Lecture 5 – Chapt 3, sections 1-3

Remind about grad school thing today at 4:00

Outline:

Three coins in a fountain

Boltzmann \[ P_j = \frac{e^{-\beta E_j}}{\sum e^{-\beta E_i}} \]

Partition function

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

Today we are really getting moving into statistical thermodynamics. This is really great stuff, but we are really going to roll, so please keep up. I am also doing things quite differently than the book so it would be good to read these sections carefully to give you two different perspectives.

Everybody get a coin while I get spreadsheet up and running.

You are all going to flip 8 times and keep track on paper: e.g. HHTHTTHT.

Go through spreadsheet... hopefully gets close to 50% heads as more trials are done

Go back and get exact order of first 4 tosses. Point out that all 16 possible configurations are equally likely

**But if all we care about is total # heads, how does this change things?** Each specific configuration is equally likely, but since coins are indistinguishable, all of the 2-2 configurations are equivalent to us, that makes it more likely. Thus, for 4 coins, we don’t really have 16 configurations, there are really only 5 distinguishable configurations, weighted 1/16, 4/16, 6/16, 4/16, 1/16

Super, but what if we had a mole of coins, we need some kind of formula. We want something like (weight of configuration) / (total # configurations)

**Can anyone see what the denominator is?** \( 2^N \) == the total number of configurations

What about numerator? Let’s say we have 4 coins (A, B, C, and D): **how many ways can we arrange them?** 4 choices for first, 3 for second, 2 for third, 1 for fourth, so \( 4 \times 3 \times 2 \times 1 = 4! = 24 \). This is total # arrangements, so we need to divide out the number of equivalent ones. This is the same type of thing, so we get (# heads)! * (# tails)!

so the final formula is \[ P(N,h) = \frac{N!}{h!(N-h)!} \frac{2^N}{2^N} \]

Try it out \(( 4! / 3! 1! ) / 2^4 = (24 / 6) / 16 = 4 / 16 \) –> perfect

What if we were rolling five dice (like Yahtzee!) \[ P = \frac{n_1!n_2!n_3!n_4!n_5!n_6!}{6!} \]
Let’s notice a couple more things about coins. What if we flipped 2 coins ->

\[ P(\text{half}) = \frac{2}{4} = 0.50 \]

but notice ratio of \( P(\text{half heads}) : P(\text{zero heads}) \) = \( 2 : 1 = 2 \)

What if we flipped 4 coins:

\[ P(\text{half}) = \frac{6}{16} = 0.375 \]

But again, ratio of \( P(\text{half}) : P(\text{zero}) \) = \( 6 : 1 = 6 \)

Go back to spreadsheet and show for # flips going up to 150. Probability of the dominant contribution falls off, but ratio of most likely to least likely increases dramatically.

For 100,000 flips, 49,000 - 51,000 heads contains 99.99999993% of the distribution.

**VERY IMPORTANT** – as \( N \) becomes huge, the distribution gets very narrow.

So, if we have something like \( 10^{23} \) particles, then even though we can’t know the energy of any particular particle at all, we can know the most probable energy and the average energy very well.

Thus far we have considered situations where every configuration is equally likely. We need to consider particle energy, which will change probability of each configuration.

Boltzmann tells us how energy affects probability. The book does a nice job of deriving the following, so I’ll just give result – **we will use this a million times VERY IMPORTANT**:

\[
P_j = \frac{e^{-\beta E_j}}{\sum_l e^{-\beta E_l}}
\]
We encounter the denominator in that Boltzmann expression often, and it actually tells us all we need to know about a system. We call it the **PARTITION FUNCTION**.

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

It turns out that \( \beta \) is closely related to temperature \( \beta = 1 / k_B T \)

So, \( P \) and \( Q \) can also be written in terms of temperature (see book), but \( \beta \) is often easier to deal with.

Back to the spreadsheet to show probability vs. \( E \) at several temps. **What are the ramifications of this to NMR?** Low B-field means 2 spin states are close in energy, so populations are very similar. High B-field means larger energy difference, so significantly fewer protons in upper state.

**\( Q \) is a weighted sum of the total # of configurations in the system.** In other words, it represents the number of configurations that are accessible at the current \( T, V, \) and \( N \).

Of course, what we are really interested in is the average energy, not just the probability of any particular individual energy. **What is the average of any quantity (in terms of probability)?**

\[ \langle X \rangle = \sum_i P_i X_i \]

So, average energy is:

\[ \langle E \rangle = \sum_i P_i E_i \]

I’ll relate this average energy to \( Q \), but do it in reverse, because it will make more sense:

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

\[ \frac{\partial}{\partial \beta} = \frac{\partial}{\partial x} \]

**derivative of sums is sum of derivatives**

So, then we have the second most important equation we have gotten to so far (second to the probability equation that we just did):

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

(Eq. 3.20 in book, Eq. 3.21 is the \( k_B T \) version)
Quickly now before you go – details in book. For N non-interacting particles

$$Q = \frac{q^N}{N!}$$

$q$ is the partition function for an individual molecule

For non-interacting particles, consider only translation. Just trust me:

$$q = \left( \frac{2\pi M}{h^2\beta} \right)^{\frac{3}{2}V}$$

Ok, then take ln of above equation:

$$\ln Q = \ln \left( \frac{q^N}{N!} \right)$$

$$= \ln \left( q^N \right) - \ln \left( N! \right)$$

$$= N \ln q - \ln \left( N! \right)$$

$$= N \ln \left( \frac{2\pi M}{h^2\beta} \right)^{\frac{3}{2}V} - \ln \left( N! \right)$$

$$= \frac{3}{2} N \ln \frac{1}{\beta} + \frac{3}{2} N \ln \left( \frac{2\pi M}{h^2} \right)^{\frac{3}{2}V} - \ln \left( N! \right)$$

Note that only the first term has any $\beta$ dependence. Remember that we are looking for energy.

So, let’s take the derivative of $\ln Q$

$$\left( \frac{\partial \ln Q}{\partial \beta} \right) = - \frac{\partial}{\partial \beta} \left( \frac{3}{2} N \ln \beta \right) + \frac{\partial}{\partial \beta} \left( \text{Constant} \right)$$

$$= - \frac{3}{2} N \frac{1}{\beta}$$

$$= - \frac{3}{2} \frac{N}{\beta}$$

$$= - \frac{3}{2} N k_b T$$

So, if the assumptions we put into $Q$ (noninteracting, monatomic particles) are OK, then

$$\langle E \rangle = \frac{3}{2} N k_b T = \frac{3}{2} nRT$$

**Anything interesting?** Energy depends only on # of molecules, but not anything about them! Molar energy: $$\langle \overline{E} \rangle = \frac{3}{2} RT$$

Often denote average energy $\langle E \rangle$ by $U$, the experimentally observed energy.

Please take note of example 3.2 in text. What we did above is for monatomic ideal gas, this example is for diatomic ideal gas.