The exponential $e^{-E_n/kT}$ is called a *Boltzmann factor*, and the sum of the Boltzmann factors of all the microstates of the system

$$\boxed{Z = \sum_n e^{-E_n/kT}} \tag{8}$$

is called the *partition function* of the system.

[EOC, Mon. 3/13/2006, #27; HW08 closed, due Mon. 3/27/2006]

The importance of these results cannot be overemphasized. When we calculated the entropy of one of our toy systems, we needed to have a thorough understanding of the multiplicities of its states, which we arrived at by combinatorial arguments. Such arguments were simple enough for those toy systems, but they become prohibitively complex in most other cases. Our new formalism is almost breathtakingly simple when applied to a small, simple system, such as an individual atom. All we need to know is the set of allowed energy states of the atom and the temperature of the reservoir in order to obtain the probabilities that the atom will be in each of its possible states. The ratios of probabilities of individual states of the atom require even less—the energies of the other states are not needed, since the partition function factors out of the ratio. There is nothing we need to know about the reservoir itself beyond its temperature; in particular, there is no need to be able to calculate the multiplicities of its macrostates. That is an enormous and very powerful simplification.

Now, let's add our new results to the table we presented near the beginning of this discussion:

Type of contact	State weight	Norm.	Massieu function	Thermodynamic potential
Isolated	1	Ω	$S(U,V,N) = k\ln\Omega$	$U(S,V,N)$
Thermal	$e^{-E_n/kT}$	Z	$S - \frac{U}{T}$	$F = U - TS$

HW Problem. Schroeder problem 6.5, p. 225.

HW Problem. Schroeder problem 6.10, p. 228.

HW Problem. Schroeder problem 6.11, p. 228.

The repeated appearance of $1/kT$ in many expressions in thermal physics becomes tiresome to write, so it is common to make the definition

$$\beta = \frac{1}{kT}\,. \tag{9}$$

In terms of β, the probability to find the system in microstate n is

$$\mathcal{P}_n = \frac{e^{-\beta E_n}}{Z} \quad \text{with} \quad Z = \sum_n e^{-\beta E_n}\,. \tag{10}$$

Example. Consider a single quantum harmonic oscillator in thermal contact with a reservoir at temperature T. We'll calculate the probability of finding the oscillator in the state with quantum number (or occupation number) n.

The energy of the oscillator in state n is

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \,, \tag{11}$$

so the partition function is

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} \\ &= e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty} x^n \,, \end{aligned} \tag{12}$$

where $x = e^{-\beta\hbar\omega}$.

Next, we need to sum the infinite geometric series. One way to do that is to start with a finite geometric series, which collapses to just two terms when multiplied by $1 - x$:

$$\begin{aligned} (1-x)\sum_{n=0}^{N} x^n &= 1 + x + x^2 + \cdots + x^N - x - x^2 - x^3 - \cdots - x^{N+1} \\ &= 1 - x^{N+1} \,. \end{aligned} \tag{13}$$

The sum of the finite series is then

$$\sum_{n=0}^{N} x^n = \frac{1 - x^{N+1}}{1 - x} \,. \tag{14}$$

Now if $|x| < 1$, we can take the large-N limit to get the sum for the infinite series:

$$\lim_{N\to\infty}\sum_{n=0}^{N} x^n = \frac{1}{1-x} \,. \tag{15}$$

Since our $x = e^{-\beta\hbar\omega}$ is less than 1, the series limit exists, and the partition function reduces to

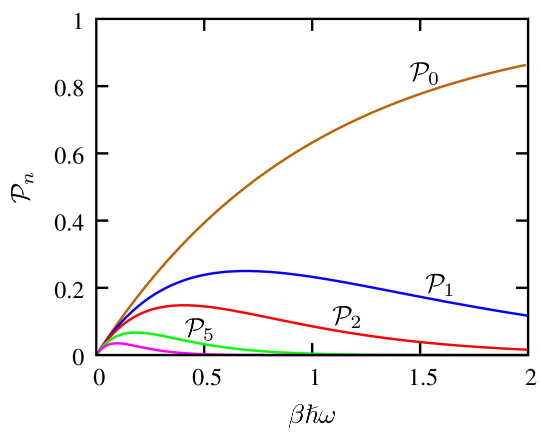
$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \,. \tag{16}$$

Finally, the probability of finding the oscillator in state n is

$$\begin{aligned} \mathcal{P}_n &= \frac{1 - e^{-\beta\hbar\omega}}{e^{-\beta\hbar\omega/2}}\, e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} \\ &= e^{-n\beta\hbar\omega}\left(1 - e^{-\beta\hbar\omega}\right) \,. \end{aligned} \tag{17}$$

Let's take a look at that result. As $T \to 0$, or $\beta \to \infty$, every state approaches zero probability, except the state $n = 0$, whose probability goes to 1. This is a clear demonstration of the quantum freeze-out effect, which we noted was responsible for the vanishing of the heat capacity of an Einstein crystal. Here, of course, we're considering a very small system, consisting of just a single oscillator.

As T becomes large, or β small, each of the $\mathcal{P}_n$ grows at the expense of those with smaller n until reaching a peak, beyond which the growth of those of larger n begins to reduce the value of $\mathcal{P}_n$. Here's a plot of several of the probabilities as a function of $\beta\hbar\omega$:



0.1.1 Average values

Once we've found the probability distribution for the microstates of a system, it's a simple matter to calculate the average values of variables using the probability distribution as a weight function:

$$\langle \alpha \rangle = \sum_n \alpha(n) \mathcal{P}_n \,. \tag{18}$$

However, there are sometimes useful tricks that can be used to make the evaluation of the sum easier.

Example. Again considering a single quantum harmonic oscillator in thermal contact with a reservoir having temperature T, we'll find the average occupation number, n, of the oscillator. We'll do this in two different but equivalent ways, the first providing an easy introduction to one of the tricks we'll find useful repeatedly, and the second placing more explicit emphasis on the partition function, which proves to be of central importance in the statistical mechanics of systems in contact with thermal reservoirs.

In the first approach, we make immediate use of the expression we've already found for the probability distribution for the states of the oscillator:

$$\begin{aligned}\langle n\rangle &= \sum_{n=0}^{\infty} nP_n \\ &= \left(1-e^{-\beta\hbar\omega}\right)\sum_{n=0}^{\infty} ne^{-n\beta\hbar\omega}\,,\end{aligned} \tag{19}$$

To simplify the notation, we'll let $\xi = \beta\hbar\omega$, so we can write the series as

$$\sum_{n=0}^{\infty} ne^{-n\beta\hbar\omega} = \sum_{n=0}^{\infty} ne^{-n\xi}\,. \tag{20}$$

Now this is almost a geometric series like the one we summed in our calculation of $\mathcal{P}_n$ for this system, except that each term is multiplied by n. But you'll notice that the exponent also contains an n, so if we were to differentiate each term of the analogous geometric series with respect to, say, ξ, that would create a series very close to the one we have here. Thus,

$$\begin{aligned}\sum_{n=0}^{\infty} ne^{-n\xi} &= -\sum_{n=0}^{\infty}\frac{\partial}{\partial\xi}e^{-n\xi} \\ &= -\frac{\partial}{\partial\xi}\sum_{n=0}^{\infty}e^{-n\xi} \\ &= -\frac{\partial}{\partial\xi}\sum_{n=0}^{\infty}x^n\,,\end{aligned} \tag{21}$$

where $x = e^{-\xi}$. The interchange of the derivative and the sum is allowable as long as the resulting series is still convergent. That's not a problem here, provided we stay away from infinite temperature, $\beta = 0$, where the series diverges.

The conclusion then is that we can obtain the sum of the series simply by differentiating the sum of the corresponding geometric series:

$$\begin{aligned}\sum_{n=0}^{\infty} ne^{-n\xi} &= -\frac{\partial}{\partial\xi}\frac{1}{1-e^{-\xi}} \\ &= \frac{e^{-\xi}}{\left(1-e^{-\xi}\right)^2}\,.\end{aligned} \tag{22}$$

Thus, the mean value of the occupation number of the oscillator is

$$\begin{aligned}\langle n\rangle &= (1-e^{-\beta\hbar\omega})\frac{e^{-\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)^2} \\ &= \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \\ &= \frac{1}{e^{\beta\hbar\omega}-1}\,.\end{aligned} \tag{23}$$

The second approach makes use of the partition function symbolically for much of the way, which gives it the flavor of a more general calculation, even though we will make use of the specific form of the energy states of the oscillator fairly early. We begin by writing the mean occupation number in terms of Boltzmann factors and the partition function:

$$\langle n \rangle = \sum_n n\mathcal{P}_n = \frac{\sum_n n e^{-\beta E_n}}{Z}\,, \tag{24}$$

where $Z = \sum_n e^{-\beta E_n}$. For the harmonic oscillator, the energies are just $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$, so

$$\langle n \rangle = \frac{\sum_{n=0}^{\infty} n e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}}{Z} \quad \text{with} \quad Z = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}\,. \tag{25}$$

Again, we see two infinite series, the one in the numerator being closely related to a derivative of the series giving Z. As before, we'll let $\xi = \beta\hbar\omega$ and differentiate the series for Z with respect to ξ. But notice that we need to divide the result by Z itself to get $\langle n \rangle$, which we can accomplish automatically by differentiating $\ln Z$, rather than Z itself. Thus,

$$\begin{aligned}
\frac{\partial}{\partial\xi}\ln Z &= \frac{1}{Z}\frac{\partial}{\partial\xi}\sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)\xi} \\
&= -\frac{1}{Z}\sum_{n=0}^{\infty}\left(n+\frac{1}{2}\right)e^{-\left(n+\frac{1}{2}\right)\xi} \\
&= \underbrace{-\frac{1}{Z}\sum_{n=0}^{\infty} n e^{-\left(n+\frac{1}{2}\right)\xi}}_{\langle n \rangle} - \frac{1}{2Z}\underbrace{\sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)\xi}}_{Z}\,.
\end{aligned} \tag{26}$$

The two copies of Z in the last term cancel, and we can solve for $\langle n \rangle$ to get

$$\langle n \rangle = -\frac{\partial}{\partial\xi}\ln Z - \frac{1}{2}\,. \tag{27}$$

Notice that we've gotten this far without having to evaluate the series for Z, and the only series that must be evaluated is that for Z, as in our first approach.

The series for Z has already been evaluated in the previous example:

$$Z = \frac{e^{-\xi/2}}{1 - e^{-\xi}}\,, \tag{28}$$

and its logarithmic derivative is easy to calculate:

$$\begin{aligned}
\frac{\partial}{\partial\xi}\ln Z &= \frac{\partial}{\partial\xi}\left[-\frac{\xi}{2} - \ln\left(1 - e^{-\xi}\right)\right] \\
&= -\frac{1}{2} - \frac{e^{-\xi}}{1 - e^{-\xi}}\,.
\end{aligned} \tag{29}$$

Finally, the mean occupation number is

$$\langle n \rangle = \frac{e^{-\xi}}{1 - e^{-\xi}} = \frac{1}{1 - e^{-\xi}} = \frac{1}{e^{\beta\hbar\omega - 1}} \,, \tag{30}$$

which is the same result we found by the first approach.

HW Problem. Schroeder problem 6.17, p. 231.

HW Problem. Schroeder problem 6.18, p. 231.

HW Problem. Schroeder problem 6.19, p. 231.

Exercise.

(a) Using methods similar to those used in the last example, show that the mean value of the energy of any system in thermal contact with a reservoir having temperature T is:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \,. \tag{31}$$

(b) Show that for a single harmonic oscillator in thermal contact with a reservoir,

$$\langle E \rangle = \left(\langle n \rangle + \frac{1}{2} \right) \hbar\omega \,. \tag{35}$$

[EOC, Wed. 3/15/2006, #28]
