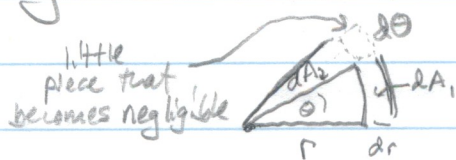


Partial Derivatives (cont.)

1.8

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 θ in radians.

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

If we had done this geometrically we would have had the

same thing: $dA = \underbrace{\frac{\theta(r+dr)^2}{2} - \frac{\theta r^2}{2}}_{dA_1 = \frac{2r\theta}{2} dr} + \underbrace{\frac{(\theta+d\theta)r^2}{2} - \frac{\theta r^2}{2}}_{dA_2 = \frac{r^2}{2} d\theta} + \text{little piece that becomes negligible}$

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 $\frac{\partial^2 z}{\partial x \partial y} = \left[\frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y}\right)_x\right]_y = \left[\frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x}\right)_y\right]_x = \frac{\partial^2 z}{\partial y \partial x}$

also $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y$ which means: $\underbrace{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y}_{\text{Chain Rule p.38}} = -1$

Chain Rule p.38

1.9

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: $\left(\frac{\partial V}{\partial T}\right)_p \dots \left(\frac{\partial V}{\partial p}\right)_T \dots$ 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): $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ "coef. of volume expansion", and

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \rightarrow \text{the "isothermal compressibility"}$$

*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:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial T}{\partial V}\right)_p} = \frac{-\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p}{\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha}{\kappa} \quad \checkmark$$

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" for 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. $PV = NkT$)
- We like the graph on p. 26 b/c it reassures us that all gases were created equal with certain unalienable properties (van der Waals, v.d.W.)
- We took a brief detour into phase change to understand T_c, P_c, V_c for p. 26
- We also detoured into Lennard-Jones to understand $a+b$ in v.d.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"...

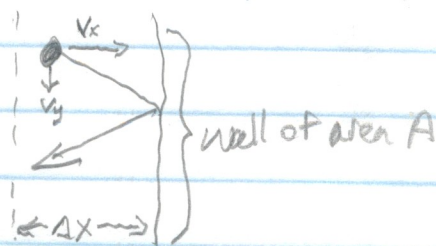
Kinetic Theory of Gases

1.11

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

Bernoulli said " $p = \frac{mn v_{avg}^2}{3}$ " where m is molecular mass, n is number of molecules per unit volume, p is pressure, & v 's velocity.

Let's derive this!



Start with a layer of gas

molecules Δx 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 $v_{x,avg}$ is what we use to calculate momentum imparted to the wall:

$$= 2m v_{x,avg} \left(\frac{A \Delta x \cdot n}{2} \right)$$

← # of particles in layer
← half moving toward wall

elastic collision gives 2x the momentum!

We remember that $F = \frac{\text{momentum imparted}}{\Delta t}$, $\Delta t = \frac{\Delta x}{v_{x,avg}}$

$$\text{So, } F = \frac{m v_{x,avg} A \Delta x \cdot n}{\Delta x / v_{x,avg}} = m v_{x,avg}^2 n A \quad \text{and} \quad p = \frac{F}{A} = m v_{x,avg}^2 n$$

but since velocity is symmetric in $x, y + z$, $v_{avg}^2 = v_{x,avg}^2 + v_{y,avg}^2 + v_{z,avg}^2 = 3v_{x,avg}^2$

so $p = m \left(\frac{v_{avg}^2}{3} \right) n$, which is what Bernoulli said! (also: $mn = \frac{M}{V} = \frac{M}{V} \cdot \frac{N}{N} = \frac{M N}{V}$)

an interesting corollary is that $pV = \frac{1}{3} v_{avg}^2 (M \frac{N}{V}) = NRT$, but $R = k_B N_A$ and $M = m N_A$, so $\frac{1}{3} m v_{avg}^2 = k_B T$ or $\frac{1}{2} m v_{avg}^2 = \frac{3}{2} k_B T$ (see p. 31)

* Equipartition Theorem: each degree of freedom contributes $\frac{1}{2} k_B T$

We saw this happen when we plugged $p = \frac{1}{3} m n v_{avg}^2$ into $PV = NRT$ and ended up with $\frac{1}{2} m v_{avg}^2 = \frac{3}{2} k_B T = 3(\frac{1}{2} k_B T)$ for 3 DoF

We'll also see that for diatomic gases the total Energy = $\frac{3}{2} k_B T + \frac{2}{2} k_B T$, the first term is for the x, y, z translation, the 2nd is for 2 axes of rotation

Now, let's find out more about v_{avg}^2 , what is the distribution of v 's?

for that, we'll need serious stat. mech.; the Boltzmann principle:

"The probability of a particle being at energy E , is proportional to $e^{-E/k_B T}$ "

Ignoring electron-energy, etc., a monoatomic gas' energy = $\frac{1}{2} m v^2$, so we write:

$$P(v) dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{1}{2} m v^2 / k_B T} dv_x dv_y dv_z$$

Probability of finding a particle with velocity, v "volume" in velocity space in which you're looking normalization so that $P(v=-\infty \rightarrow v=\infty) = 1$ from the Boltzmann principle

A graph of this is Fig. 1.10a on p. 35

however, the y-axis is confusing, I like the version in "lecture 3.ppt" which makes the "mesh width" explicit, ie. says "probability of finding it in 1 m/s " intervals

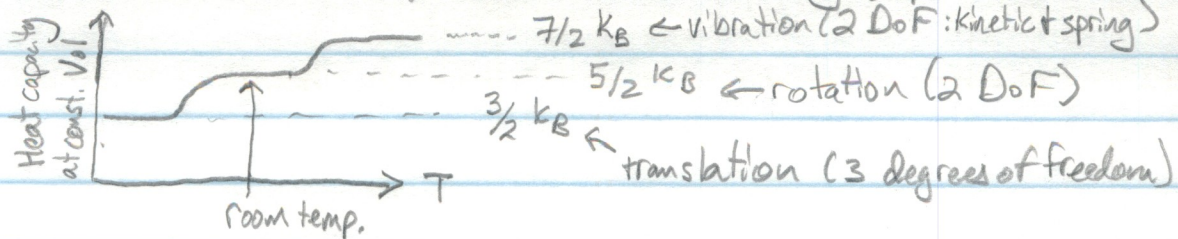
But what about speed?

For that, we change from x, y, z to v, θ, ϕ and integrate $\phi: 0 \rightarrow 2\pi, \theta: 0 \rightarrow \pi$
 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 $4\pi v^2$ (this part comes from switching to spherical coord.)

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 \rightarrow 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 $P(\vec{v})$ over all velocity space we get 1.
- if we integrate $v \cdot P(\vec{v})$, we get v_{avg} ; if we integrate $\frac{1}{2}mv^2 P(\vec{v})$ we get E_{avg}
- $E_{avg} = \frac{3}{2} k_B T$ for a monoatomic particle or $= \frac{5}{2} k_B T$ 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 $>2000\text{ K}$ \rightarrow quantized levels become accessible