Boltzmann and Partition Function Examples

These are the examples to be used along with the powerpoint lecture slides. The problems are numbered to match the tags in the the lower left hand corner of the powerpoint slides. The numbers of the examples are # the in the EX-Boltz# tags on the slides.

1 Relative probability of two states

(From pages 107-109 Gold or 695-697 Red in McQuarrie and Simon, Molecular Thermodynamics)

Derive the Boltzmann distribution based on simple math arguments.

The relative number of systems in a given state must, in the most general terms, depend on the energy of that state. Consider the ratio of the number of systems in two different states. This must be a function of the energy of those states,

\[ \frac{a_2}{a_1} = f(E_2, E_1) \]

The question now becomes,

WHAT IS THIS FUNCTION? \( \longrightarrow f(E_2, E_1) \)

First we realize that energy must be referenced to some zero, and the choice of that zero is arbitrary. Since the ratio of the number of systems in two different states should not depend on an arbitrary zero, this function must only be related to the difference in energy between the two states,

\[ f(E_2, E_1) = f(E_1 - E_2) \]

This should be true for any two states, so consider a third state relative to the first two,

\[ \frac{a_3}{a_2} = f(E_2 - E_3) \quad \frac{a_3}{a_1} = f(E_1 - E_3) \]

Of course we can write the ratio of \( a_3 \) to \( a_2 \) in terms of the ratios with the other states,

\[ \frac{a_3}{a_1} = \frac{a_3}{a_2} \cdot \frac{a_2}{a_1} \quad \text{which means} \quad f(E_1 - E_3) = f(E_2 - E_3)f(E_1 - E_2) \]

Leaving use to answer the question,

WHAT FUNCTION SATISFIES THIS FORM? \( \longrightarrow f(E_1 - E_3) = f(E_2 - E_3)f(E_1 - E_2) \)
(See if the class has any suggestions)
The answer is an exponential,
\[ e^{x+y} = e^x \cdot e^y \]

So if \( f(E) \) has the form \( e^{\beta E} \) where \( \beta \) is a constant to be determined later, then,
\[ e^{\beta(E_1-E_3)} = e^{\beta(E_2-E_3)} e^{\beta(E_1-E_2)} \]

So now consider our ratio of the number of systems in two different states,
\[ \frac{a_2}{a_1} = e^{\beta(E_1-E_2)} \]

and since there is nothing special about states 1 and 2, this should be general for any set of states \( n \) and \( m \),
\[ \frac{a_n}{a_m} = e^{\beta(E_m-E_n)} \]

[The following can also be left to the next slide...]
And this implies our final result,
\[ \boxed{a_j = C e^{-\beta E_j}} \]

where \( C \) is some (normalization) constant. (Put this back into the expression for \( \frac{a_n}{a_m} = e^{\beta(E_m-E_n)} \) and convince yourself that it works!)

This is the number of systems in state \( j \). If we have a large ensemble, then the number of systems in a given state \( j \) divided by the total number systems in all states must be the fraction in state \( j \), and in the limit of a very large system this is the \textit{probability} that a system is in state \( j \),
\[ p_j = \frac{a_j}{A} = \frac{a_j}{\sum_j a_j} = \frac{C e^{-\beta E_j}}{C \sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \]

See the next slide...

2 Probability: You grab a random beer

Now let us consider a very large cooler (say it contains \( \sim 10^6 \) beers). As an illustration let there be 4 possible states for any beer, i.e. every beer is in one of 4 available states. We want to calculate the probability of a randomly chosen beer being in each of the 4 possible states at a given temperature, and we will consider how temperature affects the probabilities.
The 4 states have the following energies (chosen to be similar to typical molecular energies, but otherwise arbitrary for illustration),
To calculate the probabilities we will use the Boltzmann distribution,

\[ p_j = \frac{e^{-E_j/kT}}{Q} = \frac{e^{-E_j/kT}}{\sum_j e^{-E_j/kT}} \]

At 200 K: Consider state 1,

\[ p_1 = \frac{e^{-E_1/kT}}{\sum_{j=1}^{4} e^{-E_j/kT}} = \frac{e^{-(3\times10^{-22} \text{ J})/(1.38\times10^{-23} \text{ J K}^{-1})(200 \text{ K})}} {e^{-(3\times10^{-22} \text{ J})/kT} + e^{-(6\times10^{-22} \text{ J})/kT} + e^{-(10\times10^{-22} \text{ J})/kT} + e^{-(20\times10^{-22} \text{ J})/kT}} \]

\[ p_1 = \frac{0.897}{0.897 + 0.805 + 0.696 + 0.485} = \frac{0.897}{2.883} = 0.311 \]

And for the other 3 states, just put in the values,

\[ p_2 = \frac{0.805}{2.883} = 0.279 \]
\[ p_3 = \frac{0.696}{2.883} = 0.241 \]
\[ p_4 = \frac{0.485}{2.883} = 0.168 \]

So what is the probability that you are in one of states 1, 2, 3, or 4? (Add them up and you should get 1 since you must be in one of the possible states!)

What happens if someone left the beer out in the sun (if the temperature goes up)? (Let the class take a shot at the qualitative change in probabilities, have them consider both the numerator and denominator.)

At 500 K: If you plug in the numbers,

\[ p_1 = \frac{0.957}{0.957 + 0.917 + 0.865 + 0.748} = \frac{0.957}{3.488} = 0.275 \]

\[ p_1 = 0.27 \quad p_2 = 0.263 \quad p_3 = 0.248 \quad p_4 = 0.215 \]

Note that the numerator for all 4 probabilities went up with the higher energy states changing more, but the denominator also went up with an overall result that the probabilities became closer together.

Now what if you get the beer really cold? (Let class take a shot.)
3 WHAT CAN I USE THE PARTITION FUNCTION FOR?

At 10 K:

\[ p_1 = \frac{0.114}{0.114 + 0.013 + 0.0007 + 0.000} = 0.114 = 0.893 \]

Now calculate all the values and compare the 3 temperatures,

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( p_1 )</th>
<th>( p_2 )</th>
<th>( p_3 )</th>
<th>( p_4 )</th>
<th>( Q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.893</td>
<td>0.102</td>
<td>0.056</td>
<td>( 4 \times 10^{-6} )</td>
<td>0.128</td>
</tr>
<tr>
<td>200</td>
<td>0.311</td>
<td>0.279</td>
<td>0.241</td>
<td>0.168</td>
<td>2.883</td>
</tr>
<tr>
<td>500</td>
<td>0.275</td>
<td>0.263</td>
<td>0.248</td>
<td>0.215</td>
<td>3.488</td>
</tr>
<tr>
<td>( \rightarrow \infty )</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>4</td>
</tr>
</tbody>
</table>

At low temperature, the majority of the probability is in the lowest energy state. As the temperature increases, the probability becomes more evenly distributed into the states.

**Question:** Can the probability of the lowest state ever become less than the probability of any other (higher energy) state given our expression?

**Answer:** No, the denominator is the same for all probabilities, and the exponential numerator will always have the largest value for the smallest energy. Note that as \( T \rightarrow \infty \) the probabilities of all the states will become equal.

Note that as the temperature goes up so does \( Q \), and as \( T \) goes up so does the probability that I am not in the ground state. One way to interpret \( Q \) is that it must be a measure of the system’s ability to escape from the ground energy state.

### 3 What can I use the partition function for?

Can I calculate thermodynamics quantities such as the average energy of the entire ensemble of beers (molecules) from the partition function? Let’s have a look and do a little math.

\[ Q(N,V,\beta) = \sum_j e^{-\beta E_j} \]

We have seen that the partition function changes with temperature, and we can figure that the average energy of the ensemble changes with temperature, so perhaps the change of \( Q \) with temperature is related to the average energy.

Consider how the partition function changes with temperature, or in this form how it changes
with $\beta$. Consider the derivative of $\ln Q$ with respect to $\beta$ (Why? Because I know where I’m going),

$$\left(\frac{\partial \ln Q(N, V, \beta)}{\partial \beta}\right)_{N, V} = \frac{1}{Q(N, V, \beta)} \left(\frac{\partial \sum_j e^{-\beta E_j(N, V)}}{\partial \beta}\right)_{N, V}$$

Remember some calculus,

$$\frac{d}{dx} \ln f(x) = \frac{1}{f(x)} \cdot f'(x)$$

$$\frac{d}{dx} e^{h(x)} = h'(x) \cdot e^{h(x)}$$

and apply this to the right hand side of our equation we get,

$$\left(\frac{\partial \ln Q(N, V, \beta)}{\partial \beta}\right)_{N, V} = \frac{1}{Q(N, V, \beta)} \sum_j (-E_j(N, V)) e^{-\beta E_j(N, V)} = -\sum_j E_j(N, V) e^{-\beta E_j(N, V)}$$

Note that the right is now of the form of the average energy,

$$-\sum_j \frac{E_j(N, V) e^{-\beta E_j(N, V)}}{Q(N, V, \beta)} = -\sum_j \frac{e^{-\beta E_j(N, V)}}{Q(N, V, \beta)} E_j(N, V) = -\sum_j p_j(N, V, \beta) E_j(N, V) = -\langle E \rangle$$

leading to our result,

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N, V}$$

This is a great result! We have demonstrated a link from a microscopic (molecular) quantity, the partition function, to the macroscopic property of the average energy of our ensemble, a thermodynamics property. Note that if the individual systems are molecules, then the energy levels are the quantum energy levels, and with these energy levels we can calculate $Q$. From $Q$ we can calculate any thermodynamic property (examples to come)!!

Now we can convert our result from $\beta$ to $T$:

Using the chain rule (might be good to set up and challenge the class to complete),

$$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial \beta} \frac{\partial \beta}{\partial T} = \frac{\partial f}{\partial \beta} \frac{d \left(\frac{1}{kT}\right)}{dT} = -\frac{1}{kT^2} \frac{\partial f}{\partial \beta}$$

$$\frac{\partial f}{\partial \beta} = -kT^2 \frac{\partial f}{\partial T}$$

so for $\langle E \rangle$,

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N, V} = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N, V}$$
4 Calculate EOS from Q

Example 3-4 on pg. 118 Gold or Example 17-4 on pg. 706 Red of McQuarrie and Simon.

If I can calculate $P$ from $Q$, then given the form of $Q$ I should be able to calculate an equation of state, EOS, $P$ as a function of $T$ and $V$. Let’s try it. You are given,

$$Q(N,V,\beta) = \frac{1}{N!} \left( \frac{2\pi m}{\hbar^2 \beta} \right)^{3N/2} (V-Nr)^N e^{\beta sN^2/V}$$

where $s$ and $r$ are constants.

To get the EOS, calculate $P_{\text{macroscopic}} = \langle P \rangle,$

$$\langle P \rangle = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,\beta}$$

Consider the $\ln Q$ derivative,

$$\ln Q = \ln \left( \frac{1}{N!} \left( \frac{2\pi m}{\hbar^2 \beta} \right)^{3N/2} \right) + \ln [(V-Nr)^N] + \ln [e^{\beta sN^2/V}]$$

$$\ln Q = \text{[terms independent of } V\text{]} + N \ln (V-Nr) + \frac{\beta sN^2}{V}$$

taking the derivative,

$$\left( \frac{\partial \ln Q}{\partial V} \right)_{N,\beta} = 0 + \frac{N}{V-Nr} - \frac{\beta sN^2}{V^2}$$

and put back the complete expression,

$$\langle P \rangle = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,\beta} = \frac{kTN}{V-Nr} - \frac{kT\beta sN^2}{V^2}$$

$$P = \frac{NkT}{V-Nr} - \frac{sN^2}{V^2}$$

$$P + \frac{sN^2}{V^2} = \frac{NkT}{V-Nr}$$

$$\left( P + \frac{sN^2}{V^2} \right) (V-Nr) = NkT$$

If we change the labels on the constants such that $s = a$ and $b = r$ we find,

$$\left( P + \frac{a}{V^2} \right) (V-b) = RT$$

and this is the van der Waals equation of state. (So we started with $Q$ for the van der Waals EOS).
5 The rotational partition function

Consider the rotational partition function. We need the rotational energy levels and if we sum over the levels rather than the states then we need the degeneracy of each level,

\[ \varepsilon_j = \frac{\hbar^2}{2I} J(J+1) \]

\[ g_j = 2J + 1 \]

write down the molecular rotational partition function, where you sum over all levels \((J = 0, 1, 2, \ldots)\),

\[ q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J + 1) \exp \left( -\frac{\hbar^2 J(J+1)}{2I kT} \right) \]

Notice how we include the degeneracy when summing over levels rather than states. Consider the first two levels (ie \(J = 0, 1, \ldots\)) and compare the two different ways to sum.

- If you sum over levels,

\[ q_{\text{rot}}(T) = \sum_{\text{levels, } J} (2J + 1) \exp \left( -\frac{E_J}{kT} \right) = (1) e^{-E_{J=0}/kT} + (3) e^{-E_{J=1}/kT} + \cdots \]

- If you sum over states,

\[ q_{\text{rot}}(T) = \sum_{\text{states}} \exp \left( -\frac{E_J}{kT} \right) = e^{-E_{J=0}/kT} + e^{-E_{J=1}/kT} + e^{-E_{J=1}/kT} + \cdots \]

there are 3 states for level \(J=1\)