Lecture 5 – Chapter 3 and 4  Second Law, First Law, Random Walk

Outline:

Second Law
work and heat
First Law of Thermodynamics
Random Walk
Molecular collisions
  mean free path
  total collisions

Review –

The above ‘general’ form further generalized for \( t \) different possible events (rather than 2 for coins or 6 for dice) is:

\[
P(N,h) = p_1^{n_1} p_2^{n_2} p_3^{n_3} \ldots p_t^{n_t} \left( \frac{N!}{n_1! n_2! n_3! \ldots n_t!} \right)
\]

(remember this is for \( N \) dice of \( t \) sides each)

We also talked about minima and maxima, local and global and that systems tend to minimize energy while maximizing entropy. Let me put my little 5-particle lattice model up again.

So, evenly mixed is the most likely to occur. Again, each possible configuration is equally likely, it is just the fact that there are more configurations for the equally mixed composition(s) that makes them most likely. Remember – this is entropy, drive from ordered (top) to disordered (bottom).

**This is the second law of thermodynamics!** Your book drives this point home by looking at heat flow – pay attention to this.
OK, now to new stuff.

- Your book does a fair bit defining force, work, and various energies, so I won’t do much of that here. I do want to really quickly mention **conservative forces**. Can someone name a **conservative force**? gravity, force from spring, force from electric field, etc.

- With all these things you fight against the force (field), but then you can get the energy back. Like you work to ride your bike up a hill (building up potential energy), but then you can coast back down for free (converting potential to kinetic).

- Can someone name a **non-conservative force**? friction. When you fight against friction, all your energy dissipates as heat (kinetic E). You don’t store any up as potential energy.

- Note also that total energy is always conserved – shouldn’t be news to anyone.

Now onto heat and work.

- the text gives a really nice description of some of the history behind heat.

- The key final experiments were done by Joule. **What did they show?** That heat could be created by doing work, therefore the amount of heat was not constant (conserved).

- This leads to understanding that heat is simply another form of energy and that heat and work can be interconverted, giving us the **First Law of Thermodynamics**. **Anyone?**

\[ U = q + w \] (probably a good thing to remember)

In other words: energy is neither produced or consumed, simply converted between heat and work. In yet another way, \( q \) and \( w \) are the only ways to change energy.

Let’s contrast heat and work from a microscopic perspective. Think about a piston and some gas molecules. If we move the piston, we do work – an organized transfer of energy from the piston to the gas. If we just heat the system up, then we also increase the energy, but now we’ve done it in a random, unorganized way.
Another way to view the two is with particles occupying various energy levels
• When heat is transferred we change how many particles are at various energy levels, but the levels themselves stay the same.
• When work is done then the particles stay at the same energy levels, but the levels themselves change their energy.
Both heat and work change the energy, but in different ways.

OK, let’s sum up quickly. We talked about the First Law and just barely mentioned the Second Law.

First? \[ U = q + w \]
Heat and work are different expressions of energy

Second? systems tend to want to maximize their multiplicity.

Chapter 4

The text spends quite a bit of time talking about series approximations. Recall we did a bit on this in the math review. I am not going to do this here, but make sure you work through what he does in the text… don't just look at it and say "That makes sense." Actually work out the details!

Your book then gets into the Random walk. We'll do it a bit differently here, so don't get confused. Random walk is really quite important - used to describe diffusion and polymer behavior among others. We won't get into molecular transport (diffusion) in earnest until chapter 18. But, if we have time today, I'll try to connect things just a bit with some of the kinetic molecular theory that you see/will see in PChem lab.

Random Walk

Consider someone walking on a sidewalk who is unable to decide at each step whether to step forward or back (say a President’s daughter or someone). Each step is therefore random and we would consider this a one-dimensional random walk. Consider the following six random steps:

In this case, the random walker returned to the starting position.

Obviously if we take \( N \) steps and the probability of forward \( (p) \) and backward \( (q) \) steps are the same, then on average the total distance traveled should be zero.
But, if \( N \) is very large, then we don't expect the number of forward steps \( (m) \) to exactly match the number of backward steps \( (N-m) \). So, individual molecules will drift away from the starting point.

Keep in mind that we are doing this because we can consider the movement of molecules as a three dimensional random walk. Each random step is the direction and distance traveled between collisions (this can be either in a gaseous or liquid medium).

So, what we want to know is the probability that, after \( N \) total steps, we will end up some number of steps \( (m - (N-m) = 2m - N) \) away from where we started.

**What's the probability we have the sequence \( fffbbbf \)?**

\[
ppqqqp = p^m q^{N-m}
\]

That is the probability of that sequence. But, of course, any sequence with \( m \) forward and \( N-m \) backward steps has the same probability.

Of course, this is our old friend the binomial distribution

\[
P(N, m) = p^m q^{N-m} \frac{N!}{m!(N-m)!}
\]

**What if we wanted to know the average \( m \)?** Remember \( \langle x \rangle = \int x f(x) dx \)

\[
\langle m \rangle = \int m P(N, m) dm
\]

but \( m \) is discreet so...

\[
\langle m \rangle = \sum_{m=0}^{N} m P(N, m)
\]

and

\[
\langle m^2 \rangle = \sum_{m=0}^{N} m^2 P(N, m)
\]

**What if \( p = q = \frac{1}{2} \)?** Then \( \langle m \rangle = \frac{N}{2} \)

(text proves this using Stirling's approx. - very important: \( \ln N! = N\ln N - N \))

(Stirling's approx is valid when \( N \) is large.)

OK, we really care about the displacement. **How do we connect these?**
\[ d = (m - (N - m))l = (2m - N)l \]
\[ \langle d \rangle = (2\langle m \rangle - N)l \]
\[ \langle d \rangle = \left( 2 \frac{N}{2} - N \right)l = 0 \]

Not surprising – on average nothing should move.

What about RMS deviation?
\[ \langle d^2 \rangle = \langle (2m - N)^2 \rangle l^2 \]
\[ \langle d^2 \rangle = \langle 4\langle m^2 \rangle - N^2 \rangle l^2 \]

(to get here we substituted \( \langle m \rangle = N/2 \))

I won’t derive this, but:
\[ \langle m^2 \rangle = \frac{N(N + 1)}{4} \]

This leads us to
\[ \langle d^2 \rangle = \left( 4 \frac{N^2 + N}{4} - N^2 \right) l^2 = Nl^2 \]
\[ d_{RMS} = \sqrt{\langle d^2 \rangle} = l\sqrt{N} \]

What do these results for \( d \) and \( d_{RMS} \) mean?

If we have many particles, their average position will be zero, but each of the particles is moving. Any individual particle on average will move by the square root of \( N \).

2 particles starting at zero

\[ \bullet \]
\[ \bullet \]

have moved, but avg. still zero

\[ \bullet \]
\[ \bullet \]

For example:
<table>
<thead>
<tr>
<th># steps</th>
<th>sequences</th>
<th>result</th>
<th>$\langle d \rangle$</th>
<th>$\sqrt{\langle d^2 \rangle}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L R</td>
<td>+1</td>
<td>$0 \quad 2 = 0$</td>
<td>$\sqrt{\frac{1^2 + 1^2}{2}} = \sqrt{1}$</td>
</tr>
<tr>
<td>2</td>
<td>LL LR, RL RR</td>
<td>+2</td>
<td>$0 \quad 4 = 0$</td>
<td>$\sqrt{\frac{8}{4}} = \sqrt{2}$</td>
</tr>
<tr>
<td>3</td>
<td>LLL LLR, LRL, RLL RRL, RLR, LRR RRR</td>
<td>+3</td>
<td>$0 \quad 8 = 0$</td>
<td>$\sqrt{\frac{24}{8}} = \sqrt{3}$</td>
</tr>
</tbody>
</table>

To connect these random walk results to real life:

- **Replace the number of steps per second** by the collision rate, $z_A$
- **Replace average step size** by the mean free path, $\lambda$