Lecture 13   – Chapt 10

Announcements:
• Friday, HUGE!!!   Science division dedication thing.
• HW is posted – short, but non-zero. Back on normal schedule next week.
• The week after is fall break!

Outline:
Boltzmann distribution
partition function

review:

We have introduced almost all of the tools to start doing serious things. (Today and Monday are good stuff!) We’ll get back to probabilities today. We’ll visit our friend, Boltzmann, and his pet the partition function. We’ll also see a few new tricks the partition function can do. Recall...

\[ U = \langle E \rangle = \sum_i E_i p_i \]

\[ dU = d\langle E \rangle = \sum_i E_i dp_i + \sum_i p_i dE_i \]

We take it as one of the postulates of quantum mechanics that the microscopic energy levels \( E_i \), do not depend on temperature – only the populations \( p_i \). Thus, \( E \) depends only on \( V \) and \( N \). **When \( V \) and \( N \) are constant?**, \( dE = 0 \) and also note that work = 0.

Thus?, \( dU = \partial q \) and \( dU = \text{Edp term} \).

\[ \sum_i E_i dp_i = \text{heat} \quad \sum_i p_i dE_i = \text{work} \]

I had described microscopic heat and work before, now we have shown in more detail that heat deals with changes in populations and work with changes in the energy levels themselves.

Now, in a HW set a bit back, you all derived some probabilities based on weighted dice. Not surprisingly there are some applications to molecules as well.

Recall with the dice that we knew the average value of many rolls and the value of each side of the die. We then were able to calculate the most likely set of probabilities to explain that average.

Let’s shift gears a bit and say that we know the average energy over many microstates \( \langle E \rangle \) and the energy of each microstate \( E_i \). Shouldn’t we then be able to calculate the most likely set of probabilities to explain that average?
How did we find the answer for the dice? Lagrange multipliers. What did the answer look like? exponential. So, if we assume we know $\langle E \rangle$ and all the $E_i$, we just use maximum entropy to solve for all the $p_i$. What do you think we get?

Boltzmann!
\[ p_j = \frac{e^{-\beta E_j}}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta E_j}}{Q} \]

and of course we all know that $\beta$ turns out to be $1/kT$.

Dill does a nice job of explaining how this relates to our familiar notion that things tend toward minimum energy. If we look at the individual microstates, any one molecule is likely to be at any of several energy levels. It is the fact that our system (ensemble) of molecules are restricted (constrained) to some energy that makes them tend toward lower energy. Lower energy per particle allows more arrangements of the particles given the same total (or average) energy.

Again, let’s take a minute to think about the partition function.

$Q$ is the number of ‘effectively accessible states’. If $T$ is high, then $Q \sim \# \text{ of states}$. If $T$ is low, then $Q \sim 1$ (just ground state contributes). $Q$ tells you how energy is partitioned in the system.

The state’s energy compared to $kT$ tells you how accessible the state is.

Clarify microstates (states) vs. macrostates (levels)

microstates are all the possible distinguishable arrangements of the system.
macrostates are all the possible energetically different arrangements of the system.
So, there can be many microstates per macrostate.
our normal definition of $Q$ is in terms of microstates. $Q$ always counts microstates.
However, it is often convenient to deal with macrostates – energy levels – instead. Something like:

\[ W_0 = 3, \quad \varepsilon = \varepsilon_0 \]
\[ W_1 - 1, \quad \varepsilon - \varepsilon_1 \]
\[ W_2: 2, \quad \varepsilon, \quad \varepsilon_2 \]
Can someone think of a good think to call \( W \)? degeneracy. Note that many people use \( g \) for this. If we do want to do things in terms of energy level, then it might be good to recast \( Q \) in terms of energy level.

\[
Q = \sum_i e^{-E_i/kT} = \varepsilon_0 + \varepsilon_0 + \varepsilon_1 + \varepsilon_2 + \varepsilon_2 = 3\varepsilon_0 + 1\varepsilon_1 + 2\varepsilon_2
\]

\begin{align*}
\text{does anyone see how to recast this in general, summing over levels and using } W? \\
Q = \sum_j W_j e^{-E_j/kT} \\
\text{where the } E_j \text{ are now energy levels rather than individual states.}
\end{align*}

We have done everything so far in terms of \( Q \) – the partition function for the system. What if we are concerned with the partition function of an individual particle? (Note that we will get to individual particle energies on Monday.)

Let’s call this \( q \).

Let’s assume that the total energy of the system is just the sum of all the molecular energies

\[
E_i = \varepsilon_i^a + \varepsilon_i^b + \varepsilon_i^c + ... \\
\text{(} i \text{ is over states of the system, } a, b, c, \text{ indicate different particles, and } j, k, l \text{ are different states of each of those particles.)}
\]

Is this valid? only if particles are non-interacting, i.e. ideal gas. But, cross terms are small in most systems, so this is still reasonable in most real systems.

\[
Q = \sum_i e^{-\beta E_i} \\
= \sum_{j,k,l} e^{-\beta(\varepsilon_j^a + \varepsilon_k^b + \varepsilon_l^c + ...)} \\
= \sum_j e^{-\beta \varepsilon_j^a} \sum_k e^{-\beta \varepsilon_k^b} \sum_l e^{-\beta \varepsilon_l^c} ...
\]

If we define the molecular partition function \( q \):

\[
q_a = \sum_j e^{-\beta \varepsilon_j^a}
\]

then

\[
Q = q_a q_b q_c ...
\]

But, usually all the particles we have in our system (if its homogeneous) have essentially the same energy levels available to them. Then what can we say? \( q_a = q_b \) and so on.

\[
Q(N,V,T) = q(V,T)^N
\]
The above is true for independent, distinguishable particles (different atoms or molecules).

**Is this true in general?** No. If particles are indistinguishable (e.g. ideal gas) then we have over counted a bit because we can’t tell the difference between particle $a$ with $\varepsilon = 27$ and $b$ with $\varepsilon = 11$ from the opposite arrangement.

$$\varepsilon_a^2 + \varepsilon_b^2 + \varepsilon_c^2 + \ldots = \varepsilon_a^2 + \varepsilon_b^2 + \varepsilon_c^2 + \ldots$$

**How does this change things?**

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

(It is our old over-counting friend from binomial days.)

Please take time to look over Table 10.1 – everything in terms of $Q$. (connecting microscopic to macroscopic)

$$U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$S = k \ln Q + \frac{U}{T}$$

$$F = U - TS = -kT \ln Q$$

and so on.
Let’s take a little break to spend some time talking about recent newsworthy events.

What is going on this time of year that is hugely important?

Nobel Prizes! Woo-hooo!

Of all the science-ish ones the first is Medicine and Physiology:

Anyone know what this was about? The olfactory system, particularly the connections between scent and memory. It was awarded to Richard Axel of Columbia and Linda Buck who was a researcher at Columbia and then at Harvard for a long time and recently at Fred Hutchinson Cancer Research Center, Seattle.

What is the second award announced. Anyone? Physics.

David Gross, UC Santa Barbara; H. David Politzer, Caltech; Frant Wilczek, MIT. They developed first theory of asymptotic freedom, which describes interaction between quarks. As the particles get closer the force gets weaker, asymptotically approaching free motion. This led to quantum chromodynamics which is crucial to the “Standard Model”, the current state-of-the-art for describing electromagnetism and the closest thing we have to a true unified model.

And the last and most important science prize? Chemistry. That will be announced today and we’ll talk about it on Monday.