25.2: Fermi-Dirac Statistics and the Fermi-Dirac Distribution Function

Let us consider the total probability sum for a system of particles that follows Fermi-Dirac statistics. As before, we let ϵ_1, ϵ_2,…, ϵ_i,…. be the energies of the successive energy levels. We let g_1, g_2,…, g_i,…. be the degeneracies of these levels. We let N_1, N_2,…, N_i,…. be the number of particles in all of the degenerate quantum states of a given energy level. The probability of finding a particle in a quantum state depends on the number of particles in the system; we have $\rho\left(N_i,\epsilon_i\right)$ rather than $\rho\left(\epsilon_i\right)$. Consequently, we cannot generate the total probability sum by expanding an equation like

$$1=\ \left(P_1+P_2+\dots +P_i+\dots \right)^{\ N}.$$

However, we continue to assume:

1. A finite subset of the population sets available to the system accounts for nearly all of the probability when the system is held in a constant-temperature environment.
2. Essentially the same finite subset of population sets accounts for nearly all of the probability when the system is isolated.
3. All of the microstates that have a given energy have the same probability. We let this probability be $\rho^{FD}_{MS,N,E}$.

As before, the total probability sum will be of the form

$$1=\sum_{\left\{N_i\right\}}{W^{FD}\left(N_i,\epsilon_i\right)}\rho^{FD}_{MS,N,E}$$

Each such term reflects the fact that there are $W^{FD}\left(N_i,\epsilon_i\right)$ ways to put N_1 particles in the g_1 quantum states of energy level ϵ_1, and N_2 particles in the g_2 quantum states of energy level ϵ_2, and, in general, N_i particles in the g_i quantum states of energy level ϵ_i. Unlike Boltzmann statistics, however, the probabilities are different for successive particles, so the coefficient W^{FD} is different from the polynomial coefficient, or thermodynamic probability, W. Instead, we must discover the number of ways to put N_i indistinguishable particles into the g_i-fold degenerate quantum states of energy ϵ_i when a given quantum state can contain at most one particle.

These conditions can be satisfied only if $g_i\ge N_i$. If we put N_i of the particles into quantum states of energy ϵ_i, there are

1. g_i ways to place the first particle, but only
2. g_i-1 ways to place the second, and
3. g_i-2 ways to place the third, and
4. …
5. $g_i-\left(N_i-1\right)$ ways to place the last one of the N_i particles.

This means that there are

$$\left(g_i\right)\left(g_i-1\right)\left(g_i-2\right)\dots \left(g_i-\left(N_i+1\right)\right)=$$

$$=\frac{\left(g_i\right)\left(g_i-1\right)\left(g_i-2\right)\dots \left(g_i-\left(N_i+1\right)\right)\left(g_i-N_i\right)\dots \left(1\right)}{\left(g_i-N_i\right)!}=\frac{g_i!}{\left(g_i-N_i\right)!}$$

ways to place the N_i particles. Because the particles cannot be distinguished from one another, we must exclude assignments which differ only by the way that the N_i particles are permuted. To do so, we must divide by $N_i!$. The number of ways to put N_i indistinguishable particles into g_i quantum states with no more than one particle in a quantum state is

$$\frac{g_i!}{\left(g_i-N_i\right)!N_i!}$$

The number of ways to put indistinguishable Fermi-Dirac particles of the population set $\left\{N_1,\ N_2,\dots ,\ N_i,\dots \right\}$ into the available energy states is

$$W^{FD}\left(N_i,g_i\right)=\left[\frac{g_1!}{\left(g_1-N_1\right)!N_1!}\right]\times \left[\frac{g_2!}{\left(g_2-N_2\right)!N_2!}\right]\times \dots \times \left[\frac{g_i!}{\left(g_i-N_i\right)!N_i!}\right]\times \dots =\prod^{\infty}_{i=1}{\left[\frac{g_i!}{\left(g_i-N_i\right)!N_i!}\right]}$$

so that the total probability sum for a Fermi-Dirac system becomes

$$1=\sum_{\{N_j\}}\prod_{i=1}^{\infty}\left[\frac{g_i!}{(g_i-N_i)!N_i!}\right]\left[\rho^{FD}\left(\epsilon_i\right)\right]^{N_i}$$

To find the Fermi-Dirac distribution function, we seek the population set $\{N_1,\ N_2,\ldots,\ N_i,\ldots\}$ for which W^{FD} is a maximum, subject to the constraints

$$N=\sum_{i=1}^{\infty}N_i$$

and

$$E=\sum_{i=1}^{\infty}N_i\epsilon_i$$

The mnemonic function becomes

$$F_{mn}^{FD}=\sum_{i=1}^{\infty}\ln g_i!\ -\sum_{i=1}^{\infty}\left[(g_i-N_i)\ln(g_i-N_i)\ -(g_i-N_i)\right]-\sum_{i=1}^{\infty}\left[N_i\ln N_i-N_i\ \right]+\alpha\left[N-\sum_{i=1}^{\infty}N_i\right]$$
$$+\ \beta\left[E-\sum_{i=1}^{\infty}N_i\epsilon_i\right]$$

We seek the $N_i^\bullet$ for which F_{mn}^{FD} is an extremum; that is, the $N_i^\bullet$ satisfying

$$\begin{aligned}0\ &=\frac{\partial F_{mn}^{FD}}{\partial N_i}=\frac{g_i-N_i^\bullet}{g_i-N_i^\bullet}+\ln\left(g_i-N_i^\bullet\right)\ -1-\frac{N_i^\bullet}{N_i^\bullet}-\ln N_i^\bullet\ +1-\alpha-\beta\epsilon_i\\&=\ln\left(g_i-N_i^\bullet\right)\ -\ln N_i^\bullet\ -\alpha-\beta\epsilon_i\end{aligned}$$

Solving for $N_i^\bullet$, we find

$$N_i^\bullet=\frac{g_ie^{-\alpha}e^{-\beta\epsilon_i}}{1+e^{-\alpha}e^{-\beta\epsilon_i}}$$

or, equivalently,

$$\frac{N_i^\bullet}{g_i}=\frac{1}{1+e^{\alpha}e^{\beta\epsilon_i}}$$

If $1\gg e^{-\alpha}e^{-\beta\epsilon_i}$ (or $1\ll e^{\alpha}e^{\beta\epsilon_i}$), the Fermi-Dirac distribution function reduces to the Boltzmann distribution function. It is easy to see that this is the case. From

$$N_i^\bullet=\frac{g_ie^{-\alpha}e^{-\beta\epsilon_i}}{1+e^{-\alpha}e^{-\beta\epsilon_i}}\approx g_ie^{-\alpha}e^{-\beta\epsilon_i}$$

and $N=\sum_{i=1}^{\infty}N_i^\bullet$, we have

$$N=e^{-\alpha}\sum_{i=1}^{\infty}g_ie^{-\beta\epsilon_i}=e^{-\alpha}z$$

It follows that $e^{\alpha}=z/N$. With $\beta=1/kT$, we recognize that $N_i^\bullet/N$ is the Boltzmann distribution. For occupied energy levels, $e^{-\beta\epsilon_i}=e^{-\epsilon_i}/kT\approx 1$; otherwise, $e^{-\beta\epsilon_i}=e^{-\epsilon_i/kT}<1$. This means that the Fermi-Dirac distribution simplifies to the Boltzmann distribution whenever $1\gg e^{-\alpha}$. We can illustrate that this is typically the case by considering the partition function for an ideal gas.

Using the translational partition function for one mole of a monatomic ideal gas from Section 24.3, we have

$$\begin{aligned} e^{\alpha} &= \frac{z_t}{N} = \left[\frac{2\pi mkT}{h^2}\right]^{3/2} \frac{\overline{V}}{\overline{N}} \\ &= \left[\frac{2\pi mkT}{h^2}\right]^{3/2} \frac{kT}{P^0} \end{aligned}$$

For an ideal gas of molecular weight 40 at 300 K and 1 bar, we find $e^{\alpha} = 1.02 \times 10^7$ and $e^{-\alpha} = 9.77 \times 10^{-8}$. Clearly, the condition we assume in demonstrating that the Fermi-Dirac distribution simplifies to the Boltzmann distribution is satisfied by molecular gases at ordinary temperatures. The value of e^{α} decreases as the temperature and the molecular weight decrease. To find $e^{\alpha} \approx 1$ for a molecular gas, it is necessary to consider very low temperatures.

Nevertheless, the Fermi-Dirac distribution has important applications. The behavior of electrons in a conductor can be modeled on the assumption that the electrons behave as a Fermi-Dirac gas whose energy levels are described by a particle-in-a-box model.
