QUANTUM PHYSICS

OF ATOMS, MOLECULES, SOLIDS, NUCLEI, AND PARTICLES

Second Edition

$$\frac{1}{\sqrt{2}}\left[\psi_\alpha(x_1)\psi_\beta(x_2) - \psi_\beta(x_1)\psi_\alpha(x_2)\right]$$

Robert Eisberg
Robert Resnick

Useful Constants and Conversion Factors

Quoted to a useful number of significant figures.

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	$= 0.6582 \times 10^{-15}$ eV-sec
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Fine-structure constant	$\alpha = e^2/4\pi\epsilon_0 \hbar c = 7.30 \times 10^{-3} \simeq 1/137$
kT at room temperature	$k300°K = 0.0258$ eV $\simeq 1/40$ eV

1 eV $= 1.602 \times 10^{-19}$ joule		1 joule $= 6.242 \times 10^{18}$ eV
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QUANTUM PHYSICS

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The figure on the cover is from Section 9-4, where it is used to show the tendency for two identical spin 1/2 particles (such as electrons) to avoid each other if their spins are essentially parallel. This tendency, or its inverse for the antiparallel case, is one of the recurring themes in quantum physics explanations of the properties of atoms, molecules, solids, nuclei, and particles.
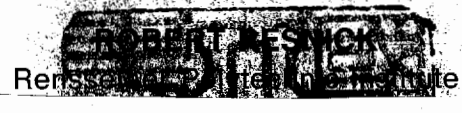
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Appendix C
THE BOLTZMANN DISTRIBUTION

We present here a simple numerical argument that leads to an approximation of the Boltzmann distribution, and then an even simpler general argument that verifies the exact form of the distribution. Consider a system containing a large number of physical entities of the same kind that are in thermal equilibrium at temperature T. To be in equilibrium they must be able to exchange energy with each other. In the exchanges the energies of the entities will fluctuate, and at any time some will have more than the average energy and some will have less. However, the classical theory of statistical mechanics demands that these energies $\mathscr{E}$ be distributed according to a definite probability distribution, whose form is specified by T. One reason is that the average value $\bar{\mathscr{E}}$ of the energy of each entity is determined by the probability distribution, and $\bar{\mathscr{E}}$ should have a definite value for a particular T.

To illustrate these ideas, consider a system consisting of entities, of the same kind, which can contain energy. An example would be a set of identical coil springs, each of which contains energy if its length is vibrating. Assume the system is isolated from the surrounding environment so that the total energy content is constant, and assume also that the entities can exchange energy with each other through some mechanism so that the constituents of the system can come into thermal equilibrium with each other. Purely for the purpose of simplifying the subsequent calculations, we shall, for the moment, also assume that the energy of any entity is restricted to one of the values $\mathscr{E} = 0, \Delta\mathscr{E}, 2\Delta\mathscr{E}, 3\Delta\mathscr{E}, 4\Delta\mathscr{E}, \ldots$ Later we shall let the interval $\Delta\mathscr{E}$ go to zero so that all the values of energy are permitted. For additional simplicity, we shall at first also consider that there are only four (an arbitrarily chosen small number) entities in the system and that the total energy of the system has the value $3\Delta\mathscr{E}$ (which is also chosen arbitrarily to be a small one of the integral multiples of $\Delta\mathscr{E}$ that the total energy must, by the above assumption, necessarily be). Later we shall generalize to systems having a large number of entities and any total energy.

Because the four entities can exchange energy with one another, all possible divisions of the total energy $3\Delta\mathscr{E}$ between the four entities can occur. In Figure C-1 we show all the possible divisions, the divisions being labelled by the letter i. For $i = 1$, three entities have $\mathscr{E} = 0$ and the fourth entity has $\mathscr{E} = 3\Delta\mathscr{E}$, giving us the required total energy of $3\Delta\mathscr{E}$. Actually we can distinguish among four different ways of getting such a division, because any one of the four entities can be the one in the energy state $\mathscr{E} = 3\Delta\mathscr{E}$. We indicate this in the figure in the column marked "number of distinguishable duplicate divisions." A second possible type of division, labelled $i = 2$, is one in which two entities have $\mathscr{E} = 0$, the third entity has $\mathscr{E} = \Delta\mathscr{E}$, and the fourth has $\mathscr{E} = 2\Delta\mathscr{E}$. There are twelve distinguishable duplicate divisions in this case, as we verify in the next paragraph. The third possible division, labelled $i = 3$, also has four distinguishable duplicate ways of letting one entity have $\mathscr{E} = 0$ and the other three have $\mathscr{E} = \Delta\mathscr{E}$, giving the required total energy $3\Delta\mathscr{E}$.

In evaluating the number of duplicate divisions we count as distinguishable duplicates any rearrangement of entities between different energy states. However, any rearrangement of entities in the same energy state is not counted as a duplicate, because entities of the same kind having the same energy cannot be distinguished experimentally from one another. That is, *the identical entities are treated as if they are distinguishable*, except for rearrangements within the same energy state. The total number of rearrangements (permutations) of the four entities is $4! \equiv 4 \times 3 \times 2 \times 1$. (The number of different ways of ordering four objects is $4!$ since there are four choices of which object is taken first, three choices of which of the remaining

Label of divisions	$\mathcal{E} = 0$	$\mathcal{E} = \Delta\mathcal{E}$	$\mathcal{E} = 2\Delta\mathcal{E}$	$\mathcal{E} = 3\Delta\mathcal{E}$	$\mathcal{E} = 4\Delta\mathcal{E}$	Number of distinguishable duplicate divisions	P_i
$i = 1$	✓✓✓			✓		4	4/20
$i = 2$	✓✓	✓	✓			12	12/20
$i = 3$	✓	✓✓✓				4	4/20

$n'(\mathcal{E})$ 40/20   24/20   12/20   4/20   0/20

Figure C-1   Illustrating a simple calculation leading to an approximation to the Boltzmann distribution.

objects is taken next, two choices of which is taken next, and one choice only for the last object. The total number of choices is $4 \times 3 \times 2 \times 1 \equiv 4!$. For n objects the number of different orderings is $n! \equiv n(n-1)(n-2) \cdots 1$.) But rearrangements within the same energy state do not count. Hence, for example, in the case $i = 2$, the number of distinguishable duplicate divisions is reduced from $4!$ to $4!/2! = 12$ because there are $2!$ rearrangements within the state $\mathcal{E} = 0$ that do not count as distinguishable. In cases $i = 1$, or $i = 3$, the number of such divisions is reduced from $4!$ to $4!/3! = 4$ since there are $3!$ rearrangements within the state $\mathcal{E} = 0$, or the state $\mathcal{E} = \Delta\mathcal{E}$, that do not count as distinguishable.

We now make the final assumption: *all possible divisions of the energy of the system occur with the same probability.* Then the probability that the divisions of a given type (or label) will occur is proportional to the number of distinguishable duplicate divisions of that type. The relative probability, P_i, is just equal to that number divided by the total number of such divisions. The relative probabilities are listed in the column marked P_i in Figure C-1.

Next let us calculate $n'(\mathcal{E})$, the probable number of entities in the energy state $\mathcal{E}$. Consider the energy state $\mathcal{E} = 0$. For divisions of the type $i = 1$, there are three entities in this state, and the relative probability P_i that these divisions occur is 4/20; for $i = 2$ there are two entities in this state, and P_i is 12/20; for $i = 3$ there is one entity, and P_i is 4/20. Thus $n'(0)$, the probable number of entities in the state $\mathcal{E} = 0$, is $3 \times (4/20) + 2 \times (12/20) + 1 \times (4/20) = 40/20$. The values of $n'(\mathcal{E})$ calculated in the same way for the other values of $\mathcal{E}$ are listed on the bottom of Figure C-1, marked $n'(\mathcal{E})$. (Note that the sum of these numbers is four, so that we find a correct total of four entities in all the states.) The values of $n'(\mathcal{E})$ are also plotted as points in Figure C-2. The solid curve in Figure C-2 is the decreasing exponential function

$$n(\mathcal{E}) = Ae^{-\mathcal{E}/\mathcal{E}_0} \tag{C-1}$$

where A and $\mathcal{E}_0$ are constants which have been adjusted to give the best fit of the curve to the points representing the results of our calculation. The rapid drop in $n'(\mathcal{E})$ with increasing $\mathcal{E}$ reflects the fact that, if one entity takes a larger share of the total energy of the system, the remainder of the system must necessarily have a reduced energy, and so a considerably reduced number of ways of dividing that energy between its constituents. That is, there are many fewer divisions of the total energy of the system in situations where a relatively large part of the energy is concentrated on one entity.
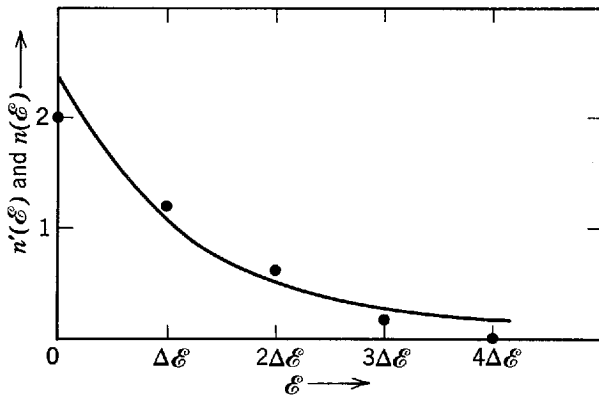
Figure C-2 A comparison of the results of a simple calculation and the Boltzmann distribution.

Imagine now that we successively make $\Delta\mathscr{E}$ smaller and smaller, increasing the number of allowed states at the same time so as to keep the total energy at its previous value. The result of such a process is that the calculated function $n'(\mathscr{E})$ becomes defined for values of $\mathscr{E}$ which are closer and closer together. (That is, we get more points on our distribution.) In the limit as $\Delta\mathscr{E} \to 0$, the energy $\mathscr{E}$ of an entity becomes a continuous variable, as classical physics demands, and the distribution $n'(\mathscr{E})$ becomes a continuous function. If, finally, we allow the number of entities in the system to become large, this function is found to be identical with the decreasing exponential $n(\mathscr{E})$ of (C-1). (That is, as the points become closer and closer together, they no longer scatter about the decreasing exponential but fall right on it.) To verify this, by a straightforward extension of our calculation to the case of a very large number of energy states and entities, involves some formidable bookkeeping in enumerating the distinguishable divisions that have the required values of total energy and number of entities, and then calculating the many relative probabilities. We shall verify the validity of the probability distribution given in (C-1) by a more subtle, but much simpler, procedure.

Consider a system of many identical entities in thermal equilibrium with each other, enclosed in walls which isolate it from the surroundings. Equilibrium requires that the entities be able to exchange energy. For instance, in interacting with the walls of the system, the entities can exchange energy with the walls and so indirectly exchange energy with each other. Thus the entities interact with each other in that if one gains energy, it does so at the expense of the total energy content of the remainder of the system (all the other entities, plus the walls). Except for this energy conservation constraint, the entities are independent of each other. *The presence of one entity in some particular energy state in no way inhibits or enhances the chance that another identical entity will be in that state.* Now consider two of these entities. Let the probability of finding one of them in an energy state at energy $\mathscr{E}_1$ be given by $p(\mathscr{E}_1)$. Then the probability of finding the other in a state at energy $\mathscr{E}_2$ will be given by the same probability distribution function, since the entities have identical properties, but evaluated at the energy $\mathscr{E}_2$. The probability will be $p(\mathscr{E}_2)$. Because of the independent behavior of the entities, these two probabilities are independent of each other. As a consequence, the probability that the energy of one entity will be $\mathscr{E}_1$ *and* that the energy of the other will be $\mathscr{E}_2$ is given by $p(\mathscr{E}_1)p(\mathscr{E}_2)$. The reason is that independent probabilities are multiplicative. (If the probability of obtaining heads in one flip of a coin is $1/2$, then the probability of obtaining heads in each of two flips is $(1/2) \times (1/2) = 1/4$, since the flips are independent.)

Next consider all divisions of the energy of the system in which the sum of the energies of the two entities has the same fixed value $\mathscr{E}_1 + \mathscr{E}_2$ as in the particular case just discussed, but in which the two entities take different shares of that energy. Since the total energy of the isolated system is constant, for all of these divisions the remainder of the system will also have a fixed value of energy. So for all of them there are the same possible number of ways for the remainder of the system to divide its energy between its constituents. As a consequence, the probability of those divisions in which there is a certain sharing of the energy $\mathscr{E}_1 + \mathscr{E}_2$ between the two entities can differ from the probability of other divisions, in which there is a different sharing of that energy, only if these different sharings occur with different probabilities. If we again assume that *all possible divisions of the energy of the system occur with the same probability* we see that this cannot be, and we conclude that all divisions in which the same energy

$\mathscr{E}_1 + \mathscr{E}_2$ is shared between the two entities in different ways occur with the same probability. In other words, the probability of all such divisions is a function only of $\mathscr{E}_1 + \mathscr{E}_2$ and so can be written as, say, $q(\mathscr{E}_1 + \mathscr{E}_2)$. However, we concluded earlier that the probability for a particular case can also be written as $p(\mathscr{E}_1)p(\mathscr{E}_2)$. Thus we find that $p(\mathscr{E}_1)p(\mathscr{E}_2) = q(\mathscr{E}_1 + \mathscr{E}_2)$.

The essential point here is that the probability distribution function $p(\mathscr{E})$ has the property that the product of two of these functions, evaluated at two different values of the variables, $\mathscr{E}_1$ and $\mathscr{E}_2$, is a function of the sum, $\mathscr{E}_1 + \mathscr{E}_2$, of these variables. But an exponential function, and only an exponential function, has this property. Recall that the product of two exponentials with different exponents is an exponential whose exponent is the sum of the two exponents. Specifically, if we take the probability $p(\mathscr{E})$ of finding an entity in a state at energy $\mathscr{E}$ to be proportional to the probable number $n(\mathscr{E})$ of entities in that state, as it certainly should be, and use (C-1) to evaluate $n(\mathscr{E})$, we have the function

$$p(\mathscr{E}) = Be^{-\mathscr{E}/\mathscr{E}_0} \tag{C-2}$$

where B is proportional to the A in (C-1). This function demonstrates the required property since

$$p(\mathscr{E}_1)p(\mathscr{E}_2) = Be^{-\mathscr{E}_1/\mathscr{E}_0}Be^{-\mathscr{E}_2/\mathscr{E}_0} = B^2 e^{-(\mathscr{E}_1+\mathscr{E}_2)/\mathscr{E}_0} = q(\mathscr{E}_1 + \mathscr{E}_2)$$

(There is no loss of generality in choosing e to be the base of the exponential function instead of some other number, such as 10. The reason is that an exponential function using any other base b can be transformed into an exponential with base e by the relation $b^x = e^{x \ln b}$. Hence changing the base amounts to no more than changing the as-yet-not-evaluated constant $\mathscr{E}_0$.) Our argument does not actually prove that $n(\mathscr{E})$ is a decreasing, instead of increasing, exponential, but an increasing exponential can be ruled out on physical grounds as its value goes to infinity for large values of $\mathscr{E}$. Thus we have verified the general validity of (C-1).

Now we shall evaluate the constant $\mathscr{E}_0$ in (C-1)

$$n(\mathscr{E}) = Ae^{-\mathscr{E}/\mathscr{E}_0}$$

By treating a system containing two different kinds of entities in thermal equilibrium, it is not difficult to prove that the value of $\mathscr{E}_0$ does not depend on the type of entities comprising a system. Thus we shall use in our argument entities with the simplest properties. Since $n(\mathscr{E})$ is the probable number of entities of the system in an energy state at $\mathscr{E}$, the number of entities whose energies would be found in the interval from $\mathscr{E}$ to $\mathscr{E} + d\mathscr{E}$ equals $n(\mathscr{E})$ times the number of states in that interval. If that number is independent of the value of $\mathscr{E}$ (i.e., if the states are uniformly distributed in energy), then the number will be proportional to the size $d\mathscr{E}$ of the interval. This is the case if the entities are simple harmonic oscillators, like the coil springs mentioned earlier. So the probable number of simple harmonic oscillators with an energy from $\mathscr{E}$ to $\mathscr{E} + d\mathscr{E}$, in an equilibrium system containing many of them, is proportional to $n(\mathscr{E})d\mathscr{E}$. If the multiplicative constant A is given the proper value, this probability can be made equal to $n(\mathscr{E})d\mathscr{E}$. Then the average energy of one of the oscillators is

$$\bar{\mathscr{E}} = \frac{\displaystyle\int_0^\infty \mathscr{E}\,n(\mathscr{E})\,d\mathscr{E}}{\displaystyle\int_0^\infty n(\mathscr{E})\,d\mathscr{E}}$$

The integral in the numerator has an integrand which is the energy weighted by the number of oscillators having that energy; the integral in the denominator is just the total number of oscillators. If we evaluate $n(\mathscr{E})$ from (C-1), we have

$$\bar{\mathscr{E}} = \frac{\displaystyle\int_0^\infty A\mathscr{E}e^{-\mathscr{E}/\mathscr{E}_0}\,d\mathscr{E}}{\displaystyle\int_0^\infty Ae^{-\mathscr{E}/\mathscr{E}_0}\,d\mathscr{E}}$$

(Note that we do not need to know the actual value of A.) By proceeding in a manner completely analogous to what is done in Example 1-4, except that integrals are involved instead of sums, we find

$$\bar{\mathscr{E}} = \mathscr{E}_0 \qquad \text{(C-3)}$$

But according to the classical law of equipartition of energy, as expressed in (1-16), for simple harmonic oscillators in equilibrium at temperature T

$$\bar{\mathscr{E}} = kT \qquad \text{(C-4)}$$

where *Boltzmann's constant* $k = 1.38 \times 10^{-23}$ joule/°K. Combining (C-3) and (C-4), we have

$$\mathscr{E}_0 = kT \qquad \text{(C-5)}$$

This result is correct for entities of any type, even though we have obtained it for the particular case of simple harmonic oscillators. Therefore we may write (C-1) as

$$n(\mathscr{E}) = Ae^{-\mathscr{E}/kT} \qquad \text{(C-6)}$$

This is the famous *Boltzmann distribution*. Since the value of A is not specified, (C-6) actually tells us about a proportionality: the probable number of entities of a system in equilibrium at temperature T that will be in a state of energy $\mathscr{E}$ is proportional to $e^{-\mathscr{E}/kT}$. Expressed in different terms: the probability that the state of energy $\mathscr{E}$ will be occupied by an entity is proportional to $e^{-\mathscr{E}/kT}$.

The value chosen for the constant A is dictated by convenience. In Chapter 1 we apply the Boltzmann distribution to a system of simple harmonic oscillators. As discussed here, in such a system $n(\mathscr{E})\,d\mathscr{E}$ is proportional to the probable number of oscillators with energy in the range $\mathscr{E}$ to $\mathscr{E} + d\mathscr{E}$, since the states of a simple harmonic oscillator are uniformly distributed in energy. Of course, $n(\mathscr{E})\,d\mathscr{E}$ is also proportional to the probability $P(\mathscr{E})\,d\mathscr{E}$ of finding a particular one of the oscillators with energy in this range. Thus we have

$$P(\mathscr{E}) = Ce^{-\mathscr{E}/\mathscr{E}_0}$$

providing the constant C is properly chosen. This is done by setting

$$\int_0^\infty P(\mathscr{E})\,d\mathscr{E} = \int_0^\infty Ce^{-\mathscr{E}/\mathscr{E}_0}\,d\mathscr{E} = C\int_0^\infty e^{-\mathscr{E}/\mathscr{E}_0}\,d\mathscr{E} = 1 \qquad \text{(C-7)}$$

That is, we define $P(\mathscr{E})\,d\mathscr{E}$ to be the probability of finding a particular simple harmonic oscillator with energy from $\mathscr{E}$ to $\mathscr{E} + d\mathscr{E}$, and so for consistency we must then demand that $\int_0^\infty P(\mathscr{E})\,d\mathscr{E}$ have the value one because the integral is just the probability of finding it with any energy. By evaluating $\int_0^\infty e^{-\mathscr{E}/\mathscr{E}_0}\,d\mathscr{E}$ in (C-7), and then solving for C, we find $C = 1/kT$. Then we have a special form of the Boltzmann distribution

$$P(\mathscr{E}) = \frac{e^{-\mathscr{E}/\mathscr{E}_0}}{kT} \qquad \text{(C-8)}$$

which is used in Chapter 1.

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