

**HW Problem.** Schroeder problem 6.37, p. 246.

**HW Problem.** Schroeder problem 6.39, p. 246.

### 0.1.5 Connecting Boltzmann statistics to thermodynamics

The formalism of Boltzmann statistics provides us with a statistical tool for calculating the probabilities of the states of a system in thermal contact with a reservoir that sets the temperature. This is analogous to, and we showed it to follow from, our earlier formalism in which the probabilities of macrostates of an isolated system are given by the ratios of their multiplicities to the total multiplicity of the system. The partition function

$$Z = \sum_n e^{-\beta E_n} \quad (79)$$

in the new formalism, being the normalization constant that turns Boltzmann factors into probabilities:

$$\mathcal{P}_n = \frac{e^{-\beta E_n}}{Z}, \quad (80)$$

is analogous to the total multiplicity, which turns macrostate multiplicities into probabilities in the original formalism:

$$\mathcal{P}_{\text{macrostate}} = \frac{\Omega_{\text{macrostate}}}{\Omega_{\text{tot}}}. \quad (81)$$

Just as the Boltzmann definition of the entropy

$$S = k \ln \Omega \quad (82)$$

relates multiplicity to the thermodynamic entropy, there is a thermodynamic analog of the logarithm of the partition function. But in this case, the analogy follows directly from the earlier Boltzmann definition of the entropy, with no need to introduce a new definition.

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To make the connection, we'll use a calculation that is very similar to the one we used to show that the probabilities of the states of a system in thermal contact with a reservoir are given by (80). So, let's begin by recalling the essentials of that calculation. We said the probability of any given state  $n$  of energy  $E_n$  of the system is proportional to the multiplicity of the macrostate of the reservoir having energy  $U_{\text{tot}} - E_n$ . That multiplicity can be expressed as the exponential of the corresponding entropy, because of the Boltzmann definition of entropy:

$$\mathcal{P}_n \propto \Omega_R(U_{\text{tot}} - E_n) = e^{S_R(U_{\text{tot}} - E_n)/k}. \quad (83)$$

The entropy of the reservoir at the energy  $U_{\text{tot}} - E_n$  can be expanded in a Taylor series about the energy  $U_{\text{tot}}$ . That series is truncated to first order, with the first derivative of the reservoir entropy introducing the inverse temperature:

$$S_R(U_{\text{tot}} - E_n) \approx S_R(U_{\text{tot}}) - \frac{1}{T} E_n, \quad (84)$$

leading to the probability being proportional to a Boltzmann factor:

$$\mathcal{P}_n \propto e^{-E_n/kT}. \quad (85)$$

Normalization by direct summation of the expressions for the probability leads to the probability being given by the ratio of a Boltzmann factor to the partition function, the sum of all the Boltzmann factors.

In our new calculation, instead of arriving at the normalization constant by summing expressions to which the probability is proportional, we'll start by directly writing down the normalization constant in terms of the total multiplicity:

$$\mathcal{P}_n = \frac{\Omega_R(U_{\text{tot}} - E_n)}{\Omega_{\text{tot}}(U_{\text{tot}})} = \frac{e^{S_R(U_{\text{tot}} - E_n)/k}}{e^{S_{\text{tot}}(U_{\text{tot}})/k}}, \quad (86)$$

where the last step follows from the Boltzmann definition of the entropy.

Now, in addition to the energy  $U_{\text{tot}}$  of the combined system plus reservoir and the energy  $E_n$  of state  $n$  of the system alone, we'll also use the average energy of the system, which is its equilibrium energy,

$$\langle E \rangle = U = \sum_n E_n \mathcal{P}_n, \quad (87)$$

in two ways. First, we'll make use of the fact that entropy is extensive, so we can write the entropy of the combined system plus reservoir in the denominator of the probability in (86) as the sum of their entropies when they are in equilibrium:

$$S_{\text{tot}}(U_{\text{tot}}) = S_R(U_{\text{tot}} - U) + S(U). \quad (88)$$

Second, we'll do a Taylor series expansion of the entropy of the reservoir appearing in the numerator of the probability in (86), but now expanding about its equilibrium energy  $U_{\text{tot}} - U$ , rather than  $U_{\text{tot}}$ :

$$\begin{aligned} S_R(U_{\text{tot}} - E_n) &= S_R(U_{\text{tot}} - U + U - E_n) \\ &\approx S_R(U_{\text{tot}} - U) + \left[ \frac{\partial S_R}{\partial U} \right]_{V,N} dU \\ &= S_R(U_{\text{tot}} - U) + \frac{1}{T} (U - E_n). \end{aligned} \quad (89)$$

Now we put these two entropies back into the expression for the probability (86), obtaining

$$\begin{aligned}
\mathcal{P}_n &= \frac{e^{S_R(U_{\text{tot}}-U)/k} e^{(U-E_n)/kT}}{e^{S_R(U_{\text{tot}}-U)/k} e^{S(U)/k}} \\
&= \frac{e^{-E_n/kT}}{e^{-[U-TS(U)]/kT}} \\
&= \frac{e^{-\beta E_n}}{e^{-\beta F}} ,
\end{aligned} \tag{90}$$

where  $F = U - TS$  is the Helmholtz free energy. Comparing this to our expression for the probability in terms of the partition function (80), we conclude that

$$\boxed{-\beta F = \ln Z} \quad \text{or} \quad \boxed{F = -kT \ln Z} . \tag{91}$$

This means that all the thermodynamic power of the free energy is now at our disposal. Once we have found the partition function for a system, we can immediately obtain the free energy, which we know is minimized at equilibrium. Furthermore, we can calculate from the free energy all the thermodynamic quantities that follow from its partial derivatives. Recall that with  $F = F(T, V, N)$ , the partials are the factors of the differentials in the total differential of  $F$ :

$$\begin{aligned}
dF &= \left( \frac{\partial F}{\partial T} \right)_{V,N} dT + \left( \frac{\partial F}{\partial V} \right)_{T,N} dV + \left( \frac{\partial F}{\partial N} \right)_{T,V} dN \\
&= dU - T dS - S dT \\
&= -S dT - P dV + \mu dN .
\end{aligned} \tag{92}$$

Notice that the entropy is one of the quantities we can obtain from the free energy:

$$\begin{aligned}
S(T, V, N) &= - \left( \frac{\partial F}{\partial T} \right)_{V,N} \\
&= k \ln Z + \frac{kT}{Z} \left( \frac{\partial Z}{\partial T} \right)_{V,N} .
\end{aligned} \tag{93}$$

With that available, we can obtain the energy of the system

$$\begin{aligned}
U(T, V, N) &= F(T, V, N) + TS(T, V, N) \\
&= -kT \ln Z + kT \ln Z + \frac{kT^2}{Z} \left( \frac{\partial Z}{\partial T} \right)_{V,N} \\
&= \frac{kT^2}{Z} \left( \frac{\partial Z}{\partial T} \right)_{V,N} .
\end{aligned} \tag{94}$$

Note that this expression for the equilibrium energy is consistent with the average energy computed from the probability distribution:

$$\langle E \rangle = \sum_n E_n \mathcal{P}_n = \sum_n \frac{E_n e^{-\beta E_n}}{Z} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}, \quad (95)$$

since

$$\frac{\partial Z}{\partial T} = \frac{\partial Z}{\partial \beta} \frac{d\beta}{dT} = -\frac{1}{kT^2} \frac{\partial Z}{\partial \beta}. \quad (96)$$

The expressions for the entropy in (93) and the energy in (94) are both written with  $T$ ,  $V$ , and  $N$  as the independent variables, which are not the natural variables of either function. But with both functions available, either could be used to eliminate  $T$  and find the other in terms of its natural variables, that is,  $S(U, V, N)$  or  $U(S, V, N)$ .

Thus,  $Z$  provides full thermodynamic information about the system, either directly via the use of  $F$  to characterize the equilibrium states, or indirectly through the ability to obtain the entropy or the energy in terms of their natural variables.

**HW Problem.** Schroeder problem 6.42, p. 249.

**HW Problem.** Schroeder problem 6.43, p. 249.

**Reading assignment.** Schroeder, section 6.7.

### 0.1.6 Factorization of the partition function

One of the most endearing features of the partition function is that it can often be partitioned into factors that can be calculated independently for different parts of a system. You can easily see the general principle by considering a system for which the energy of every state can be expressed as a sum of two independent contributions

$$E_n = E_i^{(1)} + E_j^{(2)}. \quad (97)$$

These must be independent, in the sense that the probabilities of the values of each contribution do not depend on the value of the other. In that case, the index  $n$  becomes equivalent to the composite index  $(i, j)$ , which is an ordered pair. As an example, you might think of the states of an ideal gas of diatomic molecules, in quantized form. Then the translational and rotational energies of the molecules are independent, and the energy of the gas can be decomposed into a translational energy arising from the translational motion of all the molecules and a rotational energy arising from the rotational motion of all the molecules.

With such a separation of the energies of the system, the partition function becomes

$$\begin{aligned}
Z &= \sum_n e^{-\beta E_n} \\
&= \sum_{i,j} e^{-\beta(E_i^{(1)} + E_j^{(1)})} \\
&= \sum_i e^{-\beta E_i^{(1)}} \sum_j e^{-\beta E_j^{(1)}} \\
&= Z^{(1)} Z^{(2)}.
\end{aligned} \tag{98}$$

When such a factorization is possible, the free energy decomposes into a sum of terms arising from the factors:

$$\begin{aligned}
F &= -kT \ln Z \\
&= -kT \ln Z^{(1)} - kT \ln Z^{(2)} \\
&= F^{(1)} + F^{(2)}.
\end{aligned} \tag{99}$$

Now this may all seem like a trivial curiosity, but it can provide dramatic simplification in the calculation of a partition function. One especially noteworthy family of cases are those in which the energy of a system can be expressed in terms of independent contributions from noninteracting constituents. Our favorite toy systems, the Einstein solid, the two-state paramagnet, and the ideal gas are all examples of systems for which that is true. In such cases, the partition function factors into contributions from each of the constituents:

$$Z = Z^{(1)} Z^{(2)} \dots Z^{(N)}. \tag{100}$$

What's more, in many such cases, the constituent partition functions are all the same, and it is only necessary to calculate one of them:

$$Z = Z_{\text{constituent}}^N. \tag{101}$$

You can see that factorization can be extraordinarily powerful, in spite of its simplicity.

**Example.** Let's see how much easier it can be to find the partition function of a two-state paramagnet when we make use of factorization. The energies of the individual constituents, the magnetic moments, are  $\epsilon_i = \pm\mu B$ , where  $\mu$  is the magnetic moment, and  $B$  is the strength of the external magnetic field. The energy of a particular state of an  $N$ -moment system can then be written as the sum

$$E_n = \sum_{i=1}^N \sigma_i^{(n)} \mu B = \left( N_{\downarrow}^{(n)} - N_{\uparrow}^{(n)} \right) \mu B, \tag{102}$$

where

$$\sigma_i^{(n)} = \begin{cases} +1, & \text{antialigned moment} \\ -1, & \text{aligned moment.} \end{cases} \quad (103)$$

The calculation of the partition function requires a sum over all possible states, which requires enumeration of all possible sets of values of the  $\sigma_i$ :

$$Z = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_N} e^{-\beta \sum_i \sigma_i \mu B}. \quad (104)$$

You can see that direct evaluation of the sum is quite a daunting task, particularly if  $N$  is a macroscopically large number like  $10^{23}$ .

One way to simplify the sum would be to change it from a sum over microstates to a sum over energies, using the ability to express the energy in the simpler form  $(N_{\uparrow} - N_{\downarrow})\mu B$  together with our previous knowledge of the multiplicities of the energies (macrostates) of the two-state paramagnet.

It is much simpler to make use of the factorizability of the partition function. While it is straightforward to demonstrate explicitly the reduction to factorized form for this system, we'll just use what we already know: if the energy decomposes into a sum of independent contributions, the partition function factors into a product of partition functions that can be calculated independently for each contribution to the energy. Thus:

$$Z = Z^{(1)} Z^{(2)} \dots Z^{(N)} = Z_{1 \text{ moment}}^N, \quad (105)$$

where the last equality follows from that fact that all the moments are the same, so they each have the same individual contribution to the partition function. That contribution is very easy to calculate:

$$\begin{aligned} Z_{1 \text{ moment}} &= \sum_{\sigma} e^{-\beta \sigma \mu B} \\ &= e^{\beta \mu B} + e^{-\beta \mu B} \\ &= 2 \cosh(\beta \mu B). \end{aligned} \quad (106)$$

The full partition function for the system is then simply

$$Z = Z_{1 \text{ moment}}^N = [2 \cosh(\beta \mu B)]^N. \quad (107)$$

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