Partial Derivatives (cont.)

Last lecture we saw that when \( F(x,y) \) was just Area, the concept behind: \( dA = \left( \frac{\partial A}{\partial x} \right)_y \, dx + \left( \frac{\partial A}{\partial y} \right)_x \, dy \) was pretty clear.

Another way to think about it is to imagine the wedge of a circle:

The area of this wedge is \( \frac{\theta r^2}{2} \), for \( \theta \) in radians.

So, \( dA = \left( \frac{\partial A}{\partial r} \right)_\theta \, dr + \left( \frac{\partial A}{\partial \theta} \right)_r \, d\theta = \frac{r \theta \, dr}{2} + \frac{r^2 \, d\theta}{2} \).

If we had done this geometrically we would have had the same thing: \( dA = \theta(r + dr)^2 - \theta r^2 \) to the power of 2

\[ \frac{dA}{r} = 2 \pi r \theta \, dr \]
\[ dA = \frac{\pi r^2 \, d\theta}{2} \]

So the general form, \( d[f(x,y)] = \left( \frac{\partial f(x,y)}{\partial x} \right)_y \, dx + \left( \frac{\partial f(x,y)}{\partial y} \right)_x \, dy \), works for all functions of \( 2 \) variables.

Now, let's look at the neat relations of partial derivatives:

If \( f(x,y) \) is \( z \), then \( \frac{\partial^2 z}{\partial x \partial y} = \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y = \left[ \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right]_x = \frac{\partial^2 z}{\partial y \partial x} \)

Don't forget!

Also, \( \left( \frac{\partial x}{\partial y} \right)_z = \left( \frac{\partial x}{\partial y} \right) \left( \frac{\partial x}{\partial z} \right) \) which means: \( \frac{\partial^2 z}{\partial y \partial z} \left( \frac{\partial z}{\partial x} \right)_y = -1 \).

Chain Rule p.38
Now we're ready to look at how these partial derivatives help us...

We know that our first two "equations of state" - the Ideal Gas Law and the van der Waals Equation - are functions of $p$, $v$, and $T$.

To get more mileage out of these equations, we can write 6 partial derivatives:
\[
\frac{\partial U}{\partial T}_p \quad \frac{\partial V}{\partial p}_T \quad \text{etc.}
\]

but 3 of the 6 will just be "inverses" of the other 3, and 1 of the remaining 3 can be related to the other 2 by the Chain Rule, so we only need two partial derivatives for the "basic properties of matter."

These are (p. 180): $\alpha = \frac{1}{V} \left( \frac{\partial U}{\partial T}_p \right)_v$ "coef. of volume expansion", and

$K = \frac{1}{V} \left( \frac{\partial V}{\partial p}_T \right)_T$ "the "isothermal compressibility"

*For example, if we need to give an expression for the "pressure coef.", which is how much the pressure changes w/ temp. at const. volume, we write:

\[
\frac{\partial p}{\partial T}_V = \frac{1}{V} \left( \frac{\partial U}{\partial T}_p \right)_v = \frac{1}{V} \left( \frac{\partial V}{\partial p}_T \right)_T = \frac{1}{K} \alpha
\]

Partial derivatives are a great way to relate experimentally measurable quantities to other quantities that are hard to measure. We'll see lots of examples in this class, especially as we use our "Thermodynamic Octahedron" or Maxwell relations.
To summarize chapter 1,

- We study thermo b/c it's all around us, and study stat. mech. b/c it's the bridge from micro to thermo.

- We worry about systems b/c we want to talk about states, state variables, and (ultimately) equations of state (eg. AV=NRT).

- We like the graph on p. 26 b/c it reassures us that all gases were created equal with certain unalikeable properties (van der Waals, now).

- We took a brief detour into phase change to understand T_f, P_f, V_f for p. 26.

- We also detoured into Lennard-Jones to understand a+b in v.e.w.

- We need to know partial derivatives b/c they allow us to obtain hard-to-measure quantities from easier-to-measure quantities.

- We can visualize \( dU = \left( \frac{\partial U}{\partial T} \right)_{V,N} dT + \left( \frac{\partial U}{\partial V} \right)_{T,N} dV + \left( \frac{\partial U}{\partial N} \right)_{V,T} dN \) and other expressions of differentials, by visualizing a rectangle's or wedge's area.

- There are lots of nifty things you can do with partial derivatives such as the Chain Rule, and the "Euler Relation" slide in our notes.

Now let's get back to "Stat Mech Disguised as Kinetic Theory..."
Kinetic Theory of Gases

Our book starts from the historical perspective of Boyle and Bernoulli - two guys who pretty much got it right.

Bernoulli said \( p = \frac{mnv_{x,y,z}^2}{3} \) where \( m \) is molecular mass, \( n \) is number of molecules per unit volume, \( p \) is pressure, and \( v \) is velocity.

Let's derive this!

Start with a layer of gas molecules \( \Delta x \) from a wall of area \( A \), so the volume = \( A \Delta x \).

Now half the molecules in this layer are moving toward the wall, half are not. The average toward-the-wall velocity \( v_{x,y,z} \) is what we use to calculate momentum imparted to the wall:

\[
\text{momentum imparted} = 2m v_{x,y,z} (A \Delta x \cdot n) \quad \text{# of particles in layer} \\
= 2m v_{x,y,z} (A \Delta x \cdot n) / 2 = n A v_{x,y,z} \quad \text{half moving toward wall} \\
\text{elastic collision gives } 2x \text{ the momentum!}
\]

We remember that \( F = \frac{\text{momentum imparted}}{\Delta t} \), \( \Delta t = \frac{\Delta x}{v_{x,y,z}} \)

so, \( F = \frac{mv_{x,y,z} A \Delta x \cdot n}{\Delta x / v_{x,y,z}} = mnv_{x,y,z}^2 n A \) and \( p = \frac{F}{A} = mnv_{x,y,z}^2 n \)

but since velocity is symmetric in \( x, y, z \), \( v_{x,y,z}^2 = v_{x}^2 + v_{y}^2 + v_{z}^2 = 3v_{x,y,z}^2 \)

so \( p = mn \left( \frac{3}{3} \right)^n \), which is what Bernoulli said! (also: \( mn = M N_A \))

An interesting corollary is that \( p v = \frac{1}{3} v_{x,y,z}^2 (M N_A) = k_B T \), but \( R = k_B N_A \) and \( M = m N_A \), so \( \frac{1}{3} m v_{x,y,z}^2 = k_B T \) or \( \frac{1}{2} m v_{x,y,z}^2 = \frac{3}{2} k_B T \) (see p. 31)
* Equipartition Theorem: each degree of freedom contributes $\frac{1}{2}kT$ DoF

We saw this happen when we plugged $p = \frac{1}{3}mv_{xy}^2$ into $pV = NRT$ and ended up with $\frac{1}{2}mv_{xy}^2 = \frac{3}{2}kT = 3(\frac{1}{2}kT)$ for 3 DoFs

We'll also see that for diatomic gases the total energy $= \frac{3}{2}kT + \frac{3}{2}kT$

The first term is for the $x, y, z$ translation, the second is for 2 axes of rotation.

Now, let's find out more about $v^2$, what is the distribution of $v^2$?

For that, we'll need serious stat. mec.; the Boltzmann principle:

"The probability of a particle being at energy $E$, is proportional to $e^{-\frac{E}{kT}}$"

Ignoring electron-energy, etc., a non-atomic gas energy $= \frac{1}{2}mv^2$, so we write:

$$P(v)dv = \frac{1}{(2\pi kT)^{3/2}} e^{-\frac{1}{2}mv^2/kT} dv$$

"Volume" in velocity space in which you're looking $P(v=0, v=\infty) = 1$

A graph of this is Fig. 1.10a on p. 35. I like the version in lecture 3.ppt, which makes the mesh width explicit. However, the y-axis is confusing.

But what about speed?

For that, we change from $x, y, z$ to $\xi, \eta, \zeta$ and integrate $\rho \rightarrow (\xi, \eta, \zeta)$

Then the # of particles we find in each spherical shell of radius $v \rightarrow v+dv$ gives us the # of particles with a speed of $|v|$. This gives us the same $P(v)$ as above except multiplied by $4\pi v^2$.
So what have we learned from all this stat. mech?

- We can relate things we measure with thermometers, pressure gauges, etc. to velocities of molecular particles (assuming they're like tiny hard spheres).

- The mass of the particles also enters in. Heavy ones move slower at the same T and p as lighter ones.

- We can use Boltzmann's insight to plot the distribution of velocities:

- If we integrate this distribution P(v) over all velocity space we get 1.

- If we integrate v·P(v), we get \( V_{\text{avg}} \); if we integrate \( \frac{1}{2} m v^2 P(v) \) we get \( E_{\text{avg}} \).

\[
E_{\text{avg}} = \frac{3}{2} k_B T \quad \text{for a monatomic particle} \quad \text{or} \quad \frac{5}{2} k_B T \quad \text{for a diatomic particle}.
\]

- The idea of getting \( \frac{1}{2} k_B T \) of energy for each degree of freedom is called the equipartition theorem. It works for translation, rotation, vibration.

(We didn't learn this in sect. 1.6, but I find the following graph helpful.)

For a diatomic particle the heat capacity (how much heat energy is required to raise a particle's temperature by 1°C, i.e., by 1 K) changes from \( \frac{3}{2} k_B \) at 0 K to \( \frac{5}{2} k_B \) at room temp, to \( \frac{7}{2} k_B \) at greater than 2000 K, where quantized levels become accessible.)