5.4 QUANTUM STATISTICAL MECHANICS

At absolute zero, a physical system occupies its lowest allowed energy configuration. As we turn up the temperature, random thermal activity will begin to populate the excited states, and this raises the following question: If we have a large number N of particles, in thermal equilibrium at temperature T, what is the probability that a particle, selected at random, would be found to have the specific energy, E_j? Note that the "probability" in question has nothing to do with quantum indeterminacy—exactly the same question arises in *classical* statistical mechanics. The reason we must be content with a *probabilistic* answer is that we are typically dealing with enormous numbers of particles, and we could not possibly expect to keep track of each one separately, whether or *not* the underlying mechanics is deterministic.

The **fundamental assumption of statistical mechanics** is that in **thermal equilibrium** every distinct state with the same *total* energy, E, is equally probable. Random thermal motions constantly shift energy from one particle to another, and from one form (rotational, kinetic, vibrational, etc.) to another, but (absent external influences) the *total* is fixed by conservation of energy. The assumption (and it's a *deep* one, worth thinking about) is that this continual redistribution of energy does not favor any particular state. The **temperature**, T, is simply a measure of the total energy of a system in thermal equilibrium. The only new twist introduced by quantum mechanics has to do with *how we count the distinct states* (it's actually *easier* than in the classical theory, because the states are generally discrete), and this depends critically on whether the particles involved are distinguishable, identical bosons, or identical fermions. The arguments are relatively straightforward, but the *arithmetic* gets pretty dense, so I'm going to begin with an absurdly simple example, so you'll have a clear sense of what is at issue when we come to the general case.

5.4.1 An Example

Suppose we have just *three* noninteracting particles (all of mass m) in the one-dimensional infinite square well (Section 2.2). The total energy is

$$E = E_A + E_B + E_C = \frac{\pi^2\hbar^2}{2ma^2}(n_A^2 + n_B^2 + n_C^2) \qquad [5.67]$$

(see Equation 2.27), where n_A, n_B, and n_C are positive integers. Now suppose, for the sake of argument, that $E = 363(\pi^2\hbar^2/2ma^2)$, which is to say,

$$n_A^2 + n_B^2 + n_C^2 = 363. \qquad [5.68]$$

There are, as it happens, 13 combinations of three positive integers, the sum of whose squares is 363: All three could be 11, two could be 13 and one 5

(which occurs in three permutations), one could be 19 and two 1 (again, three permutations), or one could be 17, one 7, and one 5 (six permutations). Thus (n_A, n_B, n_C) is one of the following:

$$(11, 11, 11),$$

$$(13, 13, 5),\ (13, 5, 13),\ (5, 13, 13),$$

$$(1, 1, 19),\ (1, 19, 1),\ (19, 1, 1),$$

$$(5, 7, 17),\ (5, 17, 7),\ (7, 5, 17),\ (7, 17, 5),\ (17, 5, 7),\ (17, 7, 5).$$

If the particles are *distinguishable*, each of these represents a distinct quantum state, and the fundamental assumption of statistical mechanics says that in thermal equilibrium[20] they are all equally likely. But I'm not interested in knowing *which* particle is in *which* (one-particle) state, only the total *number* of particles in each state—the **occupation number**, N_n, for the state ψ_n. The collection of all occupation numbers for a given 3-particle state we will call the **configuration**. If all three are in ψ_{11}, the configuration is

$$(0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 3, 0, 0, 0, 0, 0, 0, 0, \ldots). \qquad [5.69]$$

(i.e., $N_{11} = 3$, all others zero). If two are in ψ_{13} and one is in ψ_5, the configuration is

$$(0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 2, 0, 0, 0, 0, \ldots), \qquad [5.70]$$

(i.e., $N_5 = 1$, $N_{13} = 2$, all others zero). If two are in ψ_1 and one is in ψ_{19}, the configuration is

$$(2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, \ldots), \qquad [5.71]$$

(i.e., $N_1 = 2$, $N_{19} = 1$, all others zero). And if there is one particle in ψ_5, one in ψ_7, and one in ψ_{17}, the configuration is

$$(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \ldots). \qquad [5.72]$$

(i.e., $N_5 = N_7 = N_{17} = 1$, all others zero.) Of these, the last is the *most probable* configuration, because it can be achieved in six different ways, whereas the middle two occur three ways, and the first only one.

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[20]How the particles maintain thermal equilibrium, if they really don't interact at all, is a problem I'd rather not worry about—maybe God reaches in periodically and stirs things up (being careful not to add or remove any energy). In real life, of course, the continual redistribution of energy is caused precisely by interactions between the particles, so if you don't approve of divine intervention let there be extremely weak interactions—sufficient to thermalize the system (at least, over long time periods), but too small to alter the stationary states and the allowed energies appreciably.

Returning now to my original question, if we select one of these three particles at random, what is the probability (P_n) of getting a specific (allowed) energy E_n? The only way you can get E_1 is if it's in the third configuration (Equation 5.71); the chances of the system being in that configuration are 3 in 13, and in that configuration the probability of getting E_1 is 2/3, so $P_1 = (3/13) \times (2/3) = 2/13$. You could get E_5 either from configuration 2 (Equation 5.70)—chances 3 in 13—with probability 1/3, or from configuration 4 (Equation 5.72)—chances 6 in 13—with probability 1/3, so $P_5 = (3/13) \times (1/3) + (6/13) \times (1/3) = 3/13$. You can only get E_7 from configuration 4: $P_7 = (6/13) \times (1/3) = 2/13$. Likewise, E_{11} comes only from the first configuration (Equation 5.69)—chances 1 in 13—with probability 1: $P_{11} = (1/13)$. Similarly, $P_{13} = (3/13) \times (2/3) = 2/13$, $P_{17} = (6/13) \times (1/3) = 2/13$, and $P_{19} = (3/13) \times (1/3) = 1/13$. As a check, note that

$$P_1 + P_5 + P_7 + P_{11} + P_{13} + P_{17} + P_{19} = \frac{2}{13} + \frac{3}{13} + \frac{2}{13} + \frac{1}{13} + \frac{2}{13} + \frac{2}{13} + \frac{1}{13} = 1.$$

That's when the particles are distinguishable. If in fact they are *identical fermions*, the antisymmetrization requirement (leaving aside spin, for simplicity—or assuming they are all in the *same* spin state, if you prefer) excludes the first three configurations (which assign two—or, worse still, three—particles to the same state), and there is just *one* state in the fourth configuration (see Problem 5.22(a)). For identical fermions, then, $P_5 = P_7 = P_{17} = 1/3$ (and again the sum of the probabilities is 1). On the other hand, if they are *identical bosons* the symmetrization requirement allows for *one* state in each configuration (see Problem 5.22(b)), so $P_1 = (1/4) \times (2/3) = 1/6$, $P_5 = (1/4) \times (1/3) + (1/4) \times (1/3) = 1/6$, $P_7 = (1/4) \times (1/3) = 1/12$, $P_{11} = (1/4) \times (1) = 1/4$, $P_{13} = (1/4) \times (2/3) = 1/6$, $P_{17} = (1/4) \times (1/3) = 1/12$, and $P_{19} = (1/4) \times (1/3) = 1/12$. As always, the sum is 1.

The purpose of this example was to show you how the counting of states depends on the nature of the particles. In one respect it was actually *more complicated* than the realistic situation, in which N is a huge number. For as N grows, the most probable configuration (in this example, $N_5 = N_7 = N_{17} = 1$, for the case of distinguishable particles) becomes *overwhelmingly* more likely than its competitors, so that, for statistical purposes, we can afford to ignore the others altogether:[21] *The distribution of individual particle energies, at equilibrium, is simply their distribution in the most probable configuration.* (If this were true for $N = 3$—which, obviously, it is *not*—we would conclude that $P_5 = P_7 = P_{17} = 1/3$ for the case of distinguishable particles.) I'll return to this point in Section 5.4.3, but first we need to generalize the counting procedure itself.

[21] This is an astonishing and counterintuitive fact about the statistics of large numbers. For a good discussion see Ralph Baierlein, *Thermal Physics*. Cambridge U.P. (1999). Section 2.1.

***Problem 5.22**

(a) Construct the completely antisymmetric wave function $\psi(x_A, x_B, x_C)$ for three identical fermions, one in the state ψ_5, one in the state ψ_7, and one in the state ψ_{17}.

(b) Construct the completely symmetric wave function $\psi(x_A, x_B, x_C)$ for three identical bosons, (i) if all three are in state ψ_{11}, (ii) if two are in state ψ_1 and one is in state ψ_{19}, and (iii) if one is in the state ψ_5, one in the state ψ_7, and one in the state ψ_{17}.

***Problem 5.23** Suppose you had three (noninteracting) particles, in thermal equilibrium, in a one-dimensional harmonic oscillator potential, with a total energy $E = (9/2)\hbar\omega$.

(a) If they are distinguishable particles (but all with the same mass), what are the possible occupation-number configurations, and how many distinct (three-particle) states are there for each one? What is the most probable configuration? If you picked a particle at random and measured its energy, what values might you get, and what is the probability of each one? What is the most probable energy?

(b) Do the same for the case of identical fermions (ignoring spin, as we did in Section 5.4.1).

(c) Do the same for the case of identical bosons (ignoring spin).

5.4.2 The General Case

Now consider an arbitrary potential, for which the one-particle energies are E_1, E_2, $E_3, \ldots$, with degeneracies $d_1, d_2, d_3, \ldots$ (i.e., there are d_n distinct one-particle states with energy E_n). Suppose we put N particles (all with the same mass) into this potential; we are interested in the configuration $(N_1, N_2, N_3, \ldots)$, for which there are N_1 particles with energy E_1, N_2 particles with energy E_2, and so on. *Question:* How many different ways can this be achieved (or, more precisely, how many distinct states correspond to this particular configuration)? The answer, $Q(N_1, N_2, N_3, \ldots)$, depends on whether the particles are distinguishable, identical fermions, or identical bosons, so we'll treat the three cases separately.[22]

First, assume the particles are *distinguishable*. How many ways are there to select (from the N available candidates) the N_1 to be placed in the first "bin"?

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[22]The presentation here follows closely that of Amnon Yariv, *An Introduction to Theory and Applications of Quantum Mechanics*, Wiley, New York (1982).

Answer: the **binomial coefficient**, "N choose N_1,"

$$\binom{N}{N_1} \equiv \frac{N!}{N_1!(N-N_1)!}. \qquad [5.73]$$

For there are N ways to pick the first particle, leaving $(N-1)$ for the second, and so on:

$$N(N-1)(N-2)\ldots(N-N_1+1) = \frac{N!}{(N-N_1)!}.$$

However, this counts separately the $N_1!$ different *permutations* of the N_1 particles, whereas we don't care whether number 37 was picked on the first draw, or on the 29th draw; so we divide by $N_1!$, confirming Equation 5.73. Now, how many different ways can those N_1 particles be arranged *within* the first bin? Well, there are d_1 states in the bin, so each particle has d_1 choices; evidently there are $(d_1)^{N_1}$ possibilities in all. Thus the number of ways to put N_1 particles, selected from a total population of N, into a bin containing d_1 distinct options, is

$$\frac{N!d_1^{N_1}}{N_1!(N-N_1)!}.$$

The same goes for bin 2, of course, except that there are now only $(N-N_1)$ particles left to work with:

$$\frac{(N-N_1)!d_2^{N_2}}{N_2!(N-N_1-N_2)!};$$

and so on. It follows that

$$\begin{aligned} Q(N_1, N_2, N_3, \ldots) &= \frac{N!d_1^{N_1}}{N_1!(N-N_1)!}\frac{(N-N_1)!d_2^{N_2}}{N_2!(N-N_1-N_2)!}\frac{(N-N_1-N_2)!d_3^{N_3}}{N_3!(N-N_1-N_2-N_3)!}\cdots \\ &= N!\frac{d_1^{N_1}d_2^{N_2}d_3^{N_3}\cdots}{N_1!N_2!N_3!\ldots} = N!\prod_{n=1}^{\infty}\frac{d_n^{N_n}}{N_n!}. \end{aligned} \qquad [5.74]$$

(You should pause right now and *check* this result, for the example in Section 5.4.1—see Problem 5.24.)

The problem is a lot easier for *identical fermions*. Because they are indistinguishable, it doesn't matter *which* particles are in *which* states—the antisymmetrization requirement means that there is just *one* N-particle state in which a specific set of one-particle states are occupied. Moreover, only one particle can occupy any given state. There are

$$\binom{d_n}{N_n}$$

ways to choose the N_n occupied states in the nth bin,[23] so

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}. \qquad [5.75]$$

(Check it for the example in Section 5.4.1—see Problem 5.24.)

The calculation is hardest for the case of *identical bosons*. Again, the symmetrization requirement means that there is just one N-particle state in which a specific set of one-particle states are occupied, but this time there is no restriction on the number of particles that can share the same one-particle state. For the nth bin, the question becomes: How many different ways can we assign N_n identical particles to d_n different slots? There are many tricks to solve this combinatorial problem; an especially clever method is as follows: Let dots represent particles and crosses represent partitions, so that, for example, if $d_n = 5$ and $N_n = 7$,

$$\bullet\ \bullet\ \times\ \bullet\ \times\ \bullet\ \bullet\ \bullet\ \times\ \bullet\ \times$$

would indicate that there are two particles in the first state, one in the second, three in the third, one in the fourth, and none in the fifth. Note that there are N_n dots, and $(d_n - 1)$ crosses (partitioning the dots into d_n groups). If the individual dots and crosses were *labeled*, there would be $(N_n + d_n - 1)!$ different ways to arrange them. But for our purposes the dots are all equivalent—permuting them ($N_n!$ ways) does not change the state. Likewise, the crosses are all equivalent—permuting them ($(d_n - 1)!$ ways) changes nothing. So there are in fact

$$\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} = \binom{N_n + d_n - 1}{N_n} \qquad [5.76]$$

distinct ways of assigning the N_n particles to the d_n one-particle states in the nth bin, and we conclude that

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} \qquad [5.77]$$

(Check it for the Example in Section 5.4.1—see Problem 5.24.)

***Problem 5.24** Check Equations 5.74, 5.75, and 5.77, for the example in Section 5.4.1.

****Problem 5.25** Obtain Equation 5.76 by induction. The combinatorial question is this: How many different ways can you put N identical balls into d baskets (never

[23] This should be zero, of course, if $N_n > d_n$, and it *is*, provided we consider the factorial of a negative integer to be infinite.

mind the subscript n for this problem). You could stick all N of them into the third basket, or all but one in the second basket and one in the fifth, or two in the first and three in the third and all the rest in the seventh, etc. Work it out explicitly for the cases $N = 1$, $N = 2$, $N = 3$, and $N = 4$; by that stage you should be able to deduce the general formula.

5.4.3 The Most Probable Configuration

In thermal equilibrium, every state with a given total energy E and a given particle number N is equally likely. So the *most probable configuration* $(N_1, N_2, N_3, \ldots)$ is the one that can be achieved in the largest number of different ways—it is that particular configuration for which $Q(N_1, N_2, N_3, \ldots)$ is a maximum, subject to the constraints

$$\sum_{n=1}^{\infty} N_n = N, \qquad [5.78]$$

and

$$\sum_{n=1}^{\infty} N_n E_n = E. \qquad [5.79]$$

The problem of maximizing a function $F(x_1, x_2, x_3, \ldots)$ of several variables, subject to the constraints $f_1(x_1, x_2, x_3, \ldots) = 0$, $f_2(x_1, x_2, x_3, \ldots) = 0$, etc., is most conveniently handled by the method of **Lagrange multipliers.**[24] We introduce the new function

$$G(x_1, x_2, x_3, \ldots, \lambda_1, \lambda_2, \ldots) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + \cdots, \qquad [5.80]$$

and set *all* its derivatives equal to zero:

$$\frac{\partial G}{\partial x_n} = 0; \quad \frac{\partial G}{\partial \lambda_n} = 0. \qquad [5.81]$$

In our case it's a little easier to work with the *logarithm* of Q, instead of Q itself—this turns the *products* into *sums*. Since the logarithm is a monotonic function of its argument, the maxima of Q and $\ln(Q)$ occur at the same point. So we let

$$G \equiv \ln(Q) + \alpha\left[N - \sum_{n=1}^{\infty} N_n\right] + \beta\left[E - \sum_{n=1}^{\infty} N_n E_n\right]. \qquad [5.82]$$

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[24] See, for example, Mary Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed., Wiley, New York (1983), Chapter 4, Section 9.

where α and β are the Lagrange multipliers. Setting the derivatives with respect to α and β equal to zero merely reproduces the constraints (Equations 5.78 and 5.79); it remains, then, to set the derivative with respect to N_n equal to zero.

If the particles are *distinguishable*, then Q is given by Equation 5.74, and we have

$$G = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)] + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]. \quad [5.83]$$

Assuming the relevant occupation numbers (N_n) are large, we can invoke **Stirling's approximation**:[25]

$$\ln(z!) \approx z \ln(z) - z \quad \text{for } z \gg 1, \quad [5.84]$$

to write

$$G \approx \sum_{n=1}^{\infty} [N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n] + \ln(N!) + \alpha N + \beta E. \quad [5.85]$$

It follows that

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \alpha - \beta E_n. \quad [5.86]$$

Setting this equal to zero, and solving for N_n, we conclude that the *most probable occupation numbers*, for distinguishable particles, are

$$N_n = d_n e^{-(\alpha + \beta E_n)}. \quad [5.87]$$

If the particles are *identical fermions*, then Q is given by Equation 5.75, and we have

$$G = \sum_{n=1}^{\infty} \{\ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!]\} + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]. \quad [5.88]$$

[25] Stirling's approximation can be improved by including more terms in the **Stirling series**, but the first two will suffice for our purposes. See George Arfken and Hans-Jurgen Weber, *Mathematical Methods for Physicists*, 5th ed., Academic Press, Orlando (2000), Section 10.3. If the relevant occupation numbers are *not* large—as in Section 5.4.1—then statistical mechanics simply doesn't apply. The whole point is to deal with such enormous numbers that statistical inference is a reliable predictor. Of course, there will always be one-particle states of extremely high energy that are not populated at *all*; fortunately, Stirling's approximation holds also for $z = 0$. I use the word "relevant" to exclude any stray states right at the margin, for which N_n is neither huge nor zero.

This time we must assume not only that N_n is large, but also that $d_n \gg N_n$,[26] so that Stirling's approximation applies to both terms. In that case

$$G \approx \sum_{n=1}^{\infty}\Big[\ln(d_n!) - N_n \ln(N_n) + N_n - (d_n - N_n)\ln(d_n - N_n) + (d_n - N_n) - \alpha N_n - \beta E_n N_n\Big] + \alpha N + \beta E, \qquad [5.89]$$

so

$$\frac{\partial G}{\partial N_n} = -\ln(N_n) + \ln(d_n - N_n) - \alpha - \beta E_n. \qquad [5.90]$$

Setting this equal to zero, and solving for N_n, we find the *most probable occupation numbers* for identical fermions:

$$N_n = \frac{d_n}{e^{(\alpha+\beta E_n)} + 1}. \qquad [5.91]$$

Finally, if the particles are *identical bosons*, then Q is given by Equation 5.77, and we have

$$G = \sum_{n=1}^{\infty}\{\ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!]\} + \alpha\left[N - \sum_{n=1}^{\infty} N_n\right] + \beta\left[E - \sum_{n=1}^{\infty} N_n E_n\right]. \qquad [5.92]$$

Assuming (as always) that $N_n \gg 1$, and using Stirling's approximation:

$$G \approx \sum_{n=1}^{\infty}\{(N_n + d_n - 1)\ln(N_n + d_n - 1) - (N_n + d_n - 1) - N_n \ln(N_n) + N_n - \ln[(d_n - 1)!] - \alpha N_n - \beta E_n N_n\} + \alpha N + \beta E, \qquad [5.93]$$

so

$$\frac{\partial G}{\partial N_n} = \ln(N_n + d_n - 1) - \ln(N_n) - \alpha - \beta E_n. \qquad [5.94]$$

[26] In *one* dimension the energies are nondegenerate (see Problem 2.45), but in three dimensions d_n typically increases rapidly with increasing n (for example, in the case of hydrogen, $d_n = n^2$). So it is not unreasonable to assume that for *most* of the occupied states $d_n \gg 1$. On the other hand, d_n is certainly *not* much greater than N_n at absolute zero, where all states up to the Fermi level are filled, and hence $d_n = N_n$. Here again we are rescued by the fact that Stirling's formula holds also for $z = 0$.

Setting this equal to zero, and solving for N_n, we find the *most probable occupation numbers* for identical bosons:

$$N_n = \frac{d_n - 1}{e^{(\alpha+\beta E_n)} - 1}. \qquad [5.95]$$

(For consistency with the approximation already invoked in the case of fermions, we should really drop the 1 in the numerator, and I shall do so from now on.)

Problem 5.26 Use the method of Lagrange multipliers to find the rectangle of largest area, with sides parallel to the axes, that can be inscribed in the ellipse $(x/a)^2 + (y/b)^2 = 1$. What is that maximum area?

Problem 5.27

(a) Find the percent error in Stirling's approximation for $z = 10$.

(b) What is the smallest integer z such that the error is less than 1%?

5.4.4 Physical Significance of α and β

The parameters α and β came into the story as Lagrange multipliers, associated with the total number of particles and the total energy, respectively. Mathematically, they are determined by substituting the occupation numbers (Equations 5.87, 5.91, and 5.95) back into the constraints (Equations 5.78 and 5.79). To carry out the summation, however, we need to know the allowed energies (E_n), and their degeneracies (d_n), for the potential in question. As an example, I'll work out the case of an **ideal gas**—a large number of noninteracting particles, all with the same mass, in the three dimensional infinite square well. This will motivate the physical interpretation of α and β.

In Section 5.3.1 we found the allowed energies (Equation 5.39):

$$E_k = \frac{\hbar^2}{2m}k^2, \qquad [5.96]$$

where

$$\mathbf{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z}\right).$$

As before, we convert the sum into an integral, treating $\mathbf{k}$ as a continuous variable, with one state (or, for spin s, $2s + 1$ states) per volume π^3/V of k-space. Taking

as our "bins" the spherical shells in the first octant (see Figure 5.4), the "degeneracy" (that is, the number of states in the bin) is

$$d_k = \frac{1}{8}\frac{4\pi k^2\,dk}{(\pi^3/V)} = \frac{V}{2\pi^2}k^2\,dk. \qquad [5.97]$$

For distinguishable particles (Equation 5.87), the first constraint (Equation 5.78) becomes

$$N = \frac{V}{2\pi^2}e^{-\alpha}\int_0^\infty e^{-\beta\hbar^2k^2/2m}k^2\,dk = Ve^{-\alpha}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}.$$

so

$$e^{-\alpha} = \frac{N}{V}\left(\frac{2\pi\beta\hbar^2}{m}\right)^{3/2}. \qquad [5.98]$$

The second constraint (Equation 5.79) says

$$E = \frac{V}{2\pi^2}e^{-\alpha}\frac{\hbar^2}{2m}\int_0^\infty e^{-\beta\hbar^2k^2/2m}k^4\,dk = \frac{3V}{2\beta}e^{-\alpha}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}.$$

or, putting in Equation 5.98 for $e^{-\alpha}$:

$$E = \frac{3N}{2\beta}. \qquad [5.99]$$

(If you include the spin factor, $2s+1$, in Equation 5.97, it cancels out at this point, so Equation 5.99 is correct for all spins.)

This result (Equation 5.99) is reminiscent of the classical formula for the average kinetic energy of an atom at temperature T:[27]

$$\frac{E}{N} = \frac{3}{2}k_BT, \qquad [5.100]$$

where k_B is the Boltzmann constant. This suggests that β is related to the *temperature*:

$$\beta = \frac{1}{k_BT}. \qquad [5.101]$$

To prove that this holds in general, and not simply for distinguishable particles in the three-dimensional infinite square well, we would have to demonstrate that different substances in thermal equilibrium with one another have the same value of β. The argument is sketched in many books,[28] but I shall not reproduce it here—I will simply adopt Equation 5.101 as the *definition* of T.

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[27] See, for example, David Halliday, Robert Resnick, and Jearl Walker, *Fundamentals of Physics*, 5th ed., Wiley, New York (1997), Section 20-5.

[28] See, for example, Yariv (footnote 22), Section 15.4.

It is customary to replace α (which, as is clear from the special case of Equation 5.98, is a function of T) by the so-called **chemical potential**,

$$\mu(T) \equiv -\alpha k_B T, \qquad [5.102]$$

and rewrite Equations 5.87, 5.91, and 5.95 as formulas for the *most probable number of particles in a particular (one-particle) state with energy* ϵ (to go from the number of particles with a given energy to the number of particles in a particular *state* with that energy, we simply divide by the degeneracy of the state):

$$\boxed{n(\epsilon) = \begin{cases} e^{-(\epsilon-\mu)/k_B T} & \text{MAXWELL-BOLTZMANN} \\ \dfrac{1}{e^{(\epsilon-\mu)/k_B T}+1} & \text{FERMI-DIRAC} \\ \dfrac{1}{e^{(\epsilon-\mu)/k_B T}-1} & \text{BOSE-EINSTEIN} \end{cases}} \qquad [5.103]$$

The **Maxwell-Boltzmann distribution** is the classical result, for *distinguishable* particles; the **Fermi-Dirac distribution** applies to *identical fermions*, and the **Bose-Einstein distribution** is for *identical bosons*.

The Fermi-Dirac distribution has a particularly simple behavior as $T \to 0$:

$$e^{(\epsilon-\mu)/k_B T} \to \begin{cases} 0, & \text{if } \epsilon < \mu(0), \\ \infty, & \text{if } \epsilon > \mu(0), \end{cases}$$

so

$$n(\epsilon) \to \begin{cases} 1, & \text{if } \epsilon < \mu(0), \\ 0, & \text{if } \epsilon > \mu(0). \end{cases} \qquad [5.104]$$

All states are filled, up to an energy $\mu(0)$, and none are occupied for energies above this (Figure 5.8). Evidently the chemical potential at absolute zero is precisely the Fermi energy:

$$\mu(0) = E_F. \qquad [5.105]$$

As the temperature rises, the Fermi-Dirac distribution "softens" the cutoff, as indicated by the rounded curve in Figure 5.8.

Returning now to the special case of an ideal gas, for distinguishable particles we found that the total energy at temperature T is (Equation 5.99)

$$E = \frac{3}{2} N k_B T. \qquad [5.106]$$

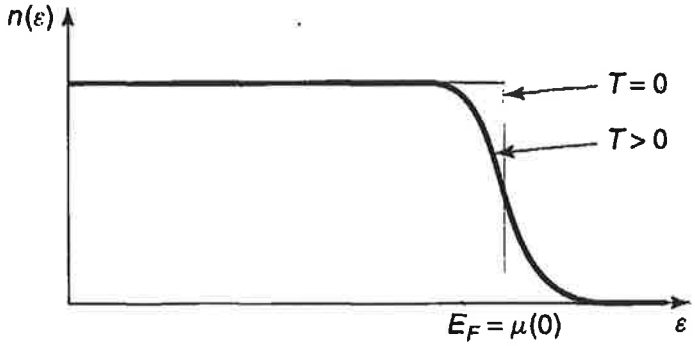

FIGURE 5.8: Fermi-Dirac distribution for $T = 0$ and for T somewhat above zero.

while (from Equation 5.98) the chemical potential is

$$\mu(T) = k_B T \left[\ln\left(\frac{N}{V}\right) + \frac{3}{2} \ln\left(\frac{2\pi\hbar^2}{mk_B T}\right) \right]. \qquad [5.107]$$

I would *like* to work out the corresponding formulas for an ideal gas of identical fermions and bosons, using Equations 5.91 and 5.95 in place of Equation 5.87. The first constraint (Equation 5.78) becomes

$$N = \frac{V}{2\pi^2} \int_0^\infty \frac{k^2}{e^{[(\hbar^2 k^2/2m)-\mu]/k_B T} \pm 1} dk, \qquad [5.108]$$

(with the plus sign for fermions and minus for bosons), and the second constraint (Equation 5.79) reads

$$E = \frac{V}{2\pi^2} \frac{\hbar^2}{2m} \int_0^\infty \frac{k^4}{e^{[(\hbar^2 k^2/2m)-\mu]/k_B T} \pm 1} dk. \qquad [5.109]$$

The first of these determines $\mu(T)$, and the second determines $E(T)$ (from the latter we obtain, for instance, the heat capacity: $C = \partial E/\partial T$). Unfortunately, these integrals cannot be evaluated in terms of elementary functions, and I shall leave it for you to explore the matter further (see Problems 5.28 and 5.29).

Problem 5.28 Evaluate the integrals (Equations 5.108 and 5.109) for the case of identical fermions at absolute zero. Compare your results with Equations 5.43 and 5.45. (Note that for electrons there is an extra factor of 2 in Equations 5.108 and 5.109, to account for the spin degeneracy.)