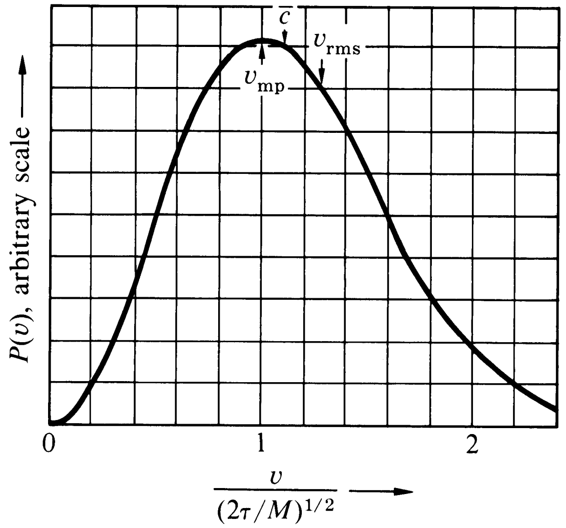

Figure 7: *The Maxwell velocity distribution as a function of molecular speed in units of the most probable speed ($v_{\rm mp}$) . Also shown are the mean speed ($\bar{c}$) and the root mean square speed ($v_{\rm rms}$).*

The mean molecular speed is given by

$$\bar{v} = \frac{1}{n}\int_0^\infty F(v)\,v\,dv. \tag{7.186}$$

Thus, we obtain

$$\bar{v} = 4\pi \left(\frac{m}{2\pi k T}\right)^{3/2} \int_0^\infty v^3 \exp(-m v^2/2\,k T)\,dv, \tag{7.187}$$

or

$$\bar{v} = 4\pi\left(\frac{m}{2\pi\,k\,T}\right)^{3/2}\left(\frac{2\,k\,T}{m}\right)^{2}\int_0^\infty y^3\exp(-y^2)\,dy. \tag{7.188}$$

Now

$$\int_0^\infty y^3\exp(-y^2)\,dy = \frac{1}{2}, \tag{7.189}$$

so

$$\bar{v} = \sqrt{\frac{8}{\pi}\frac{k\,T}{m}}. \tag{7.190}$$

A similar calculation gives

$$v_{\rm rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3\,k\,T}{m}}. \tag{7.191}$$

However, this result can also be obtained from the equipartition theorem. Since

$$\overline{\frac{1}{2}\,m\,v^2} = \overline{\frac{1}{2}\,m\,(v_x^{\,2}+v_y^{\,2}+v_z^{\,2})} = 3\left(\frac{1}{2}\,k\,T\right), \tag{7.192}$$

then Eq. (7.191) follows immediately. It is easily demonstrated that the most probable molecular speed (*i.e.*, the maximum of the Maxwell distribution function) is

$$\tilde{v} = \sqrt{\frac{2\,k\,T}{m}}. \tag{7.193}$$

The speed of sound in an ideal gas is given by

$$c_s = \sqrt{\frac{\gamma\,p}{\rho}}, \tag{7.194}$$

where γ is the ratio of specific heats. This can also be written

$$c_s = \sqrt{\frac{\gamma\,k\,T}{m}}, \tag{7.195}$$

since $p = n\,k\,T$ and $\rho = n\,m$. It is clear that the various average speeds which we have just calculated are all of order the sound speed (*i.e.*, a few hundred meters per second at room temperature). In ordinary air ($\gamma = 1.4$) the sound speed is about 84% of the most probable molecular speed, and about 74% of the mean molecular speed. Since sound waves ultimately propagate via molecular motion, it makes sense that they travel at slightly less than the most probable and mean molecular speeds.

Figure 7 shows the Maxwell velocity distribution as a function of molecular speed in units of the most probable speed. Also shown are the mean speed and the root mean square speed.

It is difficult to directly verify the Maxwell velocity distribution. However, this distribution can be verified indirectly by measuring the velocity distribution of atoms exiting from a small hole in an oven. The velocity distribution of the escaping atoms is closely related to, but slightly different from, the velocity distribution inside the oven, since high velocity atoms escape more readily than low velocity atoms. In fact, the predicted velocity distribution of the escaping atoms varies like $v^3 \exp(-m v^2/2\,k\,T)$, in contrast to the $v^2 \exp(-m v^2/2\,k\,T)$ variation of the velocity distribution inside the oven. Figure 8 compares the measured and theoretically predicted velocity distributions of potassium atoms escaping from an oven at 157° C. There is clearly very good agreement between the two.

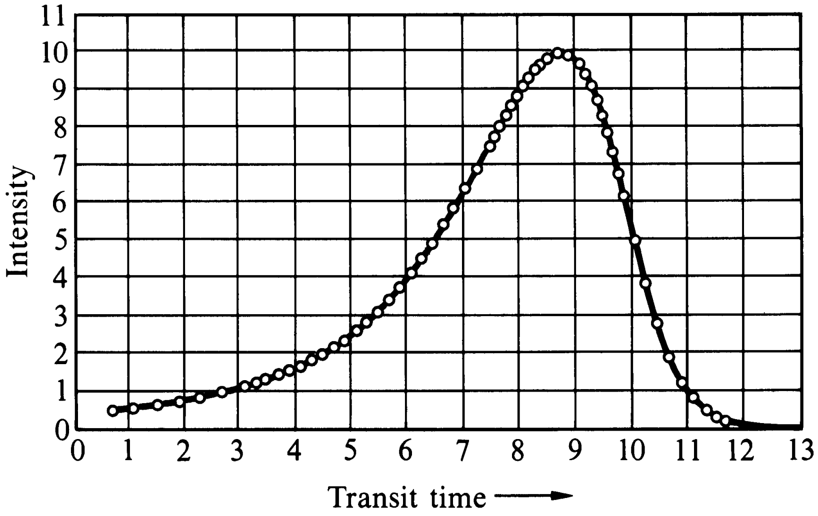

Figure 8: *Comparison of the measured and theoretically predicted velocity distributions of potassium atoms escaping from an oven at* 157° *C. Here, the measured transit time is directly proportional to the atomic speed.*

8 Quantum statistics

8.1 Introduction

Previously, we investigated the statistical thermodynamics of ideal gases using a rather *ad hoc* combination of classical and quantum mechanics (see Sects. 7.6 and 7.7). In fact, we employed classical mechanics to deal with the translational degrees of freedom of the constituent particles, and quantum mechanics to deal with the non-translational degrees of freedom. Let us now discuss ideal gases from a purely quantum mechanical standpoint. It turns out that this approach is necessary to deal with either low temperature or high density gases. Furthermore, it also allows us to investigate completely non-classical "gases," such as photons or the conduction electrons in a metal.

8.2 Symmetry requirements in quantum mechanics

Consider a gas consisting of N *identical*, non-interacting, structureless particles enclosed within a container of volume V. Let Q_i denote collectively all the coordinates of the ith particle: *i.e.*, the three Cartesian coordinates which determine its spatial position, as well as the spin coordinate which determines its internal state. Let s_i be an index labeling the possible quantum states of the ith particle: *i.e.*, each possible value of s_i corresponds to a specification of the three momentum components of the particle, as well as the direction of its spin orientation. According to quantum mechanics, the overall state of the system when the ith particle is in state s_i, *etc.*, is *completely determined* by the complex *wave-function*

$$\Psi_{s_1,\cdots,s_N}(Q_1, Q_2, \cdots, Q_N). \tag{8.1}$$

In particular, the probability of an observation of the system finding the ith particle with coordinates in the range Q_i to $Q_i + dQ_i$, *etc.*, is simply

$$|\Psi_{s_1,\cdots,s_N}(Q_1, Q_2, \cdots, Q_N)|^2 \, dQ_1 \, dQ_2 \cdots dQ_N. \tag{8.2}$$

One of the fundamental postulates of quantum mechanics is the essential *indistinguishability* of particles of the same species. What this means, in practice, is that we cannot *label* particles of the same species: *i.e.*, a proton is just a proton—we cannot meaningfully talk of proton number 1 and proton number 2, *etc*. Note that no such constraint arises in classical mechanics. Thus, in classical mechanics particles of the same species are regarded as being *distinguishable*, and can, therefore, be labelled. Of course, the quantum mechanical approach is the correct one.

Suppose that we *interchange* the ith and jth particles: *i.e.*,

$$Q_i \leftrightarrow Q_j, \tag{8.3}$$

$$s_i \leftrightarrow s_j. \tag{8.4}$$

If the particles are truly indistinguishable then nothing has changed: *i.e.*, we have a particle in quantum state s_i and a particle in quantum state s_j both before and after the particles are swapped. Thus, the probability of observing the system in a given state also cannot have changed: *i.e.*,

$$|\Psi(\cdots Q_i \cdots Q_j \cdots)|^2 = |\Psi(\cdots Q_j \cdots Q_i \cdots)|^2. \tag{8.5}$$

Here, we have omitted the subscripts $s_1, \cdots, s_N$ for the sake of clarity. Note that we cannot conclude that the wave-function Ψ is unaffected when the particles are swapped, because Ψ cannot be observed experimentally. Only the *probability density* $|\Psi|^2$ is observable. Equation (8.5) implies that

$$\Psi(\cdots Q_i \cdots Q_j \cdots) = A\,\Psi(\cdots Q_j \cdots Q_i \cdots), \tag{8.6}$$

where A is a complex constant of modulus unity: *i.e.*, $|A|^2 = 1$.

Suppose that we interchange the ith and jth particles a second time. Swapping the ith and jth particles twice leaves the system completely unchanged: *i.e.*, it is equivalent to doing nothing to the system. Thus, the wave-functions before and after this process must be identical. It follows from Eq. (8.6) that

$$A^2 = 1. \tag{8.7}$$

Of course, the only solutions to the above equation are $A = \pm 1$.

We conclude, from the above discussion, that the wave-function Ψ is either completely *symmetric* under the interchange of particles, or it is completely *anti-symmetric*. In other words, either

$$\Psi(\cdots Q_i \cdots Q_j \cdots) = +\Psi(\cdots Q_j \cdots Q_i \cdots), \tag{8.8}$$

or

$$\Psi(\cdots Q_i \cdots Q_j \cdots) = -\Psi(\cdots Q_j \cdots Q_i \cdots). \tag{8.9}$$

In 1940 the Nobel prize winning physicist Wolfgang Pauli demonstrated, via arguments involving relativistic invariance, that the wave-function associated with a collection of identical integer-spin (*i.e.*, spin $0, 1, 2$, *etc.*) particles satisfies Eq. (8.8), whereas the wave-function associated with a collection of identical half-integer-spin (*i.e.*, spin $1/2, 3/2, 5/2$, *etc.*) particles satisfies Eq. (8.9). The former type of particles are known as *bosons* [after the Indian physicist S.N. Bose, who first put forward Eq. (8.8) on empirical grounds]. The latter type of particles are called *fermions* (after the Italian physicists Enrico Fermi, who first studied the properties of fermion gases). Common examples of bosons are photons and He^4 atoms. Common examples of fermions are protons, neutrons, and electrons.

Consider a gas made up of identical bosons. Equation (8.8) implies that the interchange of any two particles does not lead to a new state of the system. Bosons must, therefore, be considered as genuinely indistinguishable when enumerating the different possible states of the gas. Note that Eq. (8.8) imposes no restriction on how many particles can occupy a given single-particle quantum state s.

Consider a gas made up of identical fermions. Equation (8.9) implies that the interchange of any two particles does not lead to a new physical state of the system (since $|\Psi|^2$ is invariant). Hence, fermions must also be considered genuinely indistinguishable when enumerating the different possible states of the gas. Consider the special case where particles i and j lie in the same quantum state. In this case, the act of swapping the two particles is equivalent to leaving the system unchanged, so

$$\Psi(\cdots Q_i \cdots Q_j \cdots) = \Psi(\cdots Q_j \cdots Q_i \cdots). \tag{8.10}$$

However, Eq. (8.9) is also applicable, since the two particles are fermions. The only way in which Eqs. (8.9) and (8.10) can be reconciled is if

$$\Psi = 0 \tag{8.11}$$

wherever particles i and j lie in the same quantum state. This is another way of saying that it is *impossible* for any two particles in a gas of fermions to lie in the same single-particle quantum state. This proposition is known as the *Pauli exclusion principle*, since it was first proposed by W. Pauli in 1924 on empirical grounds.

Consider, for the sake of comparison, a gas made up of identical classical particles. In this case, the particles must be considered distinguishable when enumerating the different possible states of the gas. Furthermore, there are no constraints on how many particles can occupy a given quantum state.

According to the above discussion, there are *three* different sets of rules which can be used to enumerate the states of a gas made up of identical particles. For a boson gas, the particles must be treated as being indistinguishable, and there is no limit to how many particles can occupy a given quantum state. This set of rules is called *Bose-Einstein statistics*, after S.N. Bose and A. Einstein, who first developed them. For a fermion gas, the particles must be treated as being indistinguishable, and there can never be more than one particle in any given quantum state. This set of rules is called *Fermi-Dirac statistics*, after E. Fermi and P.A.M. Dirac, who first developed them. Finally, for a classical gas, the particles must be treated as being distinguishable, and there is no limit to how many particles can occupy a given quantum state. This set of rules is called *Maxwell-Boltzmann statistics*, after J.C. Maxwell and L. Boltzmann, who first developed them.

8.3 An illustrative example

Consider a very simple gas made up of two identical particles. Suppose that each particle can be in one of three possible quantum states, $s = 1, 2, 3$. Let us enumerate the possible states of the whole gas according to Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics, respectively.

For the case of Maxwell-Boltzmann (MB) statistics, the two particles are considered to be distinguishable. Let us denote them A and B. Furthermore, any number of particles can occupy the same quantum state. The possible different states of the gas are shown in Tab. 6. There are clearly 9 distinct states.

1	2	3
AB	$\cdots$	$\cdots$
$\cdots$	AB	$\cdots$
$\cdots$	$\cdots$	AB
A	B	$\cdots$
B	A	$\cdots$
A	$\cdots$	B
B	$\cdots$	A
$\cdots$	A	B
$\cdots$	B	A

Table 6: *Two particles distributed amongst three states according to Maxwell-Boltzmann statistics.*

For the case of Bose-Einstein (BE) statistics, the two particles are considered to be indistinguishable. Let us denote them both as A. Furthermore, any number of particles can occupy the same quantum state. The possible different states of the gas are shown in Tab. 7. There are clearly 6 distinct states.

1	2	3
AA	$\cdots$	$\cdots$
$\cdots$	AA	$\cdots$
$\cdots$	$\cdots$	AA
A	A	$\cdots$
A	$\cdots$	A
$\cdots$	A	A

Table 7: *Two particles distributed amongst three states according to Bose-Einstein statistics.*

Finally, for the case of Fermi-Dirac (FD) statistics, the two particles are considered to be indistinguishable. Let us again denote them both as A. Furthermore, no more than one particle can occupy a given quantum state. The possible different states of the gas are shown in Tab. 8. There are clearly only 3 distinct states.

It follows, from the above example, that Fermi-Dirac statistics are more restrictive (*i.e.*, there are less possible states of the system) than Bose-Einstein statistics,

1	2	3
A	A	$\cdots$
A	$\cdots$	A
$\cdots$	A	A

Table 8: *Two particles distributed amongst three states according to Fermi-Dirac statistics.*

which are, in turn, more restrictive than Maxwell-Boltzmann statistics. Let

$$\xi \equiv \frac{\text{probability that the two particles are found in the same state}}{\text{probability that the two particles are found in different states}}. \tag{8.12}$$

For the case under investigation,

$$\xi_{\rm MB} = 1/2, \tag{8.13}$$

$$\xi_{\rm BE} = 1, \tag{8.14}$$

$$\xi_{\rm FD} = 0. \tag{8.15}$$

We conclude that in Bose-Einstein statistics there is a greater relative tendency for particles to cluster in the same state than in classical statistics. On the other hand, in Fermi-Dirac statistics there is less tendency for particles to cluster in the same state than in classical statistics.

8.4 Formulation of the statistical problem

Consider a gas consisting of N identical non-interacting particles occupying volume V and in thermal equilibrium at temperature T. Let us label the possible quantum states of a single particle by r (or s). Let the energy of a particle in state r be denoted ϵ_r. Let the number of particles in state r be written n_r. Finally, let us label the possible quantum states of the whole gas by R.

The particles are assumed to be non-interacting, so the total energy of the gas in state R, where there are n_r particles in quantum state r, *etc.*, is simply

$$E_R = \sum_r n_r\,\epsilon_r, \tag{8.16}$$

where the sum extends over all possible quantum states r. Furthermore, since the total number of particles in the gas is known to be N, we must have

$$N = \sum_r n_r. \tag{8.17}$$

In order to calculate the thermodynamic properties of the gas (*i.e.*, its internal energy or its entropy), it is necessary to calculate its *partition function*,

$$Z = \sum_R e^{-\beta\,E_R} = \sum_R e^{-\beta\,(n_1\,\epsilon_1+n_2\,\epsilon_2+\cdots)}. \tag{8.18}$$

Here, the sum is over all possible states R of the whole gas: *i.e.*, over all the various possible values of the numbers $n_1, n_2, \cdots$.

Now, $\exp[-\beta\,(n_1\,\epsilon_1 + n_2\,\epsilon_2 + \cdots)]$ is the relative probability of finding the gas in a particular state in which there are n_1 particles in state 1, n_2 particles in state 2, *etc*. Thus, the mean number of particles in quantum state s can be written

$$\bar{n}_s = \frac{\sum_R n_s\,\exp[-\beta\,(n_1\,\epsilon_1 + n_2\,\epsilon_2 + \cdots)]}{\sum_R \exp[-\beta\,(n_1\,\epsilon_1 + n_2\,\epsilon_2 + \cdots)]}. \tag{8.19}$$

A comparison of Eqs. (8.18) and (8.19) yields the result

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_s}. \tag{8.20}$$

Here, $\beta \equiv 1/k\,T$.

8.5 Fermi-Dirac statistics

Let us, first of all, consider Fermi-Dirac statistics. According to Eq. (8.19), the average number of particles in quantum state s can be written

$$\bar{n}_s = \frac{\sum_{n_s} n_s\,e^{-\beta\,n_s\,\epsilon_s}\ \sum^{(s)}_{n_1,n_2,\cdots} e^{-\beta\,(n_1\,\epsilon_1+n_2\,\epsilon_2+\cdots)}}{\sum_{n_s} e^{-\beta\,n_s\,\epsilon_s}\ \sum^{(s)}_{n_1,n_2,\cdots} e^{-\beta\,(n_1\,\epsilon_1+n_2\,\epsilon_2+\cdots)}}. \tag{8.21}$$

Here, we have rearranged the order of summation, using the multiplicative properties of the exponential function. Note that the first sums in the numerator and denominator only involve n_s, whereas the last sums omit the particular state s from consideration (this is indicated by the superscript s on the summation symbol). Of course, the sums in the above expression range over all values of the numbers $n_1, n_2, \cdots$ such that $n_r = 0$ and 1 for each r, subject to the overall constraint that

$$\sum_r n_r = N. \tag{8.22}$$

Let us introduce the function

$$Z_s(N) = \sum_{n_1,n_2,\cdots}^{(s)} e^{-\beta\,(n_1\,\epsilon_1 + n_2\,\epsilon_2 + \cdots)}, \tag{8.23}$$

which is defined as the partition function for N particles distributed over all quantum states, *excluding* state s, according to Fermi-Dirac statistics. By explicitly performing the sum over $n_s = 0$ and 1, the expression (8.21) reduces to

$$\bar{n}_s = \frac{0 + e^{-\beta\,\epsilon_s}\,Z_s(N-1)}{Z_s(N) + e^{-\beta\,\epsilon_s}\,Z_s(N-1)}, \tag{8.24}$$

which yields

$$\bar{n}_s = \frac{1}{[Z_s(N)/Z_s(N-1)]\,e^{\beta\,\epsilon_s} + 1}. \tag{8.25}$$

In order to make further progress, we must somehow relate $Z_s(N-1)$ to $Z_s(N)$. Suppose that $\Delta N \ll N$. It follows that $\ln Z_s(N - \Delta N)$ can be Taylor expanded to give

$$\ln Z_s(N-\Delta N) \simeq \ln Z_s(N) - \frac{\partial \ln Z_s}{\partial N}\,\Delta N = \ln Z_s(N) - \alpha_s\,\Delta N, \tag{8.26}$$

where

$$\alpha_s \equiv \frac{\partial \ln Z_s}{\partial N}. \tag{8.27}$$

As always, we Taylor expand the slowly varying function $\ln Z_s(N)$, rather than the rapidly varying function $Z_s(N)$, because the radius of convergence of the latter Taylor series is too small for the series to be of any practical use. Equation (8.26) can be rearranged to give

$$Z_s(N-\Delta N) = Z_s(N)\,e^{-\alpha_s\,\Delta N}. \tag{8.28}$$

Now, since $Z_s(N)$ is a sum over very many different quantum states, we would not expect the logarithm of this function to be sensitive to which particular state s is excluded from consideration. Let us, therefore, introduce the approximation that α_s is independent of s, so that we can write

$$\alpha_s \simeq \alpha \tag{8.29}$$

for all s. It follows that the derivative (8.27) can be expressed approximately in terms of the derivative of the full partition function $Z(N)$ (in which the N particles are distributed over *all* quantum states). In fact,

$$\alpha \simeq \frac{\partial \ln Z}{\partial N}. \tag{8.30}$$

Making use of Eq. (8.28), with $\Delta N = 1$, plus the approximation (8.29), the expression (8.25) reduces to

$$\bar{n}_s = \frac{1}{e^{\,\alpha+\beta\,\epsilon_s} + 1}. \tag{8.31}$$

This is called the *Fermi-Dirac distribution*. The parameter α is determined by the constraint that $\sum_r \bar{n}_r = N$: *i.e.*,

$$\sum_r \frac{1}{e^{\,\alpha+\beta\,\epsilon_r} + 1} = N. \tag{8.32}$$

Note that $\bar{n}_s \to 0$ if ϵ_s becomes sufficiently large. On the other hand, since the denominator in Eq. (8.31) can never become less than unity, no matter how small ϵ_s becomes, it follows that $\bar{n}_s \leq 1$. Thus,

$$0 \leq \bar{n}_s \leq 1, \tag{8.33}$$

in accordance with the Pauli exclusion principle.

Equations (8.20) and (8.30) can be integrated to give

$$\ln Z = \alpha\,N + \sum_r \ln\left(1 + e^{-\alpha-\beta\,\epsilon_r}\right), \tag{8.34}$$

where use has been made of Eq. (8.31).

8.6 Photon statistics

Up to now, we have assumed that the number of particles N contained in a given system is a fixed number. This is a reasonable assumption if the particles possess non-zero mass, since we are not generally considering relativistic systems in this course. However, this assumption breaks down for the case of photons, which are *zero-mass* bosons. In fact, photons enclosed in a container of volume V, maintained at temperature T, can readily be absorbed or emitted by the walls. Thus, for the special case of a gas of photons there is no requirement which limits the total number of particles.

It follows, from the above discussion, that photons obey a simplified form of Bose-Einstein statistics in which there is an unspecified total number of particles. This type of statistics is called *photon statistics*.

Consider the expression (8.21). For the case of photons, the numbers $n_1, n_2, \cdots$ assume all values $n_r = 0, 1, 2, \cdots$ for each r, without any further restriction. It follows that the sums $\sum^{(s)}$ in the numerator and denominator are identical and, therefore, cancel. Hence, Eq. (8.21) reduces to

$$\bar{n}_s = \frac{\sum_{n_s} n_s\, e^{-\beta\, n_s\, \epsilon_s}}{\sum_{n_s} e^{-\beta\, n_s\, \epsilon_s}}. \tag{8.35}$$

However, the above expression can be rewritten

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_s}\left(\ln \sum_{n_s} e^{-\beta\, n_s\, \epsilon_s}\right). \tag{8.36}$$

Now, the sum on the right-hand side of the above equation is an infinite geometric series, which can easily be evaluated. In fact,

$$\sum_{n_s=0}^{\infty} e^{-\beta\, n_s\, \epsilon_s} = 1 + e^{-\beta\, \epsilon_s} + e^{-2\,\beta\, \epsilon_s} + \cdots = \frac{1}{1 - e^{-\beta\, \epsilon_s}}. \tag{8.37}$$

Thus, Eq. (8.36) gives

$$\bar{n}_s = \frac{1}{\beta}\frac{\partial}{\partial \epsilon_s} \ln\left(1 - e^{-\beta\, \epsilon_s}\right) = \frac{e^{-\beta\, \epsilon_s}}{1 - e^{-\beta\, \epsilon_s}}, \tag{8.38}$$

or

$$\bar{n}_s = \frac{1}{e^{\beta\,\epsilon_s} - 1}. \tag{8.39}$$

This is known as the *Planck distribution*, after the German physicist Max Planck who first proposed it in 1900 on purely empirical grounds.

Equation (8.20) can be integrated to give

$$\ln Z = -\sum_r \ln\,(1 - e^{-\beta\,\epsilon_r}), \tag{8.40}$$

where use has been made of Eq. (8.39).

8.7 Bose-Einstein statistics

Let us now consider Bose-Einstein statistics. The particles in the system are assumed to be massive, so the total number of particles N is a fixed number.

Consider the expression (8.21). For the case of massive bosons, the numbers $n_1, n_2, \cdots$ assume all values $n_r = 0, 1, 2, \cdots$ for each r, subject to the constraint that $\sum_r n_r = N$. Performing explicitly the sum over n_s, this expression reduces to

$$\bar{n}_s = \frac{0 + e^{-\beta\,\epsilon_s}\,Z_s(N-1) + 2\,e^{-2\,\beta\,\epsilon_s}\,Z_s(N-2) + \cdots}{Z_s(N) + e^{-\beta\,\epsilon_s}\,Z_s(N-1) + e^{-2\,\beta\,\epsilon_s}\,Z_s(N-2) + \cdots}, \tag{8.41}$$

where $Z_s(N)$ is the partition function for N particles distributed over all quantum states, *excluding* state s, according to Bose-Einstein statistics [*cf.*, Eq. (8.23)]. Using Eq. (8.28), and the approximation (8.29), the above equation reduces to

$$\bar{n}_s = \frac{\sum_s n_s\,e^{-n_s\,(\alpha+\beta\,\epsilon_s)}}{\sum_s e^{-n_s\,(\alpha+\beta\,\epsilon_s)}}. \tag{8.42}$$

Note that this expression is identical to (8.35), except that $\beta\,\epsilon_s$ is replaced by $\alpha + \beta\,\epsilon_s$. Hence, an analogous calculation to that outlined in the previous subsection yields

$$\bar{n}_s = \frac{1}{e^{\alpha+\beta\,\epsilon_s} - 1}. \tag{8.43}$$

This is called the *Bose-Einstein distribution*. Note that $\bar{n}_s$ can become very large in this distribution. The parameter α is again determined by the constraint on the total number of particles: *i.e.*,

$$\sum_r \frac{1}{e^{\alpha+\beta\,\epsilon_r}-1} = N. \tag{8.44}$$

Equations (8.20) and (8.30) can be integrated to give

$$\ln Z = \alpha\,N - \sum_r \ln\left(1-e^{-\alpha-\beta\,\epsilon_r}\right), \tag{8.45}$$

where use has been made of Eq. (8.43).

Note that photon statistics correspond to the special case of Bose-Einstein statistics in which the parameter α takes the value zero, and the constraint (8.44) does not apply.

8.8 Maxwell-Boltzmann statistics

For the purpose of comparison, it is instructive to consider the purely classical case of Maxwell-Boltzmann statistics. The partition function is written

$$Z = \sum_R e^{-\beta\,(n_1\,\epsilon_1+n_2\,\epsilon_2+\cdots)}, \tag{8.46}$$

where the sum is over all distinct states R of the gas, and the particles are treated as distinguishable. For given values of $n_1, n_2, \cdots$ there are

$$\frac{N!}{n_1!\,n_2!\,\cdots} \tag{8.47}$$

possible ways in which N distinguishable particles can be put into individual quantum states such that there are n_1 particles in state 1, n_2 particles in state 2, *etc*. Each of these possible arrangements corresponds to a distinct state for the whole gas. Hence, Eq. (8.46) can be written

$$Z = \sum_{n_1,n_2,\cdots} \frac{N!}{n_1!\,n_2!\,\cdots} e^{-\beta\,(n_1\,\epsilon_1+n_2\,\epsilon_2+\cdots)}, \tag{8.48}$$

where the sum is over all values of $n_r = 0, 1, 2, \cdots$ for each r, subject to the constraint that

$$\sum_r n_r = N. \tag{8.49}$$

Now, Eq. (8.48) can be written

$$Z = \sum_{n_1, n_2, \cdots} \frac{N!}{n_1!\, n_2!\, \cdots} (e^{-\beta\,\epsilon_1})^{n_1}\, (e^{-\beta\,\epsilon_2})^{n_2} \cdots, \tag{8.50}$$

which, by virtue of Eq. (8.49), is just the result of expanding a polynomial. In fact,

$$Z = (e^{-\beta\,\epsilon_1} + e^{-\beta\,\epsilon_2} + \cdots)^N, \tag{8.51}$$

or

$$\ln Z = N\,\ln\left(\sum_r e^{-\beta\,\epsilon_r}\right). \tag{8.52}$$

Note that the argument of the logarithm is simply the partition function for a single particle.

Equations (8.20) and (8.52) can be combined to give

$$\bar{n}_s = N\,\frac{e^{-\beta\,\epsilon_s}}{\sum_r e^{-\beta\,\epsilon_r}}. \tag{8.53}$$

This is known as the *Maxwell-Boltzmann distribution*. It is, of course, just the result obtained by applying the Boltzmann distribution to a single particle (see Sect. 7).

8.9 Quantum statistics in the classical limit

The preceding analysis regarding the quantum statistics of ideal gases is summarized in the following statements. The mean number of particles occupying quantum state s is given by

$$\bar{n}_s = \frac{1}{e^{\,\alpha+\beta\,\epsilon_s} \pm 1}, \tag{8.54}$$

where the upper sign corresponds to Fermi-Dirac statistics and the lower sign corresponds to Bose-Einstein statistics. The parameter α is determined via

$$\sum_r \bar{n}_r = \sum_r \frac{1}{e^{\,\alpha+\beta\,\epsilon_r} \pm 1} = N. \tag{8.55}$$

Finally, the partition function of the gas is given by

$$\ln Z = \alpha\,N \pm \sum_r \ln\left(1 \pm e^{-\alpha-\beta\,\epsilon_r}\right). \tag{8.56}$$

Let us investigate the magnitude of α in some important limiting cases. Consider, first of all, the case of a gas at a given temperature when its concentration is made sufficiently low: *i.e.*, when N is made sufficiently small. The relation (8.55) can only be satisfied if each term in the sum over states is made sufficiently small; *i.e.*, if $\bar{n}_r \ll 1$ or $\exp\,(\alpha + \beta\,\epsilon_r) \gg 1$ for all states r.

Consider, next, the case of a gas made up of a fixed number of particles when its temperature is made sufficiently large: *i.e.*, when β is made sufficiently small. In the sum in Eq. (8.55), the terms of appreciable magnitude are those for which $\beta\,\epsilon_r \ll \alpha$. Thus, it follows that as $\beta \rightarrow 0$ an increasing number of terms with large values of ϵ_r contribute substantially to this sum. In order to prevent the sum from exceeding N, the parameter α must become large enough that each term is made sufficiently small: *i.e.*, it is again necessary that $\bar{n}_r \ll 1$ or $\exp\,(\alpha + \beta\,\epsilon_r) \gg 1$ for all states r.

The above discussion suggests that if the concentration of an ideal gas is made sufficiently low, or the temperature is made sufficiently high, then α must become so large that

$$e^{\,\alpha+\beta\,\epsilon_r} \gg 1 \tag{8.57}$$

for all r. Equivalently, this means that the number of particles occupying each quantum state must become so small that

$$\bar{n}_r \ll 1 \tag{8.58}$$

for all r. It is conventional to refer to the limit of sufficiently low concentration, or sufficiently high temperature, in which Eqs. (8.57) and Eqs. (8.58) are satisfied, as the *classical limit*.

According to Eqs. (8.54) and (8.57), both the Fermi-Dirac and Bose-Einstein distributions reduce to

$$\bar{n}_s = e^{-\alpha-\beta\,\epsilon_s} \tag{8.59}$$

in the classical limit, whereas the constraint (8.55) yields

$$\sum_r e^{-\alpha-\beta\,\epsilon_r} = N. \tag{8.60}$$

The above expressions can be combined to give

$$\bar{n}_s = N\,\frac{e^{-\beta\,\epsilon_s}}{\sum_r e^{-\beta\,\epsilon_r}}. \tag{8.61}$$

It follows that in the classical limit of sufficiently low density, or sufficiently high temperature, the quantum distribution functions, whether Fermi-Dirac or Bose-Einstein, reduce to the Maxwell-Boltzmann distribution. It is easily demonstrated that the physical criterion for the validity of the classical approximation is that the mean separation between particles should be much greater than their mean de Broglie wavelengths.

Let us now consider the behaviour of the partition function (8.56) in the classical limit. We can expand the logarithm to give

$$\ln Z = \alpha\,N \pm \sum_r \left(\pm e^{-\alpha-\beta\,\epsilon_r}\right) = \alpha\,N + N. \tag{8.62}$$

However, according to Eq. (8.60),

$$\alpha = -\ln N + \ln\left(\sum_r e^{-\beta\,\epsilon_r}\right). \tag{8.63}$$

It follows that

$$\ln Z = -N\,\ln N + N + N\,\ln\left(\sum_r e^{-\beta\,\epsilon_r}\right). \tag{8.64}$$

Note that this *does not* equal the partition function Z_{MB} computed in Eq. (8.52) from Maxwell-Boltzmann statistics: *i.e.*,

$$\ln Z_{MB} = N\,\ln\left(\sum_r e^{-\beta\,\epsilon_r}\right). \tag{8.65}$$

In fact,

$$\ln Z = \ln Z_{\rm MB} - \ln N!, \tag{8.66}$$

or

$$Z = \frac{Z_{\rm MB}}{N!}, \tag{8.67}$$

where use has been made of Stirling's approximation ($N! \simeq N \ln N - N$), since N is large. Here, the factor $N!$ simply corresponds to the number of different permutations of the N particles: permutations which are physically meaningless when the particles are identical. Recall, that we had to introduce precisely this factor, in an *ad hoc* fashion, in Sect. 7.7 in order to avoid the non-physical consequences of the Gibb's paradox. Clearly, there is no Gibb's paradox when an ideal gas is treated properly via quantum mechanics.

In the classical limit, a full quantum mechanical analysis of an ideal gas reproduces the results obtained in Sects. 7.6 and 7.7, except that the arbitrary parameter h_0 is replaced by Planck's constant $h = 6.61 \times 10^{-34}$ J s.

A gas in the classical limit, where the typical de Broglie wavelength of the constituent particles is much smaller than the typical inter-particle spacing, is said to be *non-degenerate*. In the opposite limit, where the concentration and temperature are such that the typical de Broglie wavelength becomes comparable with the typical inter-particle spacing, and the actual Fermi-Dirac or Bose-Einstein distributions must be employed, the gas is said to be *degenerate*.

8.10 The Planck radiation law

Let us now consider the application of statistical thermodynamics to electromagnetic radiation. According to Maxwell's theory, an electromagnetic wave is a coupled self-sustaining oscillation of electric and magnetic fields which propagates though a vacuum at the speed of light, $c = 3 \times 10^8$ m s^{-1}. The electric component of the wave can be written

$$\mathbf{E} = \mathbf{E}_0 \exp[\,i\,(\mathbf{k}\cdot\mathbf{r} - \omega\,t)], \tag{8.68}$$

where $\mathbf{E}_0$ is a constant, $\mathbf{k}$ is the wave-vector which determines the wavelength and direction of propagation of the wave, and ω is the frequency. The dispersion relation

$$\omega = k\,c \tag{8.69}$$

ensures that the wave propagates at the speed of light. Note that this dispersion relation is very similar to that of sound waves in solids [see Eq. (7.140)]. Electromagnetic waves always propagate in the direction perpendicular to the coupled electric and magnetic fields (*i.e.*, electromagnetic waves are transverse waves). This means that $\mathbf{k}\cdot\mathbf{E}_0 = 0$. Thus, once $\mathbf{k}$ is specified, there are only *two* possible independent directions for the electric field. These correspond to the two independent polarizations of electromagnetic waves.

Consider an enclosure whose walls are maintained at fixed temperature T. What is the nature of the steady-state electromagnetic radiation inside the enclosure? Suppose that the enclosure is a parallelepiped with sides of lengths L_x, L_y, and L_z. Alternatively, suppose that the radiation field inside the enclosure is periodic in the x-, y-, and z-directions, with periodicity lengths L_x, L_y, and L_z, respectively. As long as the smallest of these lengths, L, say, is much greater than the longest wavelength of interest in the problem, $\lambda = 2\pi/k$, then these assumptions should not significantly affect the nature of the radiation inside the enclosure. We find, just as in our earlier discussion of sound waves (see Sect. 7.12), that the periodicity constraints ensure that there are only a discrete set of allowed wave-vectors (*i.e.*, a discrete set of allowed modes of oscillation of the electromagnetic field inside the enclosure). Let $\rho(\mathbf{k})\,d^3\mathbf{k}$ be the number of allowed modes *per unit volume* with wave-vectors in the range $\mathbf{k}$ to $\mathbf{k}+d\mathbf{k}$. We know, by analogy with Eq. (7.146), that

$$\rho(\mathbf{k})\,d^3\mathbf{k} = \frac{d^3\mathbf{k}}{(2\pi)^3}. \tag{8.70}$$

The number of modes per unit volume for which the *magnitude* of the wave-vector lies in the range k to $k + dk$ is just the density of modes, $\rho(\mathbf{k})$, multiplied by the "volume" in $\mathbf{k}$-space of the spherical shell lying between radii k and $k+dk$. Thus,

$$\rho_k(k)\,dk = \frac{4\pi\,k^2\,dk}{(2\pi)^3} = \frac{k^2}{2\pi^2}\,dk. \tag{8.71}$$

Finally, the number of modes per unit volume whose frequencies lie between ω and $\omega + d\omega$ is, by Eq. (8.69),

$$\sigma(\omega)\, d\omega = 2\, \frac{\omega^2}{2\pi^2\, c^3}\, d\omega. \tag{8.72}$$

Here, the additional factor 2 is to take account of the two independent polarizations of the electromagnetic field for a given wave-vector **k**.

Let us consider the situation classically. By analogy with sound waves, we can treat each allowable mode of oscillation of the electromagnetic field as an independent harmonic oscillator. According to the equipartition theorem (see Sect. 7.8), each mode possesses a mean energy $k\,T$ in thermal equilibrium at temperature T. In fact, $(1/2)\,k\,T$ resides with the oscillating electric field, and another $(1/2)\,k\,T$ with the oscillating magnetic field. Thus, the classical *energy density* of electromagnetic radiation (*i.e.*, the energy per unit volume associated with modes whose frequencies lie in the range ω to $\omega + d\omega$) is

$$\overline{u}(\omega)\, d\omega = k\,T\,\sigma(\omega)\, d\omega = \frac{k\,T}{\pi^2\, c^3}\, \omega^2\, d\omega. \tag{8.73}$$

This result is known as the *Rayleigh-Jeans radiation law*, after Lord Rayleigh and James Jeans who first proposed it in the late nineteenth century.

According to Debye theory (see Sect. 7.12), the energy density of sound waves in a solid is analogous to the Rayleigh-Jeans law, with one very important difference. In Debye theory there is a cut-off frequency (the Debye frequency) above which no modes exist. This cut-off comes about because of the discrete nature of solids (*i.e.*, because solids are made up of atoms instead of being continuous). It is, of course, impossible to have sound waves whose wavelengths are much less than the inter-atomic spacing. On the other hand, electromagnetic waves propagate through a vacuum, which possesses no discrete structure. It follows that there is no cut-off frequency for electromagnetic waves, and so the Rayleigh-Jeans law holds for all frequencies. This immediately poses a severe problem. The total classical energy density of electromagnetic radiation is given by

$$U = \int_0^\infty \overline{u}(\omega)\, d\omega = \frac{k\,T}{\pi^2\, c^3} \int_0^\infty \omega^2\, d\omega. \tag{8.74}$$

This is an integral which obviously does not converge. Thus, according to classical physics, the total energy density of electromagnetic radiation inside an enclosed cavity is infinite! This is clearly an absurd result, and was recognized as such in the latter half of the nineteenth century. In fact, this prediction is known as the *ultra-violet catastrophe*, because the Rayleigh-Jeans law usually starts to diverge badly from experimental observations (by over-estimating the amount of radiation) in the ultra-violet region of the spectrum.

So, how do we obtain a sensible answer? Well, as usual, quantum mechanics comes to our rescue. According to quantum mechanics, each allowable mode of oscillation of the electromagnetic field corresponds to a *photon state* with energy and momentum

$$\epsilon = \hbar\,\omega, \tag{8.75}$$

$$\mathbf{p} = \hbar\,\mathbf{k}, \tag{8.76}$$

respectively. Incidentally, it follows from Eq. (8.69) that

$$\epsilon = p\,c, \tag{8.77}$$

which implies that photons are massless particles which move at the speed of light. According to the Planck distribution (8.39), the mean number of photons occupying a photon state of frequency ω is

$$n(\omega) = \frac{1}{e^{\beta\,\hbar\,\omega} - 1}. \tag{8.78}$$

Hence, the mean energy of such a state is given by

$$\bar{\epsilon}(\omega) = \hbar\,\omega\;n(\omega) = \frac{\hbar\,\omega}{e^{\beta\,\hbar\,\omega} - 1}. \tag{8.79}$$

Note that low frequency states (*i.e.*, $\hbar\,\omega \ll k\,T$) behave classically: *i.e.*,

$$\bar{\epsilon} \simeq k\,T. \tag{8.80}$$

On the other hand, high frequency states (*i.e.*, $\hbar\,\omega \gg k\,T$) are completely "frozen out": *i.e.*,

$$\bar{\epsilon} \ll k\,T. \tag{8.81}$$

The reason for this is simply that it is very difficult for a thermal fluctuation to create a photon with an energy greatly in excess of $k\,T$, since $k\,T$ is the characteristic energy associated with such fluctuations.

According to the above discussion, the true energy density of electromagnetic radiation inside an enclosed cavity is written

$$\bar{u}\,d\omega = \epsilon(\omega)\,\sigma(\omega)\,d\omega, \tag{8.82}$$

giving

$$\overline{u}(\omega)\,d\omega = \frac{\hbar}{\pi^2\,c^3}\frac{\omega^3\,d\omega}{\exp(\beta\,\hbar\,\omega) - 1}. \tag{8.83}$$

This is famous result is known as the *Planck radiation law*. The Planck law approximates to the classical Rayleigh-Jeans law for $\hbar\,\omega \ll k\,T$, peaks at about $\hbar\,\omega \simeq 3\,k\,T$, and falls off exponentially for $\hbar\,\omega \gg k\,T$. The exponential fall off at high frequencies ensures that the total energy density remains finite.

8.11 Black-body radiation

Suppose that we were to make a small hole in the wall of our enclosure, and observe the emitted radiation. A small hole is the best approximation in Physics to a *black-body,* which is defined as an object which absorbs, and, therefore, emits, radiation perfectly at all wavelengths. What is the power radiated by the hole? Well, the power density inside the enclosure can be written

$$\overline{u}(\omega)\,d\omega = \hbar\,\omega\;n(\omega)\,d\omega, \tag{8.84}$$

where $n(\omega)$ is the mean number of photons per unit volume whose frequencies lie in the range ω to $\omega + d\omega$. The radiation field inside the enclosure is isotropic (we are assuming that the hole is sufficiently small that it does not distort the field). It follows that the mean number of photons per unit volume whose frequencies lie in the specified range, and whose directions of propagation make an angle in the range θ to $\theta + d\theta$ with the normal to the hole, is

$$n(\omega, \theta)\,d\omega\,d\theta = \frac{1}{2}\,n(\omega)\,d\omega\;\sin\theta\,d\theta, \tag{8.85}$$

where $\sin\theta$ is proportional to the solid angle in the specified range of directions, and

$$\int_0^{\pi} n(\omega,\theta)\,d\omega\,d\theta = n(\omega)\,d\omega. \tag{8.86}$$

Photons travel at the velocity of light, so the power per unit area escaping from the hole in the frequency range ω to $\omega + d\omega$ is

$$P(\omega)\,d\omega = \int_0^{\pi/2} c\,\cos\theta\;\hbar\,\omega\;n(\omega,\theta)\,d\omega\,d\theta, \tag{8.87}$$

where $c\,\cos\theta$ is the component of the photon velocity in the direction of the hole. This gives

$$P(\omega)\,d\omega = c\,\overline{u}(\omega)\,d\omega\,\frac{1}{2}\int_0^{\pi/2}\cos\theta\,\sin\theta\,d\theta = \frac{c}{4}\,\overline{u}(\omega)\,d\omega, \tag{8.88}$$

so

$$P(\omega)\,d\omega = \frac{\hbar}{4\pi^2\,c^2}\frac{\omega^3\,d\omega}{\exp(\beta\,\hbar\,\omega) - 1} \tag{8.89}$$

is the power per unit area radiated by a black-body in the frequency range ω to $\omega + d\omega$.

A black-body is very much an idealization. The power spectra of real radiating bodies can deviate quite substantially from black-body spectra. Nevertheless, we can make some useful predictions using this model. The black-body power spectrum peaks when $\hbar\,\omega \simeq 3\,k\,T$. This means that the peak radiation frequency scales linearly with the temperature of the body. In other words, hot bodies tend to radiate at higher frequencies than cold bodies. This result (in particular, the linear scaling) is known as *Wien's displacement law*. It allows us to estimate the surface temperatures of stars from their colours (surprisingly enough, stars are fairly good black-bodies). Table 9 shows some stellar temperatures determined by this method (in fact, the whole emission spectrum is fitted to a black-body spectrum). It can be seen that the apparent colours (which correspond quite well to the colours of the peak radiation) scan the whole visible spectrum, from red to blue, as the stellar surface temperatures gradually rise.

Probably the most famous black-body spectrum is cosmological in origin. Just after the "big bang" the Universe was essentially a "fireball," with the energy as-

Name	Constellation	Spectral Type	Surf. Temp. (° K)	Colour
Antares	Scorpio	M	3300	Very Red
Aldebaran	Taurus	K	3800	Reddish
Sun		G	5770	Yellow
Procyon	Canis Minor	F	6570	Yellowish
Sirius	Canis Major	A	9250	White
Rigel	Orion	B	11,200	Bluish White

Table 9: *Physical properties of some well-known stars*

sociated with radiation completely dominating that associated with matter. The early Universe was also pretty well described by equilibrium statistical thermodynamics, which means that the radiation had a black-body spectrum. As the Universe expanded, the radiation was gradually Doppler shifted to ever larger wavelengths (in other words, the radiation did work against the expansion of the Universe, and, thereby, lost energy), but its spectrum remained invariant. Nowadays, this primordial radiation is detectable as a faint *microwave background* which pervades the whole universe. The microwave background was discovered accidentally by Penzias and Wilson in 1961. Until recently, it was difficult to measure the full spectrum with any degree of precision, because of strong microwave absorption and scattering by the Earth's atmosphere. However, all of this changed when the COBE satellite was launched in 1989. It took precisely nine minutes to measure the perfect black-body spectrum reproduced in Fig. 9. This data can be fitted to a black-body curve of characteristic temperature 2.735 ° K. In a very real sense, this can be regarded as the "temperature of the Universe."

8.12 The Stefan-Boltzmann law

The total power radiated per unit area by a black-body at *all* frequencies is given by

$$P_{\rm tot}(T) = \int_0^\infty P(\omega)\,d\omega = \frac{\hbar}{4\pi^2\,c^2}\int_0^\infty \frac{\omega^3\,d\omega}{\exp(\hbar\,\omega/k\,T)-1}, \tag{8.90}$$

or

$$P_{\rm tot}(T) = \frac{k^4\,T^4}{4\pi^2\,c^2\,\hbar^3}\int_0^\infty \frac{\eta^3\,d\eta}{\exp\eta - 1}, \tag{8.91}$$

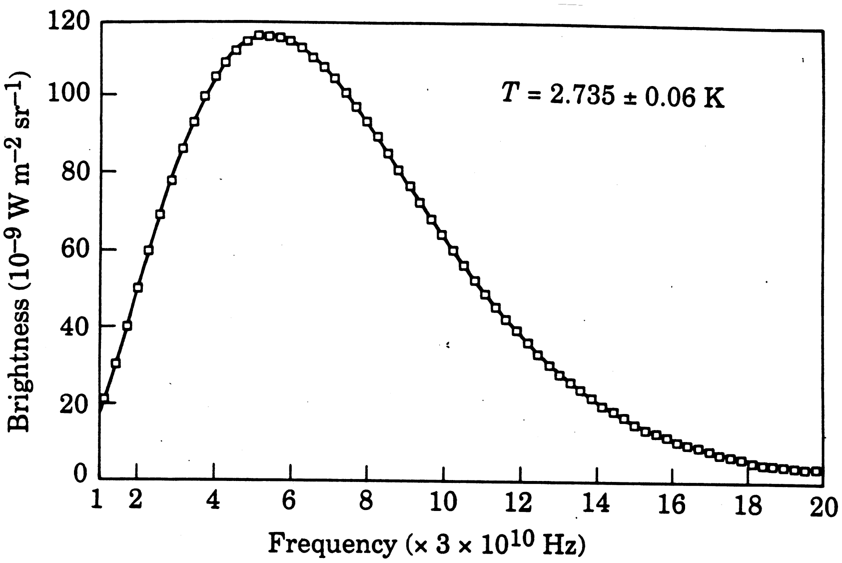

Figure 9: *Cosmic background radiation spectrum measured by the Far Infrared Absolute Spectrometer (FIRAS) aboard the Cosmic Background Explorer satellite (COBE).*

where $\eta = \hbar\,\omega/k\,T$. The above integral can easily be looked up in standard mathematical tables. In fact,

$$\int_0^\infty \frac{\eta^3\,d\eta}{\exp\eta - 1} = \frac{\pi^4}{15}. \tag{8.92}$$

Thus, the total power radiated per unit area by a black-body is

$$P_{\rm tot}(T) = \frac{\pi^2}{60}\frac{k^4}{c^2\,\hbar^3}\,T^4 = \sigma\,T^4. \tag{8.93}$$

This T^4 dependence of the radiated power is called the *Stefan-Boltzmann law*, after Josef Stefan, who first obtained it experimentally, and Ludwig Boltzmann, who first derived it theoretically. The parameter

$$\sigma = \frac{\pi^2}{60}\frac{k^4}{c^2\,\hbar^3} = 5.67\times 10^{-8}\ {\rm W\,m^{-2}\,K^{-4}}, \tag{8.94}$$

is called the *Stefan-Boltzmann constant*.

We can use the Stefan-Boltzmann law to estimate the temperature of the Earth from first principles. The Sun is a ball of glowing gas of radius $R_\odot \simeq 7\times 10^5$ km and surface temperature $T_\odot \simeq 5770^\circ$ K. Its luminosity is

$$L_\odot = 4\pi\, R_\odot^{\,2}\, \sigma\, T_\odot^{\,4}, \tag{8.95}$$

according to the Stefan-Boltzmann law. The Earth is a globe of radius $R_\oplus \sim 6000$ km located an average distance $r_\oplus \simeq 1.5 \times 10^8$ km from the Sun. The Earth intercepts an amount of energy

$$P_\oplus = L_\odot\, \frac{\pi\, R_\oplus^{\,2}/r_\oplus^{\,2}}{4\pi} \tag{8.96}$$

per second from the Sun's radiative output: *i.e.*, the power output of the Sun reduced by the ratio of the solid angle subtended by the Earth at the Sun to the total solid angle 4π. The Earth absorbs this energy, and then re-radiates it at longer wavelengths. The luminosity of the Earth is

$$L_\oplus = 4\pi\, R_\oplus^{\,2}\, \sigma\, T_\oplus^{\,4}, \tag{8.97}$$

according to the Stefan-Boltzmann law, where $T_\oplus$ is the average temperature of the Earth's surface. Here, we are ignoring any surface temperature variations between polar and equatorial regions, or between day and night. In steady-state, the luminosity of the Earth must balance the radiative power input from the Sun, so equating $L_\oplus$ and $P_\oplus$ we arrive at

$$T_\oplus = \left(\frac{R_\odot}{2\, r_\oplus}\right)^{1/2} T_\odot. \tag{8.98}$$

Remarkably, the ratio of the Earth's surface temperature to that of the Sun depends only on the Earth-Sun distance and the solar radius. The above expression yields $T_\oplus \sim 279^\circ$ K or 6° C (or 43° F). This is slightly on the cold side, by a few degrees, because of the greenhouse action of the Earth's atmosphere, which was neglected in our calculation. Nevertheless, it is quite encouraging that such a crude calculation comes so close to the correct answer.

8.13 Conduction electrons in a metal

The conduction electrons in a metal are non-localized (*i.e.*, they are not tied to any particular atoms). In conventional metals, each atom contributes a single such electron. To a first approximation, it is possible to neglect the mutual interaction of the conduction electrons, since this interaction is largely shielded out by the stationary atoms. The conduction electrons can, therefore, be treated as an *ideal gas*. However, the concentration of such electrons in a metal *far exceeds* the concentration of particles in a conventional gas. It is, therefore, not surprising that conduction electrons cannot normally be analyzed using classical statistics: in fact, they are subject to Fermi-Dirac statistics (since electrons are fermions).

Recall, from Sect. 8.5, that the mean number of particles occupying state s (energy ϵ_s) is given by

$$\bar{n}_s = \frac{1}{e^{\beta\,(\epsilon_s-\mu)}+1}, \tag{8.99}$$

according to the Fermi-Dirac distribution. Here,

$$\mu \equiv -k\,T\,\alpha \tag{8.100}$$

is termed the *Fermi energy* of the system. This energy is determined by the condition that

$$\sum_r \bar{n}_r = \sum_r \frac{1}{e^{\beta\,(\epsilon_r-\mu)}+1} = N, \tag{8.101}$$

where N is the total number of particles contained in the volume V. It is clear, from the above equation, that the Fermi energy μ is generally a function of the temperature T.

Let us investigate the behaviour of the *Fermi function*

$$F(\epsilon) = \frac{1}{e^{\beta\,(\epsilon-\mu)}+1} \tag{8.102}$$

as ϵ varies. Here, the energy is measured from its lowest possible value $\epsilon = 0$. If the Fermi energy μ is such that $\beta\,\mu \ll 1$ then $\beta\,(\epsilon-\mu) \gg 1$, and F reduces to the Maxwell-Boltzmann distribution. However, for the case of conduction electrons in a metal we are interested in the opposite limit, where

$$\beta\,\mu \equiv \frac{\mu}{k\,T} \gg 1. \tag{8.103}$$

In this limit, if $\epsilon \ll \mu$ then $\beta\,(\epsilon-\mu) \ll 1$, so that $F(\epsilon) = 1$. On the other hand, if $\epsilon \gg \mu$ then $\beta\,(\epsilon-\mu) \gg 1$, so that $F(\epsilon) = \exp[-\beta\,(\epsilon-\mu)]$ falls off exponentially

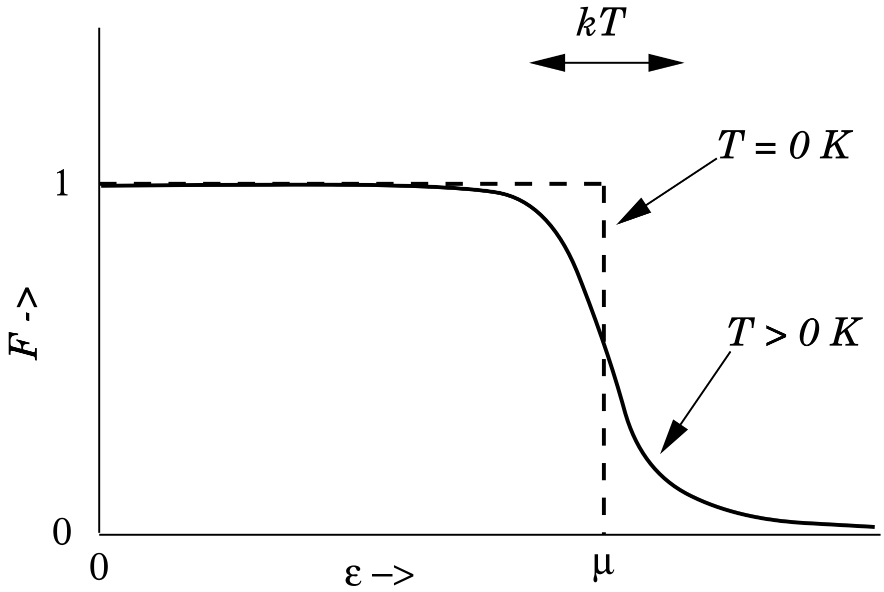

Figure 10: *The Fermi function.*

with increasing ϵ, just like a classical Boltzmann distribution. Note that $F = 1/2$ when $\epsilon = \mu$. The transition region in which F goes from a value close to unity to a value close to zero corresponds to an energy interval of order $k\,T$, centred on $\epsilon = \mu$. This is illustrated in Fig. 10.

In the limit as $T \rightarrow 0$, the transition region becomes infinitesimally narrow. In this case, $F = 1$ for $\epsilon < \mu$ and $F = 0$ for $\epsilon > \mu$, as illustrated in Fig. 10. This is an obvious result, since when $T = 0$ the conduction electrons attain their lowest energy, or *ground-state*, configuration. Since the Pauli exclusion principle requires that there be no more than one electron per single-particle quantum state, the lowest energy configuration is obtained by piling electrons into the lowest available unoccupied states until all of the electrons are used up. Thus, the last electron added to the pile has quite a considerable energy, $\epsilon = \mu$, since all of the lower energy states are already occupied. Clearly, the exclusion principle implies that a Fermi-Dirac gas possesses a large mean energy, even at absolute zero.

Let us calculate the Fermi energy $\mu = \mu_0$ of a Fermi-Dirac gas at $T = 0$. The energy of each particle is related to its momentum $\mathbf{p} = \hbar\,\mathbf{k}$ via

$$\epsilon = \frac{p^2}{2\,m} = \frac{\hbar^2\,k^2}{2\,m}, \tag{8.104}$$

where $\mathbf{k}$ is the de Broglie wave-vector. At $T = 0$ all quantum states whose energy is less than the Fermi energy μ_0 are filled. The Fermi energy corresponds to a *Fermi momentum* $p_F = \hbar\,k_F$ which is such that

$$\mu_0 = \frac{p_F^2}{2\,m} = \frac{\hbar^2\,k_F^2}{2\,m}. \tag{8.105}$$

Thus, at $T = 0$ all quantum states with $k < k_F$ are filled, and all those with $k > k_F$ are empty.

Now, we know, by analogy with Eq. (7.146), that there are $(2\pi)^{-3}\,V$ allowable translational states per unit volume of $\mathbf{k}$-space. The volume of the sphere of radius k_F in $\mathbf{k}$-space is $(4/3)\,\pi\,k_F^3$. It follows that the *Fermi sphere* of radius k_F contains $(4/3)\,\pi\,k_F^3\,(2\pi)^{-3}\,V$ translational states. The number of quantum states inside the sphere is *twice* this, because electrons possess two possible spin states for every possible translational state. Since the total number of occupied states (*i.e.*, the total number of quantum states inside the Fermi sphere) must equal the total number of particles in the gas, it follows that

$$2\,\frac{V}{(2\pi)^3}\left(\frac{4}{3}\,\pi\,k_F^3\right) = N. \tag{8.106}$$

The above expression can be rearranged to give

$$k_F = \left(3\,\pi^2\,\frac{N}{V}\right)^{1/3}. \tag{8.107}$$

Hence,

$$\lambda_F \equiv \frac{2\pi}{k_F} = \frac{2\pi}{(3\pi^2)^{1/3}}\left(\frac{V}{N}\right)^{1/3}, \tag{8.108}$$

which implies that the de Broglie wavelength λ_F corresponding to the Fermi energy is of order the mean separation between particles $(V/N)^{1/3}$. All quantum states with de Broglie wavelengths $\lambda \equiv 2\pi/k > \lambda_F$ are occupied at $T = 0$, whereas all those with $\lambda < \lambda_F$ are empty.

According to Eq. (8.105), the Fermi energy at $T = 0$ takes the form

$$\mu_0 = \frac{\hbar^2}{2\,m}\left(3\,\pi^2\,\frac{N}{V}\right)^{2/3}. \tag{8.109}$$

It is easily demonstrated that $\mu_0 \gg k\,T$ for conventional metals at room temperature.

The majority of the conduction electrons in a metal occupy a band of completely filled states with energies far below the Fermi energy. In many cases, such electrons have very little effect on the macroscopic properties of the metal. Consider, for example, the contribution of the conduction electrons to the specific heat of the metal. The heat capacity C_V at constant volume of these electrons can be calculated from a knowledge of their mean energy $\bar{E}(T)$ as a function of T: *i.e.*,

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V. \tag{8.110}$$

If the electrons obeyed classical Maxwell-Boltzmann statistics, so that $F \propto \exp(-\beta\,\epsilon)$ for *all* electrons, then the equipartition theorem would give

$$\bar{E} = \frac{3}{2}\,N\,k\,T, \tag{8.111}$$

$$C_V = \frac{3}{2}\,N\,k. \tag{8.112}$$

However, the actual situation, in which F has the form shown in Fig. 10, is very different. A small change in T does not affect the mean energies of the majority of the electrons, with $\epsilon \ll \mu$, since these electrons lie in states which are completely filled, and remain so when the temperature is changed. It follows that these electrons contribute nothing whatsoever to the heat capacity. On the other hand, the relatively small number of electrons $N_{\rm eff}$ in the energy range of order $k\,T$, centred on the Fermi energy, in which F is significantly different from 0 and 1, do contribute to the specific heat. In the tail end of this region $F \propto \exp(-\beta\,\epsilon)$, so the distribution reverts to a Maxwell-Boltzmann distribution. Hence, from Eq. (8.112), we expect each electron in this region to contribute roughly an amount $(3/2)\,k$ to the heat capacity. Hence, the heat capacity can be written

$$C_V \simeq \frac{3}{2}\,N_{\rm eff}\,k. \tag{8.113}$$

However, since only a fraction $k\,T/\mu$ of the total conduction electrons lie in the tail region of the Fermi-Dirac distribution, we expect

$$N_{\rm eff} \simeq \frac{k\,T}{\mu}\,N. \tag{8.114}$$

It follows that

$$C_V \simeq \frac{3}{2}\,N\,k\,\frac{k\,T}{\mu}. \tag{8.115}$$

Since $k\,T \ll \mu$ in conventional metals, the molar specific heat of the conduction electrons is clearly very much less than the classical value $(3/2)\,R$. This accounts for the fact that the molar specific heat capacities of metals at room temperature are about the same as those of insulators. Before the advent of quantum mechanics, the classical theory predicted incorrectly that the presence of conduction electrons should raise the heat capacities of metals by 50 percent [*i.e.*, $(3/2)\,R$] compared to those of insulators.

Note that the specific heat (8.115) is not temperature independent. In fact, using the superscript e to denote the *electronic* specific heat, the molar specific heat can be written

$$c_V^{(e)} = \gamma\,T, \tag{8.116}$$

where γ is a (positive) constant of proportionality. At room temperature $c_V^{(e)}$ is completely masked by the much larger specific heat $c_V^{(L)}$ due to lattice vibrations. However, at very low temperatures $c_V^{(L)} = A\,T^3$, where A is a (positive) constant of proportionality (see Sect. 7.12). Clearly, at low temperatures $c_V^{(L)} = A\,T^3$ approaches zero far more rapidly that the electronic specific heat, as T is reduced. Hence, it should be possible to measure the electronic contribution to the molar specific heat at low temperatures.

The total molar specific heat of a metal at low temperatures takes the form

$$c_V = c_V^{(e)} + c_V^{(L)} = \gamma\,T + A\,T^3. \tag{8.117}$$

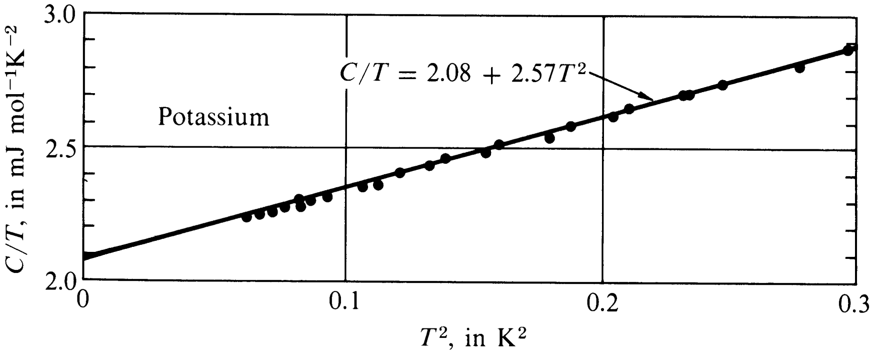

Figure 11: *The low temperature heat capacity of potassium, plotted as* C_V/T *versus* T^2. *From C. Kittel, and H. Kroemer, Themal physics (W.H. Freeman & co., New York NY, 1980).*

Hence,

$$\frac{c_V}{T} = \gamma + A\,T^2. \tag{8.118}$$

If follows that a plot of c_V/T versus T^2 should yield a *straight line* whose intercept on the vertical axis gives the coefficient γ. Figure 11 shows such a plot. The fact that a good straight line is obtained verifies that the temperature dependence of the heat capacity predicted by Eq. (8.117) is indeed correct.

8.14 White-dwarf stars

A main-sequence hydrogen-burning star, such as the Sun, is maintained in equilibrium via the balance of the gravitational attraction tending to make it collapse, and the thermal pressure tending to make it expand. Of course, the thermal energy of the star is generated by nuclear reactions occurring deep inside its core. Eventually, however, the star will run out of burnable fuel, and, therefore, start to collapse, as it radiates away its remaining thermal energy. What is the ultimate fate of such a star?

A burnt-out star is basically a gas of electrons and ions. As the star collapses, its density increases, so the mean separation between its constituent particles decreases. Eventually, the mean separation becomes of order the de Broglie wavelength of the electrons, and the electron gas becomes *degenerate*. Note, that the de Broglie wavelength of the ions is much smaller than that of the electrons, so the ion gas remains non-degenerate. Now, even at zero temperature, a degenerate electron gas exerts a substantial pressure, because the Pauli exclusion principle prevents the mean electron separation from becoming significantly smaller than the typical de Broglie wavelength (see the previous section). Thus, it is possible for a burnt-out star to maintain itself against complete collapse under gravity via the *degeneracy pressure* of its constituent electrons. Such stars are termed *white-dwarfs*. Let us investigate the physics of white-dwarfs in more detail.

The total energy of a white-dwarf star can be written

$$E = K + U, \tag{8.119}$$

where K is the total kinetic energy of the degenerate electrons (the kinetic energy of the ion is negligible) and U is the gravitational potential energy. Let us assume, for the sake of simplicity, that the density of the star is *uniform*. In this case, the gravitational potential energy takes the form

$$U = -\frac{3}{5}\frac{G\,M^2}{R}, \tag{8.120}$$

where G is the gravitational constant, M is the stellar mass, and R is the stellar radius.

Let us assume that the electron gas is highly degenerate, which is equivalent to taking the limit $T \rightarrow 0$. In this case, we know, from the previous section, that the Fermi momentum can be written

$$p_F = \Lambda\left(\frac{N}{V}\right)^{1/3}, \tag{8.121}$$

where

$$\Lambda = (3\pi^2)^{1/3}\,\hbar. \tag{8.122}$$

Here,

$$V = \frac{4\pi}{3}\,R^3 \tag{8.123}$$

is the stellar volume, and N is the total number of electrons contained in the star. Furthermore, the number of electron states contained in an annular radius of **p**-space lying between radii p and $p + dp$ is

$$dN = \frac{3\,V}{\Lambda^3}\,p^2\,dp. \tag{8.124}$$

Hence, the total kinetic energy of the electron gas can be written

$$K = \frac{3\,V}{\Lambda^3}\int_0^{p_F}\frac{p^2}{2\,m}\,p^2\,dp = \frac{3}{5}\,\frac{V}{\Lambda^3}\,\frac{p_F^5}{2\,m}, \tag{8.125}$$

where m is the electron mass. It follows that

$$K = \frac{3}{5}\,N\,\frac{\Lambda^2}{2\,m}\left(\frac{N}{V}\right)^{2/3}. \tag{8.126}$$

The interior of a white-dwarf star is composed of atoms like C^{12} and O^{16} which contain equal numbers of protons, neutrons, and electrons. Thus,

$$M = 2\,N\,m_p, \tag{8.127}$$

where m_p is the proton mass.

Equations (8.119), (8.120), (8.122), (8.123), (8.126), and (8.127) can be combined to give

$$E = \frac{A}{R^2} - \frac{B}{R}, \tag{8.128}$$

where

$$A = \frac{3}{20}\left(\frac{9\pi}{8}\right)^{2/3}\frac{\hbar^2}{m}\left(\frac{M}{m_p}\right)^{5/3}, \tag{8.129}$$

$$B = \frac{3}{5}\,G\,M^2. \tag{8.130}$$

The equilibrium radius of the star R_* is that which *minimizes* the total energy E. In fact, it is easily demonstrated that

$$R_* = \frac{2\,A}{B}, \tag{8.131}$$

which yields

$$R_* = \frac{(9\pi)^{2/3}}{8}\,\frac{\hbar^2}{m}\,\frac{1}{G\,m_p^{5/3}\,M^{1/3}}. \tag{8.132}$$

The above formula can also be written

$$\frac{R_*}{R_\odot} = 0.010\left(\frac{M_\odot}{M}\right)^{1/3}, \tag{8.133}$$

where $R_\odot = 7\times 10^5$ km is the solar radius, and $M_\odot = 2\times 10^{30}$ kg is the solar mass. It follows that the radius of a typical solar mass white-dwarf is about 7000 km: *i.e.*, about the same as the radius of the Earth. The first white-dwarf to be discovered (in 1862) was the companion of Sirius. Nowadays, thousands of white-dwarfs have been observed, all with properties similar to those described above.

8.15 The Chandrasekhar limit

One curious feature of white-dwarf stars is that their radius decreases as their mass increases [see Eq. (8.133)]. It follows, from Eq. (8.126), that the mean energy of the degenerate electrons inside the star increases strongly as the stellar mass increases: in fact, $K \propto M^{4/3}$. Hence, if M becomes sufficiently large the electrons become *relativistic*, and the above analysis needs to be modified. Strictly speaking, the non-relativistic analysis described in the previous section is only valid in the low mass limit $M \ll M_\odot$. Let us, for the sake of simplicity, consider the ultra-relativistic limit in which $p \gg m\,c$.

The total electron energy (including the rest mass energy) can be written

$$K = \frac{3\,V}{\Lambda^3}\int_0^{p_F}(p^2\,c^2 + m^2\,c^4)^{1/2}\,p^2\,dp, \tag{8.134}$$

by analogy with Eq. (8.125). Thus,

$$K \simeq \frac{3\,V\,c}{\Lambda^3}\int_0^{p_F}\left(p^3 + \frac{m^2\,c^2}{2}\,p + \cdots\right)dp, \tag{8.135}$$

giving

$$K \simeq \frac{3}{4}\frac{V\,c}{\Lambda^3}\left[p_F^4 + m^2\,c^2\,p_F^2 + \cdots\right]. \tag{8.136}$$

It follows, from the above, that the total energy of an ultra-relativistic white-dwarf star can be written in the form

$$E \simeq \frac{A - B}{R} + C\,R, \tag{8.137}$$

where

$$A = \frac{3}{8}\left(\frac{9\pi}{8}\right)^{1/3}\hbar\,c\left(\frac{M}{m_p}\right)^{4/3}, \tag{8.138}$$

$$B = \frac{3}{5}\,G\,M^2, \tag{8.139}$$

$$C = \frac{3}{4}\,\frac{1}{(9\pi)^{1/3}}\,\frac{m^2\,c^3}{\hbar}\left(\frac{M}{m_p}\right)^{2/3}. \tag{8.140}$$

As before, the equilibrium radius R_* is that which minimizes the total energy E. However, in the ultra-relativistic case, a non-zero value of R_* only exists for $A - B > 0$. When $A - B < 0$ the energy decreases monotonically with decreasing stellar radius: in other words, the degeneracy pressure of the electrons is incapable of halting the collapse of the star under gravity. The criterion which must be satisfied for a relativistic white-dwarf star to be maintained against gravity is that

$$\frac{A}{B} > 1. \tag{8.141}$$

This criterion can be re-written

$$M < M_C, \tag{8.142}$$

where

$$M_C = \frac{15}{64}\,(5\pi)^{1/2}\,\frac{(\hbar\,c/G)^{1/2}}{m_p^2} = 1.72\,M_\odot \tag{8.143}$$

is known as the *Chandrasekhar limit*, after A. Chandrasekhar who first derived it in 1931. A more realistic calculation, which does not assume constant density, yields

$$M_C = 1.4\,M_\odot. \tag{8.144}$$

Thus, if the stellar mass exceeds the Chandrasekhar limit then the star in question cannot become a white-dwarf when its nuclear fuel is exhausted, but, instead, must continue to collapse. What is the ultimate fate of such a star?

8.16 Neutron stars

At stellar densities which greatly exceed white-dwarf densities, the extreme pressures cause electrons to combine with protons to form neutrons. Thus, any star which collapses to such an extent that its radius becomes significantly less than that characteristic of a white-dwarf is effectively transformed into a gas of neutrons. Eventually, the mean separation between the neutrons becomes comparable with their de Broglie wavelength. At this point, it is possible for the degeneracy pressure of the neutrons to halt the collapse of the star. A star which is maintained against gravity in this manner is called a *neutron star*.

Neutrons stars can be analyzed in a very similar manner to white-dwarf stars. In fact, the previous analysis can be simply modified by letting $m_p \to m_p/2$ and $m \to m_p$. Thus, we conclude that non-relativistic neutrons stars satisfy the mass-radius law:

$$\frac{R_*}{R_\odot} = 0.000011 \left(\frac{M_\odot}{M}\right)^{1/3}, \tag{8.145}$$

It follows that the radius of a typical solar mass neutron star is a mere 10 km. In 1967 Antony Hewish and Jocelyn Bell discovered a class of compact radio sources, called *pulsars*, which emit extremely regular pulses of radio waves. Pulsars have subsequently been identified as rotating neutron stars. To date, many hundreds of these objects have been observed.

When relativistic effects are taken into account, it is found that there is a critical mass above which a neutron star cannot be maintained against gravity. According to our analysis, this critical mass, which is known as the *Oppenheimer-Volkoff limit*, is given by

$$M_{OV} = 4\, M_C = 6.9\, M_\odot. \tag{8.146}$$

A more realistic calculation, which does not assume constant density, does not treat the neutrons as point particles, and takes general relativity into account, gives a somewhat lower value of

$$M_{OV} = 1.5\text{—}2.5\,M_\odot. \tag{8.147}$$

A star whose mass exceeds the Oppenheimer-Volkoff limit cannot be maintained against gravity by degeneracy pressure, and must ultimately collapse to form a *black-hole*.