Leture 6 Chapter 5 – lots of multivariate calculus

Outline:

a little more on molecular collisions  
calculus  
  total differential  
  exact differential  
  state and path functions

Review:

GRE is coming up – make sure you sign up. any questions on this in general?

Remember that last time we were talking about the random walk problem and that this relates to  
diffusion (and other things).

The key results were  
\[ \langle d \rangle = \left( \frac{2N}{2} - N \right) \ell = 0 \]

and  
\[ d_{\text{RMS}} = \sqrt{\langle d^2 \rangle} = \sqrt{N} \ell \]  
(if the probability of forward and backward steps are equal)

Now, I zipped through some gas phase collision theory pretty quickly. I’d like to go over this in  
just a little more detail today meaning we’ll have less time for ch 5. That’s OK, because we’ll  
see the tools of chapt 5 as we go throughout the semester.

I sketched this flying particle last time

\[ \text{Area} = \sigma = \pi d^2 \]

and we figured out that in some short time \( dt \), that our happy particle will hit any other particle  
that is within the volume? \[ V_A = \sqrt{2} \sigma_A v_A dt \]

\( \sigma \) is called? The cross section. (technically in this case as single-particle cross section).
The rest I zipped through pretty quickly

OK, if we want to know how many collisions, we have to know how many other particles are in the volume.

Start with the density. In this case we want \# ptcls per unit volume – called the number density.

\[ n^* = \frac{N}{V} = \frac{nN_A}{V} = \frac{pN_A}{RT} = \frac{p}{k_B T} \]

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

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

So, then the number of collisions is just?  
\[ \text{density} \times \text{volume} \]

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

\[ \text{collision rate} = z_A = \frac{d(\text{collisions})}{dt} = \sqrt{2} \sigma_A \langle v_A \rangle n^* = \sqrt{2} \pi d_A^2 \langle v_A \rangle n^* \]

For \( \text{N}_2 \) 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 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:  
\( \lambda = l = \frac{\langle v_A \rangle}{z_A} \)

*(do the units work out?)*

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

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

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

For \( \text{N}_2 \) at STP, \( l = 61 \) nm. Because \( \text{N}_2 \) 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 \( \text{N}_2 \) at STP.

For \( \text{N}_2 \) 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

\[ \lambda = 60 \text{ nm} \quad z_A = 7 \times 10^9 \text{ s}^{-1} \]

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

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.

As Jason pointed out, we should always be thinking of things like this in terms of the variables they depend on. **This is a very important part of science – understanding behavior.**

So, if we want to know about diffusion, **we should look at?** \( d_{\text{RMS}} \):

\[
d_{\text{RMS}} = \sqrt{z_A \lambda} = \sqrt{z_A} \frac{\langle v_A \rangle}{\sqrt{z_A}} = \left[ \frac{\langle v_A \rangle}{\sqrt{2} \text{ cm}} \right]^{\frac{1}{2}} = \left[ \frac{\langle v_A \rangle}{\sqrt{2 \pi d^2} \frac{p}{k_B T}} \right]^{\frac{1}{2}} = \left[ \frac{\langle v_A \rangle k_B T}{\sqrt{2 \pi d^2} p} \right]^{\frac{1}{2}}
\]

Now then, **what do we have from here that is important?!**

\[ d_{\text{RMS}} \propto \sqrt{T} \quad \text{(well, sort of... why? can’t ignore velocity)} \]

\[ d_{\text{RMS}} \propto \frac{1}{\sqrt{p}} \]

\[ d_{\text{RMS}} \propto \frac{1}{d} \]

**any other variable you think should be there that isn’t?** perhaps mass? it IS there, \( v \).

OK, let’s switch gears a bit to chapter 5. Like I said, we’ll have these things again and again so I’m too worried that you have all of this down pat right now. However, I do want to make sure everyone is 100 % clear on a few things.

**Total derivative** (of some function \( f \) that depends on only \( x \) and \( y \))

\[
df = \left( \frac{\partial f}{\partial x} \right)_y \, dx + \left( \frac{\partial f}{\partial y} \right)_x \, dy
\]

(If we had \( z \)? Just add on another term... and so on.)
Exact differential?

$df$ is an exact differential if

$$\left( \frac{\partial^2 f}{\partial x \partial y} \right) = \left( \frac{\partial^2 f}{\partial y \partial x} \right)$$

notice how this relates the coefficients we had above.

If $f$ does have an exact differential, then we call it a state function. What does this mean? It means that the change in $f$ on going from point A to point B only depends on the conditions at A and B, not on the conditions of any intermediate point. Thus,

$$\int_{x_A}^{x_B} \int_{y_A}^{y_B} df(x, y) = f(x_B, y_B) - f(x_A, y_A)$$

This is true for things like? temperature, energy, pressure, location
Not true for things like? work, heat

work and heat (and others) are called? Path functions, because their value depends on path.

For example, if its 2nd and one at mid field, Culpepper can do a little QB sneak ahead for two yards and pick of the first down. The ball is now on the 48. Or, the Vikes know they have two downs left, so they can be a little crazy and run a reverse to Moss who goes the whole width of the field but only gains two yards. Same result right? First down, ball on the 48.

In this case the down and position of the ball are state functions. However, the amount of work done by the ball carrier is a path function. Duante ran a few yards, Randy ran about 40 – completely different.

So, for work and heat the above equation is not enough. You must also specify the path that you are taking. We’ll get to that more in later chapters.

Remember grad school information things tonight and you should sign up for the GRE practice test (with Stewart?)