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The basic ideas of thermodynamics and statistical mechanics

1.1 From atoms to thermodynamics

Imagine a box, a cube 10 cm on each edge, with 10^{22} atoms of helium gas in it. The atoms share among them some total energy U; say, 2×10^6 ergs, which cannot change because the box is isolated from the rest of the world. Inside the box the atoms fly around, banging into each other or the walls, exchanging energy and momentum. If there is only one atom in the box, and we know how it started out, we might imagine being able to calculate its precise trajectory for a while, predicting just where it would end up at some later time. If there are twenty atoms, the same job becomes horribly more complicated. With 10^{22} atoms it is obviously hopeless. Moreover, according to the laws of quantum mechanics, it would not be possible even in principle. If we knew precisely where the atoms were at some time, we could have no idea of how fast they were moving, according to the uncertainty principle. Obviously, a very short time after we start things off, there is not much we can say about what's going on inside the box.

Nevertheless, it is possible to make some very precise statements about the properties of the gas in the box, especially if we allow some time to pass after we start it off. For example, the gas will have some pressure, P, and some temperature, T, and, given the information we already have, these can be predicted with extreme accuracy and confidence. Temperature and pressure are macroscopic or thermodynamic quantities. The problem before us in this section is to describe the connection between these (predictable) thermodynamic quantities and the (unpredictable) microscopic quantities that somehow give rise to them.

The trick, as it usually is in physics, is to ask the right question. We cannot, even in principle, say exactly what is going on inside the box some

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time after we isolate it, but we can, in principle at least, say how many possibilities there are. Let us focus our attention on that question.

We have a box of volume V (10^3 cm^3 in our example) containing atoms of some kind (10^{22} atoms of helium) with total energy U (2×10^6 ergs). Let us call the number of things that can possibly happen Γ. That is, there are Γ ways in which N atoms can divide among them energy U while remaining in volume V. (It is not obvious that such a number exists, but it does. We shall see shortly just what we mean by "the number of possible things that can happen".)

If we change U, V or N, the number Γ will change. In other words, Γ is a function of the numbers U, V and N. It will turn out to be convenient to deal not with the (usually gigantic) number Γ but rather with its (more manageable) natural logarithm (written as "log" rather than "ln" throughout this book). We define the quantity S,

$$S = k_{\text{B}} \log \Gamma \tag{1.1.1}$$

where k_{B} here, called Boltzmann's constant, will be assigned a value later. The quantity S is called the **entropy**. Since Γ is a function of U, V and N, S is also a function of those variables. If we add more energy to the box, it seems clear that the number of ways of dividing the (larger) energy among the same number of particles must increase. Thus Γ, and hence S, should be a monotonic function of energy at a given V and N. If we knew the functional form we could therefore solve uniquely for U as a function of S, V and N. Let us write

$$U = U(S, V, N) \tag{1.1.2}$$

We are here supposed to visualize an equation with only U on the left-hand side, and on the right a mathematical form that involves, aside from constants, only the variables S, V and N (not U). Equation (1.1.2) means that any change in U comes about by means of changes of its three variables. Moreover, any small change can be constructed by changing the variables one at a time. We express that fact by writing

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \tag{1.1.3}$$

The coefficients of dS, dV and dN are called partial derivatives. They are, in effect, defined by this equation. Each partial derivative expresses

a precisely defined operation, both physically and mathematically. For example, $(\partial U/\partial S)_{V,N}$ means how much does the energy of the system change if we change the entropy by dS while holding V and N fixed? Mathematically, we are to calculate the derivative of U with respect to S while treating V and N as constants.

Example 1.1.1

Find $(\partial U/\partial S)_{V,N}$ for an ideal gas of atoms.

Solution.

For an ideal gas, Eq. (1.1.2) has the form

$$U = \frac{3}{2}Nk_{\mathrm{B}}\left(\frac{N}{V}\right)^{2/3}\exp\left[\frac{S}{(3/2)Nk_{\mathrm{B}}} - s_0\right] \qquad (1.1.4)$$

where k_{B} is Boltzmann's constant and s_0 is also a constant. So

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{N}{V}\right)^{2/3}\exp\left[\frac{S}{(3/2)Nk_{\mathrm{B}}} - s_0\right] = \frac{U}{(3/2)Nk_{\mathrm{B}}}$$

Equilibrium thermodynamics is largely an expression of the fact that the energy of a body is a unique function of S and (generally) one or two other variables such as V and N. The consequences of this fact are in turn expressed by partial derivatives. The mathematics of partial derivatives is the language of equilibrium thermodynamics.

Of the many partial derivatives that will show up in the course of our work, a few have particular significance and are therefore given special names. Among those chosen few are the three coefficients of the differentials in Eq. (1.1.3). We define

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad (1.1.5)$$

where T is called the absolute thermodynamic temperature;

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad (1.1.6)$$

where P is called the pressure; and

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \qquad (1.1.7)$$

where μ is called the chemical potential.

Example 1.1.2

For the system obeying Eq. (1.1.4) find the pressure as a function of T, V and N.

Solution.

From Example (1.1.1) we have

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{U}{(3/2)Nk_{\mathrm{B}}}$$

and also

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = +\frac{2U}{3V}$$

(since $U \propto V^{-2/3}$ with everything else held constant). Upon eliminating U between these two equations, we have

$$P = \frac{Nk_{\mathrm{B}}T}{V} \tag{1.1.8}$$

The relation involving P, T, V and N for any system is called the equation of state. Equation (1.1.8) is the equation of state of the ideal gas.

There is a technical point to take care of concerning units. The constant k_{B} is related to the temperature by

$$T = \frac{\partial U}{\partial S} = \frac{1}{k_{\mathrm{B}}}\frac{\partial U}{\partial \log \Gamma} = \frac{\Gamma}{k_{\mathrm{B}}}\frac{\partial U}{\partial \Gamma}$$

Thus $k_{\mathrm{B}}T$ has the units of energy. The choice of a value for k_{B} fixes the absolute temperature scale. We shall choose to express T in kelvins (K), which is accomplished by setting

$$k_{\mathrm{B}} = 1.38 \times 10^{-23} \text{ joules/kelvin}$$
$$= 1.38 \times 10^{-16} \text{ ergs/kelvin}$$

On the Kelvin scale, zero is the absolute zero of temperature. Water, ice and water vapor coexist at the unique temperature of 273.15 K, and the normal boiling point of water is exactly 100 K higher. Room temperature (of a rather warm room) is roughly 300 K.

The connection we set out to make has now been made. Starting from a purely microscopic idea – the number Γ of ways that N atoms could divide the available energy, we have shown what is meant by purely macroscopic ideas such as temperature and pressure. We have, of course,

not yet shown that the peculiar entities that appear in Eqs. (1.1.5) and (1.1.6) behave as we intuitively feel temperature and pressure ought to behave. That will come shortly. It is unlikely that you have any intuitive feel for chemical potential. We shall try to develop that intuition later.

Problem 1.1
For a system obeying Eq. (1.1.4), find the following functions:

$$S = S(T, V)$$
$$S = S(T, P)$$

Problem 1.2
For an ideal gas of large N and U, obeying Eq. (1.1.4), we wish to carry out the following operation. We add one atom with zero energy so that the gas has the same amount of energy but $N + 1$ atoms. We then wish to extract enough energy that the entropy of the system is the same as it was before the atom was added. How much energy must be extracted?

1.2 Counting quantum states

We have seen that, in order to connect thermodynamics to the microscopic world of atoms and molecules, the question we must answer is not what the atoms are doing, but rather, how many things can they be doing? In this section, we shall see exactly what is meant by that question and by its answer, the number Γ, in the case of the perfect gas.

The perfect gas is one whose atoms exert no forces on one another. It is a good approximation to the behavior of real matter at low densities and high temperatures. In those conditions it becomes the same as the ideal gas of Example 1.1.1. Our interest in it now, however, is as a model, an idealization that will help us form more concrete ideas about how to describe the microscopic behavior of matter.

To begin with, we consider the simpler problem of a single atom confined in an otherwise empty box in the form of a cube whose dimension is L on each edge. The energy of the atom is simply its kinetic energy, which is related to its momentum by

$$\varepsilon = \frac{p^2}{2m} \tag{1.2.1}$$

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where ε is the energy, m the mass and $\vec{p}$ the momentum is a vector with
x, y and z components, so that

$$p^2 = p_x^2 + p_y^2 + p_z^2 \tag{1.2.2}$$

In classical mechanics each component of $\vec{p}$ is a continuous variable
that can take on any positive or negative value. Thus even for the simple
problem of a single atom with fixed energy, there would be no answer to
the question of how many ways the atom could use up the energy it has.
For any finite ε there are an infinite (i.e. uncountable) number of choices
of p_x, p_y and p_z. In quantum mechanics, however, the components of the
momentum are quantized and are given in our case by

$$\begin{aligned} p_x &= n_x p_0 \\ p_y &= n_y p_0 \\ p_z &= n_z p_0 \end{aligned} \tag{1.2.3}$$

where n_x, n_y and n_z are numbers (called **quantum numbers**), and p_0 is the
quantum unit of momentum in our cubical box. The permissible values of
n_x, n_y and n_z and the size of p_0 depend on how we choose to describe the
walls of the box.

One way to describe the walls is simply to say they are impenetrable.
Thus an atom hitting one of these walls bounces off, conserving energy.
An impenetrable wall is sketched in Fig. 1.1. With this specification, each
of the ns can be any positive integer,

$$n_x, n_y, n_z = 1, 2, 3, \ldots \text{ (impenetrable walls)}$$

and p_0 is given by

$$p_0 = h/(2L) \text{ (impenetrable walls)}$$

where h is Planck's constant,

$$h = 6.62517 \times 10^{-27} \text{ erg s}$$

(We often use the symbol $\hbar = h/(2\pi) = 1.05 \times 10^{-27}$ erg s.)

All of the possible states of the atom in our box can be enumerated
by assigning positive integers to n_x, n_y and n_z. Although our description of
the problem is simple and straightforward, this set of solutions has some
bizarre aspects, even aside from the fact that ε and $\vec{p}$ are quantized. For one
thing, it is impossible for the atom to have zero kinetic energy. The lowest
value that the energy can have, say ε_m, occurs when $n_x = n_y = n_z = 1$, so that

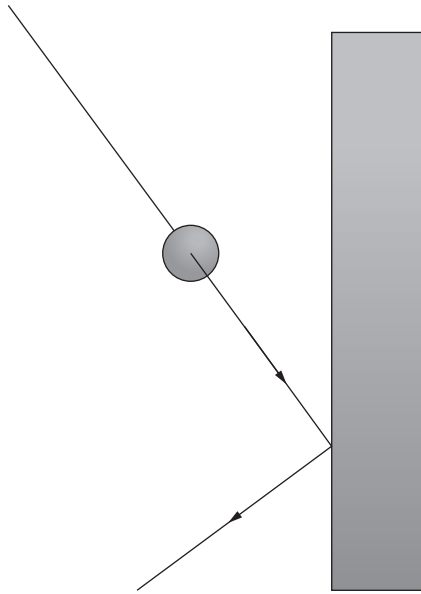$$\varepsilon_m = 3 \frac{(h/(2L))^2}{2m} = \frac{3}{8} \frac{h^2}{mL^2}$$

Figure 1.1 An impenetrable wall.

This quantity is called the *zero-point energy*, and it always occurs in quantum mechanics when a particle is confined in space. Even more peculiar, the components of momentum have only positive values. It's hard to see how we can make use of this description to discuss an atom that can fly either to the left or the right.

There is another way of describing the walls that denotes states that do not have these strange quirks. In this description, when the atom hits the wall, it does not bounce off of it at all. Instead it vanishes into the wall, reappearing with the same energy and momentum at the opposite wall, as sketched in Fig. 1.2. In other words it behaves as if the left-hand end of the box always begins just where the right-hand end stops, and there are no walls at all. A problem described this way is said to have *periodic boundary conditions*.

Strange though such a box may seem, it has all the necessary properties for our purposes. Imagine it to have N atoms in it with total energy U. That makes it suitable for thermodynamic analysis. For periodic boundary conditions, the unit of momentum is

$$p_0 = h/L \text{ (periodic boundary conditions)} \qquad (1.2.4)$$

and the allowed values of quantum numbers are

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots \text{ (periodic boundary conditions)} \qquad (1.2.5)$$
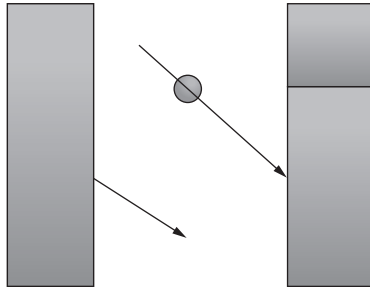
Figure 1.2 Periodic boundary conditions.

We thus have, in this case, a state of zero energy, and both positive and negative components of momentum. Because of these nice properties, we will always use periodic boundary conditions. We are now in a position to see by example, at least for the simple case of one atom in a box, what exactly is meant by the number Γ.

Example 1.2.1
Find Γ for one atom in the box we have been discussing, if the atom has 3 units of energy.

Solution.
The quantum unit of energy in the box is

$$\varepsilon_0 = p^2/(2m) = h^2/(2mL^2) \qquad (1.2.6)$$

Using Eqs. (1.2.1), (1.2.2) and (1.2.3), the possible energies of an atom in the box may be written as

$$\varepsilon = \varepsilon_0 \left(n_x^2 + n_y^2 + n_z^2\right) \qquad (1.2.7)$$

The statement that the atom has 3 units of energy means

$$n_x^2 + n_y^2 + n_z^2 = 3$$

Γ is the number of choices of (n_x, n_y, n_z) that satisfy this last equation. The choices that work are all possible combinations of $n_x = \pm 1$, $n_y = \pm 1$ and $n_z = \pm 1$. There are $2^3 = 8$ possible sets that work, so in this simple case $\Gamma = 8$.

Problem 1.3
One atom in the same box has energy $\varepsilon = B\varepsilon_0$. Find Γ if $B = 0$, and if $B = 1$ or 2 or 4. Find Γ if $B = 25$.

We do not need thermodynamics to discuss the behavior of one atom in a box. But we do need it if there are many atoms. The problem we want to analyze, the perfect gas, is formulated as follows. In the box we have been describing there are N atoms. The possible states of each atom, however, are those it would have if it were alone in the box. In other words, each atom has kinetic energy only. The kinetic energy of each atom is quantized, and its possible values are given by Eq. (1.2.7) with n_x, n_y and n_z each equal to zero or any positive or negative integer. Thus the quantum mechanical description of the problem is no different from what it was before, but the problem of counting how many ways a given amount of energy can be allocated has become dramatically more difficult.

Before going on with this discussion, we must come to grips with a purely linguistic difficulty. The problem is that the word *state* simply has too many uses. We speak of the state of a single atom, the microscopic state of a gas of atoms, the macroscopic state of a gas (i.e. its temperature and pressure), the liquid state, the solid state; and, although Philadelphia is in the Commonwealth of Pennsylvania, San Francisco is in the state of California – and you may now be in a state of confusion. In the hope of denting that confusion a little bit, we will now replace one of those uses of the word with a special term for our purposes. We will refer to a microscopic state of a single particle as a ***level***.

A level is a particular set of quantum numbers. Thus $n_x = 2$, $n_y = -3$, $n_z = 0$ is a level, which we can call "the level $(2, -3, 0)$". If a particle is in that state, we will say it "occupies the level $(2, -3, 0)$". Any atom occupying that level has energy $\varepsilon = 13\varepsilon_0 = 13h^2/(2mL^2)$. There may be many levels with the same energy for a single particle. In fact, the last part of Problem 1.3 can be restated as follows: How many levels are there with energy $25\varepsilon_0$ for one particle?

If there is more than one atom (or molecule or particle) in the box, there may be more than one atom in the same level. We will call the number of atoms in a level the ***occupation number*** of the level. Giving the occupation numbers of all of the levels specifies the microscopic state of a system of particles in a box. In other words, we need to know how many particles are in each level, but not which ones are there.

Example 1.2.2
Here is a schematic representation of one possible microscopic state of a system consisting of six atoms with a total of 7 units of energy:

n_x	n_y	n_z	Energy of each atom in this level	Occupation number	Total energy of atoms in level
0	0	0	0	2	0
1	0	0	ε_0	0	0
0	1	0	ε_0	1	ε_0
0	0	1	ε_0	0	0
-1	0	0	ε_0	0	0
0	-1	0	ε_0	0	0
0	0	-1	ε_0	0	0
$\ldots$	$\ldots$	$\ldots$			
1	1	0	$2\varepsilon_0$	3	$6\varepsilon_0$
			All other states Unoccupied		

We are now in a position to say exactly what is meant by Γ for a perfect gas in the situation which formed our starting point: N atoms in an isolated box with total energy U. For convenience we take the box to be a cube of side L, so that $V = L^3$, and $U = B\varepsilon_0$, where B is some (usually very big) number (in Example 1.2.2 above, $N = 6$ and $B = 7$). A possible microscopic state of the system is a specific set of all the occupation numbers of all the levels in the box such that all the particles get used up, and all the energy gets used up. Γ is then the number of possible microscopic states of the system.

Problem 1.4
For the situation outlined in the paragraph above, find Γ in the following cases:

$\qquad$ (a) $\quad N = 2$ and $B = 24 \quad$ (answer $\quad 4116$)

$\qquad$ (b) $\quad N = 2$ and $B = 25 \quad$ (answer $\quad 3906$)

$\qquad$ (c) $\quad N = 2$ and $B = 26 \quad$ (answer $\quad 5040$)

Hint: The problem is just to organize the job of counting. Consider, for example, the case in which $B = 25$. In every possible state of the system, two levels are occupied by one atom each (since the energies must add up to an odd number) and all other levels are empty. First consider all states in which the level $(0, 0, 0)$ is occupied. The other atom must be in some level with 25 units of energy. The possibilities are $(\pm 5, 0, 0)$, $(0, \pm 5, 0)$, $(0, 0, \pm 5)$; six levels so far. We can also reach 25 with a combination of 3^2 and 4^2. In the vector (n_x, n_y, n_z), there are three places for a 4 to appear,