Lecture 5 -- Random walk part of Chapt 4
(with bonus connection to kinetic molecular theory)

Outline:

Random Walk
Molecular collisions
  mean free path
  total collisions

Review:
- work and heat are both forms of energy
  - work is ‘organized’ heat is chaotic
- First Law of Thermodynamics: \( U = q + w \)
- Second Law of Thermodynamics: systems reorganize to maximize multiplicity

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 chapt 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 Michigan St. QB). 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 \( ffbbbf \)?**

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

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 \( \langle x \rangle = \int x f(x) dx \)

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

but \( m \) is discreet

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

and

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

Of course, \( \langle m \rangle = N/2 \) if \( p = q = \frac{1}{2} \)

(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?**

\[ d = (m-(N-m))l = (2m-N)l \]

\[ \langle d \rangle = 2\langle m \rangle - N \]

\[ \langle d \rangle = (2 \cdot \frac{N}{2} - N)l = 0 \]

What about the RMS deviation?

\[ \langle d^2 \rangle = \langle (2m-N)^2 \rangle l^2 \]

\[ \langle d^2 \rangle = 4\langle m^2 \rangle - N^2 l^2 \quad \text{(to get here we substituted } \langle m \rangle = N/2) \]
I won’t derive, but

\[ \langle m^2 \rangle = \frac{N(N+1)}{4} \]

So,

\[ \langle d^2 \rangle = \left( 4 \cdot \frac{N^2 + N}{4} - N^2 \right) = Nl^2 \]

\[ d_{\text{RMS}} = \sqrt{\langle d^2 \rangle} = \sqrt{Nl} \]

What do these results for \( d \) and \( d_{\text{RMS}} \) 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 \( \sqrt{N} \).

2 particles starting at zero

\[ \bullet \]

have moved, but avg. still zero

\[ \bullet \]

For example:

<table>
<thead>
<tr>
<th># steps</th>
<th>sequence</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</td>
<td>+1</td>
<td>0/2 = 0</td>
<td>[ \sqrt{2}/2 = \sqrt{1} ]</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>LL</td>
<td>+2</td>
<td>0/4 = 0</td>
<td>[ \sqrt{8}/4 = \sqrt{2} ]</td>
</tr>
<tr>
<td></td>
<td>LR,RL</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RR</td>
<td>-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>LLL</td>
<td>+3</td>
<td>0/8 = 0</td>
<td>[ \sqrt{24}/8 = \sqrt{3} ]</td>
</tr>
<tr>
<td></td>
<td>LLR,RLR,LRL</td>
<td>+1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RRL,RLR,LRR</td>
<td>-1</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>RRR</td>
<td>-3</td>
<td></td>
<td></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, \( \lambda \)

**Intermolecular collisions**

Consider the volume swept out by some (hard sphere) particle of diameter \( d \), in among a bunch of other particles of diameter \( d \), in the time \( dt \).
Volume of cylinder = height times area
what is height? $V_A dt$
what is area? $\pi d_A^2$ -- we call this the cross section, $\sigma_A$
note use of $d$ rather than radius – accounts for collision with other particles of same size

$V_A = \sigma_A V_A dt$

**This is nice, but we have left out one tidbit?** All particles are moving, not just our particle.

The physics trick for this is to use the reduced mass to get a relative velocity rather than just the velocity of the one particle

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2}$$

Since, in energy $m$ and $v$ are related by square root, it works out that:

$$\langle v_{rel} \rangle = \sqrt{2} \langle v_A \rangle$$

So, our effective volume then is $V_A = \sqrt{2} \sigma_A V_A dt$

**Why do we care about this volume?** We can use it to figure out # of collisions.

**How can we get the total number of collisions our happy molecule sees?** multiply this $V$ times the number of particles per unit volume – the number density – that our molecule will bump into.

$$n^* = \frac{N}{V} = \frac{n N_A}{V} = \frac{pN_A}{RT} = \frac{p}{k_B T}$$

at STP: $\rho = 2.69 \times 10^{19}$ molecules cm$^{-3}$

note that sometimes $\rho$ is used instead of $n^*$

$$\text{collisions} = \sqrt{2} \sigma_A \langle v_A \rangle n^* A dt = \sqrt{2} \pi d_A^2 \langle v_A \rangle n^* A dt$$

$$\text{collision rate} = z_A = \frac{d(\text{collisions})}{dt} = \sqrt{2} \sigma_A \langle v_A \rangle n^* A = \sqrt{2} \pi d_A^2 \langle v_A \rangle n^* A$$
For N\textsubscript{2} at STP, d = 0.370 nm so \( z_A = 7.4 \times 10^9 \) s\(^{-1} \) or one collision every 0.135 nanoseconds!

Note that the collision frequency also determines the \textbf{gas kinetic rate} of chemical reactions - no gas phase chemical reaction can proceed faster than the gas kinetic rate.

**Mean free path (\( \lambda \) or \( l \)):** the average distance a particle travels between collisions

This must be the mean speed divided by the collision frequency:  
\[
\lambda = l = \frac{\langle v_A \rangle}{z_A}
\]

Substitution yields  
\[
l = \frac{1}{\sqrt{2} \sigma A n^*_{A}} = \frac{k_B T}{\sqrt{2} \sigma A p}
\]

\textbf{Note:} that \( l \propto \frac{1}{p} \) so increasing pressure decreases distance between collisions.

However, \( l \) does not depend directly on the speed.

For N\textsubscript{2} at STP, \( l = 61 \) nm. Because N\textsubscript{2} has a molecular diameter of about 0.4 nm, \( d \ll l \) so the kinetic theory of gases holds since the molecules spend much more time apart than in collisions – this implies that the ideal gas should be a very good approximation for N\textsubscript{2} at STP.

For N\textsubscript{2} at 10\(^{-8} \) bar (a pressure achievable with the diffusion pump in the p-chem lab), \( l = 6 \) m!!! Molecules collide with the walls of system much more often than they collide with each other!

Getting back to our random walk results for displacement:

For N\textsubscript{2} at STP  
\[
\lambda = 60 \text{ nm} \quad z_A = 7 \times 10^9 \text{ s}^{-1}
\]

\[
d_{\text{RMS}} = \sqrt{Nl} = \sqrt{1 \text{ sec} \cdot 7 \times 10^9 \text{ sec}^{-1} \cdot 60 \times 10^{-9}} = 0.56 \text{ cm} \quad \text{in one second}
\]

Note that for N\textsubscript{2} at STP \( \langle v \rangle = 474 \text{ m/s} \)

So, \( d_{\text{RMS}} \) is small, not because the particles aren’t moving quickly, but because all the collisions keep reversing direction (roughly), remember 3 dimensions.