Appendix B3

Derivation of the Boltzmann Distribution

Consider an isolated system, whose total energy is therefore constant, consisting of an ensemble of identical particles[1] that can exchange energy with one another and thereby achieve thermal equilibrium. In order to simplify the numerical derivation, we shall assume that the energy E of any individual particle is restricted to one or another of the values 0, ΔE, $2\Delta E$, $3\Delta E$, . . . Later, after seeing how the distribution emerges, we can let $\Delta E \rightarrow 0$ so that the permitted energies are continuous. Simply to keep the amount of subsequent calculation manageable, we will assume that the system consists of only six particles (hardly a "large" number!) and that the total energy E_{total} of the system is $8\Delta E$, both numbers being arbitrarily chosen, the latter of necessity being an integer multiple of ΔE.

It is also convenient at this point to introduce the concept of *macrostates* and *microstates*. The term *microstate* refers to the description of the system in which the state of every individual particle is specified. For classical particles this means specifying the position and momentum, and hence energy, for each. In quantum mechanics, as we shall see in the following sections, it means specifying a complete set of quantum numbers for each particle. The macrostate for a system is a less detailed description in which only the number of particles occupying each energy state is specified.

Since the particles can exchange energy with one another, all possible macrostates, i.e., divisions of the total energy $E_{total} = 8\Delta E$ between six particles, can occur. For the example we are considering there are 20 macrostates, labeled 1 through 20 in Table B3-1. For instance, macrostate 1 has five particles with $E = 0$ and one with $E = 8\Delta E$; macrostate 2 has four particles with $E = 0$, one with $E = \Delta E$, and one with $E = 7\Delta E$; and so on. Notice that there are six different ways in which we can rearrange the particles in macrostate 1 so as to achieve that particular division of the total energy $8\Delta E$, since any one of the particles can be put into the state $8\Delta E$ with the other five in the state $E = 0$. Each of these six arrangements is different from the other because the classical particles in a microstate are identical in terms of physical properties, but distinguishable in terms of position and momentum, and hence energy. Thus, the rearrangements of the five particles in the $E = 0$ state are not distinguishable from one another, since all five have the same energy. The number of distinguishable rearrangements of the particles within a given macrostate is the number of microstates.

The way in which the number of microstates is computed is as follows. For six particles the rules of statistics tell us that there are 6! different rearrangements or permutations possible. For N particles the number is, of course $N!$. However, since rearrangements within the same energy state are not distinguishable, those must be divided out of the total:

$$\text{Number of microstates} = \frac{N!}{n_0!n_1! \cdots n_i!}$$

For macrostate 1 there are five particles in the $E = 0$ state, so the 5! rearrangements of those five must be divided out of the 6! total number for all six particles in order to obtain the number N of *distinguishable* rearrangements, or microstates, for macrostate 1. Since $6!/5! = 6$, that is how the number of microstates for macrostate 1 was determined. The following example illustrates the calculation for macrostate 6 of the system we are using for the derivation.

Example B3-1 Number of Microstate

Compute the number of microstates, i.e., distinguishable rearrangements, for macrostate 6 in Table B3-1.

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Solution

The total number of possible rearrangements of six particles is 6!; however, energy state $E = 0$ contains three particles, hence 3! indistinguishable rearrangements, and energy state $E = \Delta E$ contains two particles, hence 2! more. Therefore, the total number of microstates is

$$\frac{N!}{n_0!n_1!} = \frac{6!}{3! \times 2!} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{3 \times 2 \times 1 \times 2 \times 1} = 60$$

If we now make the reasonable assumption that all microstates occur with the same probability, then the relative probability P_j that macrostate j will occur is proportional to the number of microstates that exist for that state. For our system there are 1287 total microstates, so the relative probability P_j of occurrence for each of the 20 macrostates is the number of microstates listed in the column on the right of Table B3-1 divided by 1287. Now we are close to obtaining the approximate form of the Boltzmann distribution. Assuming that the most prob-

Table B3-1 States and occupation probabilities for six particles with total energy $8\Delta E$

Macrostate	Number of particles with energy E_i equal to $i\Delta E$									Number of
j	0	ΔE	$2\Delta E$	$3\Delta E$	$4\Delta E$	$5\Delta E$	$6\Delta E$	$7\Delta E$	$8\Delta E$	microstates
1	5	0	0	0	0	0	0	0	1	6
2	4	1	0	0	0	0	0	1	0	30
3	4	0	1	0	0	0	1	0	0	30
4	4	0	0	1	0	1	0	0	0	30
5	4	0	0	0	2	0	0	0	0	15
6	3	2	0	0	0	0	1	0	0	60
7	3	0	2	0	1	0	0	0	0	60
8	3	0	1	2	0	0	0	0	0	60
9	3	1	1	0	0	1	0	0	0	120
10	3	1	0	1	1	0	0	0	0	120
11	2	0	4	0	0	0	0	0	0	15
12*	2	2	0	2	0	0	0	0	0	90
13*	2	1	2	1	0	0	0	0	0	180
14*	2	2	1	0	1	0	0	0	0	180
15	2	3	0	0	0	1	0	0	0	60
16	1	4	0	0	1	0	0	0	0	30
17	1	3	1	1	0	0	0	0	0	120
18	1	2	3	0	0	0	0	0	0	60
19	0	4	2	0	0	0	0	0	0	15
20	0	5	0	1	0	0	0	0	0	6
$n(E_i)$	2.31	1.54	0.98	0.59	0.33	0.16	0.07	0.02	0.005	1287

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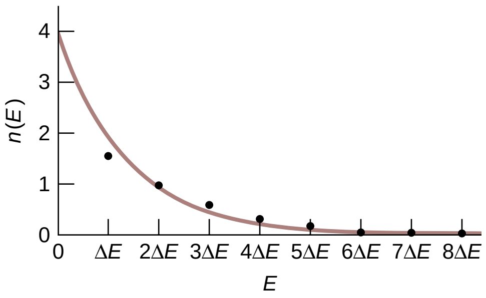

Fig. B3-1 $n(e)$ vs. E for data from Table B3-1. Solid curve is the exponential $n(E) = Be^{-E/E_c}$, where the constants B and E_c have been adjusted to give the best fit to the data points.

able distribution of the particles among the available states is that corresponding to thermal equilibrium, it remains only for us to calculate how many particles $n(E_i)$ are likely to be found in each of the nine energy states $E_0 = 0$ through $E_8 = 8\Delta E$. Consider the $E_0 = 0$ state. For macrostate 1, the probability of occurrence P_1 is $6/1287$ and there are five particles in the $E_0 = 0$ energy state; therefore, macrostate 1 will contribute $5 \times (6/1287) = 0.023$ particles to the total for $E_0 = 0$. The numbers of particles contributed by the other 19 macrostates to the $E_0 = 0$ state are computed in an identical manner and, when added, yield a total $n(0) =$ 2.31 particles, meaning that an average of 2.31 of the six particles will be found to have $E = 0$. Thus, in general the $n(E_i)$ values are given by

$$n(E_i) = \sum_j n_{ij}p_j = g_i f(E_i) \qquad \textbf{B3-1}\boldsymbol{a}$$

where g_i is the statistical weight of state i and $f(E_i)$ is the probability that a particle will have energy E_i. Clearly, then,

$$N = \sum_i n(E_i) \qquad \textbf{B3-1}\boldsymbol{b}$$

The bottom row of Table B3-1 records the result of this calculation for each of the possible energies. Note that the sum of the $n(E_i)$ values is 6, as you would expect.

In Figure B3-1 the values of $n(E_i)$ are plotted against E. The curve shown with the solid line is an exponential function fitted to the data, where B and E_c are constants:

$$n(E) = Be^{-E/E_c} \qquad \textbf{B3-2}$$

If we allow ΔE to become smaller while keeping the total energy the same as before, we get more data points on the graph. In the limit as $\Delta E \rightarrow 0$, E becomes a continuous variable and $n(E)$ a continuous function. If we also increase the number of particles to a statistically large number, we find that the data points fall exactly on the solid curve in Figure B3-1, i.e., the form of the Boltzmann distribution is correctly given by Equation B3-2. Verifying this with an extension of the calculation for six particles and $E_{\text{total}} = 8\Delta E$ to a large number of particles and energy states would be a formidable task. Fortunately, there is a much simpler, but subtle, way to show that it is correct, as has been described by Eisberg and Resnick.[2]

When a particular particle gains energy as the result of an interaction, it does so at the expense of the rest of the particles since the total energy of the system is conserved. Except for this conservation requirement, the particles are independent of one another and, in particular, there is no prohibition or constraint on more than one particle occupying the exact same energy state, as Table B3-1 illustrates. Consider just two particles from the ensemble. Let the probability of finding one of them in the energy state E_1 be given by $f(E_1)$. Since the distribution function is the same for all of the particles (because they are identical), the probability of finding the second one in an energy state E_2 is found by evaluating that function at E_2, i.e., $f(E_2)$. Since the particles are independent of one another, so are their probabilities. Consequently, according to probability theory, the probability of *both* occurrences, i.e., of finding one particle with energy E_1 and the other with energy E_2, is the product of the probabilities $f(E_1) \times f(E_2)$. (This is equivalent to the probability of obtaining heads on two successive

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coin tosses. The probability of getting heads is 1/2 on each toss, and the tosses, like the particles, are independent, so the probability of getting heads twice is $1/2 \times 1/2 = 1/4$.)

Now consider all of the macrostates of the system for which the sum of the energies of the two particles totals $E_1 + E_2$, as was just discussed, but for which the two particles share the total differently from before.[3] Since the energy is conserved, the remainder of the system has the same amount of energy (and the same number of particles) for each of these macrostates, namely, $E_{total} - (E_1 + E_2)$. So all of these remainders have the same number of ways to divide their energy among their constituent particles. Therefore, the probability for those microstates in which $E_1 + E_2$ is shared between the two particles in a certain way can differ from the probability for those microstates in which $E_1 + E_2$ is shared differently *only* if the different ways $E_1 + E_2$ can be shared occur with different probabilities. *However,* we have already assumed that all microstates occur with the same probability; therefore, we must conclude that all microstates in which $E_1 + E_2$ is shared differently between the two particles occur with the same probability. This means that the probability for such microstates occurring is some function of the sum $E_1 + E_2$, say, $h(E_1 + E_2)$. The original sharing of energy, E_1 to one particle and E_2 to the other, is certainly one of these and, hence, has probability $h(E_1 + E_2)$. But we have already shown that particular sharing to occur with probability $f(E_1) \times f(E_2)$, and we must conclude, therefore, that

$$f(E_1) \times f(E_2) = h(E_1 + E_2)$$

Thus, the probability distribution $f(E)$ that we seek has the property that the product of the results of evaluating the function $f(E)$ at two different energies is a function of the sum of those energies. The *only* mathematical function that has this property is the exponential function.[4] If we take $n(E_i)$, the average number of particles with energy E_i (again, see Table B3-1), to be proportional to $f(E_i)$, as would be expected, then we have from Equation B3-2 that

$$f(E) = Ae^{-E/E_c} \qquad \textbf{B3-3}$$

from which we conclude that the exponential form used to fit the data in Figure B3-1 is the only correct form of the distribution of identical, distinguishable particles among the available energy states of a classical system.[5]

Boltzmann used calculus of variations to do a much more general derivation of Equation B3-3 than we have done here, obtaining for the constant E_c, independent of the nature of the particles, the value

$$E_c = kT \qquad \textbf{B3-4}$$

where k is the Boltzmann constant given in Equation 8-10 and T is the absolute temperature. Inserting E_c from Equation B3-4 into Equation B3-3 gives the Boltzmann distribution f_B, the probability that a state with energy E is occupied at temperature T:

$$f_B(E) = Ae^{-E/kT} \qquad \textbf{8-13}$$

In a wave-mechanical treatment of the example system of six identical particles that we used in the optional derivation of the Boltzmann distribution above, the individual microstates that were identified for a particular macrostate cannot be distinguished from one another. Thus, rather than the 1287 distinguishable microstates listed in Table B3-1, the system of six identical, indistinguishable particles with a total energy $8\Delta E$ has only the 20 macrostates. Again assuming that each of these states occurs with equal probability, as we did with the distinguishable microstates earlier, the average number of particles in each energy state is computed just as illustrated in that example. For example, for the $E = 0$ state, state 1 contributes (see Table B3-1)

$$\frac{\text{Number of particles in state 1 with } E = 0}{\text{Number of states}} = \frac{5}{20}$$

Continued

Table B3-2 Distribution of six quantum particles with total energy $8\Delta E$									
Energy state	**0**	ΔE	$2\Delta E$	$3\Delta E$	$4\Delta E$	$5\Delta E$	$6\Delta E$	$7\Delta E$	$8\Delta E$
$n_{BE}(E)$	2.45	1.55	0.90	0.45	0.30	0.15	0.10	0.05	0.05
$n_{FD}(E)$	2.00	1.67	1.00	1.00	0.33	0	0	0	0

and the average number of particles $n_{BE}(0)$ in energy state $E = 0$ is, therefore,

$$n_{BE}(0) = \frac{[5 + (4 \times 4) + (5 \times 3) + (5 \times 2) + (3 \times 1)]}{20} = 2.45$$

Table B3-2 lists the average number of such particles $n_{BE}(E)$ in each energy state computed in the same manner as the example above. Note that the number of particles totals 6, as expected.

There is yet another condition that limits the way in which quantum-mechanical particles that obey the Pauli exclusion principle can be distributed among the energy states. If our six particles were electrons, the exclusion principle would prevent more than two (one with spin up and one with spin down) from occupying any particular energy. Since the exclusion principle applies to all particles that, like electrons, have $\frac{1}{2}$-integral spins, such as protons, neutrons, muons, and quarks, this limitation in number per energy state applies to them, also. Examining Table B3-1, we see that only the three macrostates marked with asterisks (12, 13, and 14) conform to this limitation. Thus, particles that obey the exclusion principle can occupy only those three states. Once again assuming that each is occupied with equal probability, the average number of particles $n_{FD}(E)$ in each energy state is computed as before. For example, the average number of particles in the $E = 0$ state, $n_{FD}(0)$, is

$$n_{FD}(0) = \frac{\text{number of particles with } E = 0}{\text{number of states}} = \frac{(2 + 2 + 2)}{3} = 2$$

The bottom row in Table B3-2 records the results of computing $n_{FD}(E)$ for each of the values of E for six identical, indistinguishable particles that obey the exclusion principle.

Notes for Appendix B3

1. We use the term *particles* here as a specific example. They could be molecules, grains of dust, or coil springs, for example, just as long as they are all identical and can contain energy.
2. See R. Eisberg and R. Resnick, *Quantum Physics,* 2d ed., Wiley, New York, 1985, Appendix C-4.
3. Using the particles in Table B3-1 as an example, suppose $E_1 + E_2 = 5\Delta E$. Then macrostates 4, 8, 9, 10, 13, 14, 15, 16, and 17 are all ones in which two particles have total energy $5\Delta E$, although each particle's share varies between the macrostates.
4. Recall that $e^a \times e^b = e^{(a+b)}$.
5. This argument allows both positive and negative exponentials. The positive exponential is ruled out on physical grounds, since it predicts an infinite probability that a particle will have infinite energy, which is in obvious disagreement with experimental observation.