Lecture 2: Pressure

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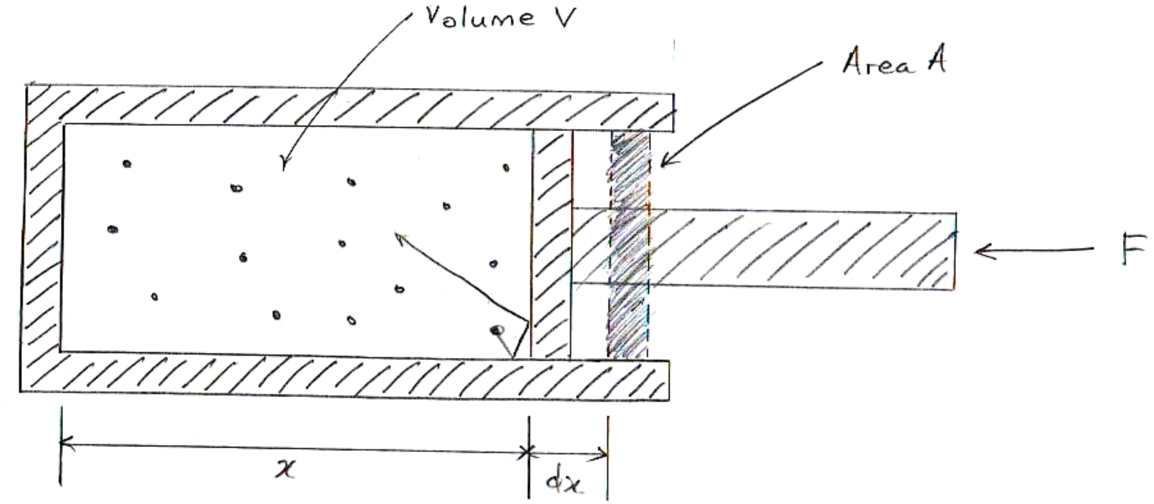
Why start this course with kinetic theory?

- Thermal physics, as its usually taught, doesn't actually begin with kinetic theory (i.e., a microscopic viewpoint).
- The main reason for that is historical. In the heyday of the subject, the late 1700s and early 1800s era of Watt, Carnot and others, people didn't know anything about the microscopic properties of systems.
- To a certain extent, these guys were flying blind in their science, they could talk about pressure and temperature, which is fine if all you care about is building a steam engine or something, but they had little idea how it worked.
- We're in a pretty fortunate position – we live in an era where we understand both the macroscopic and microscopic aspects of thermodynamics really well, so we have the luxury of learning the subject backwards, forwards, whichever way makes best sense.
- I'm going to start from kinetic theory because then we can actually see where our statistical state variables really come from, which means they're more than just meaningless numbers we can measure in a system, we know what drives their behaviour. We're going to start with the easiest one, pressure.

Pressure

- Imagine we have a frictionless piston. We have a gas of particles inside the cylinder as shown, and we can apply some force *F* to the piston to push it in (or pull it out) of the cylinder.



- Suppose there's nothing outside the cylinder (i.e., its in a vacuum). Each collision of a particle against the piston will impart some momentum to the piston, and push it out of the cylinder. To keep the piston in place, we need to apply a force F to hold it in place.

- We can now try and equate those two forces, and see where it takes us.

Force as a change in momentum

- So lets start with the force that the individual particles exert on the piston when they collide with it. You’ll remember from Newton’s 2nd law that:

$$F = ma = m\frac{dv}{dt} = \frac{dp}{dt} \qquad \textbf{(2.1)}$$

That’s right, the force is just the rate of change in momentum. In fact, from here on in physics, this definition of force will probably be more useful than mass × accel.

- OK, so we need the momentum imparted by the particles per unit time, but that’s a rather tricky thing to get. It depends on how fast the particles are moving and how many particles there are in the piston.

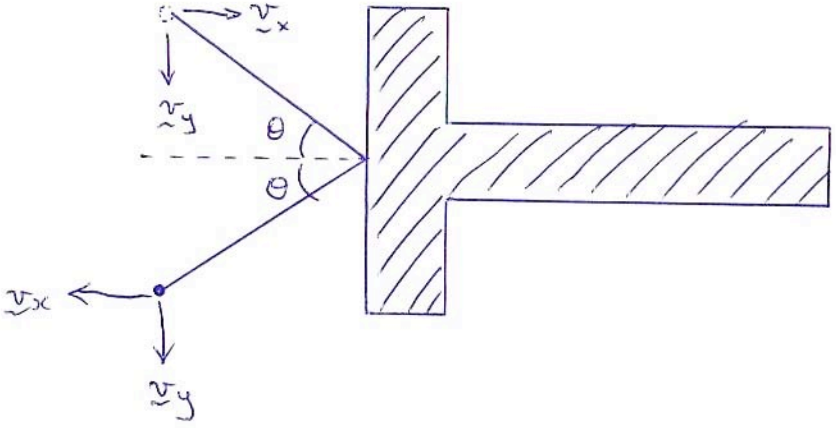
- However, we can split the derivative in Eqn. 2.1 using the number of particles that collide with the piston n_c:

$$F = \frac{dp}{dt} = \frac{dp}{dn_c}\frac{dn_c}{dt} \qquad \textbf{(2.2)}$$

These derivatives are the momentum imparted to the piston per particle dp/dn_c and the particles per time striking the piston dn_c/dt, and we can work both of these out.

Momentum per particle dp/dn_c

- To start here, we need to assume that particle collisions with the piston are elastic. At thermal equilibrium this is a very fair assumption because if it wasn't, either the gas would get cold and the walls hot or vice versa – both of which we know don't happen.



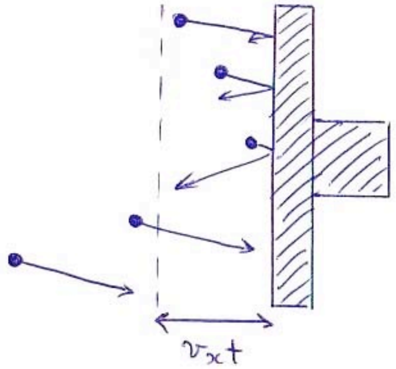
- Considering a particle colliding elastically with the piston, it comes in with (v_x,v_y) and goes out with ($-v_x$,v_y). The momentum must also be conserved, so:

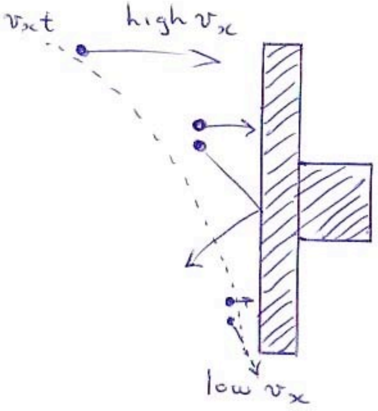
$$\Delta p = p_f - p_i = -mv_x - mv_x = -2mv_x \tag{2.3}$$

and so the momentum per particle comes out quite easily as $dp/dn_c = 2mv_x$, but note that we'll need to determine v_x soon.

Particles per time dn_c/dt

- If we watch for a time period *t*, how many of the particles in the cylinder will collide with the piston?





- Each particle has some v_x and providing it has $v_x > 0$ (i.e., it's going right) and is within a distance $v_x t$ of the piston, then it will collide with it.
- If the piston has area *A*, then particles in a volume $v_x tA$ will collide with the piston, and if the cylinder contains *N* particles in its volume *V*, or $n = N/V$ particles per unit volume, then the number colliding with the piston n_c is given by:

$$n_c = n v_x t A \tag{2.4}$$

or taking the derivative:

$$\frac{dn_c}{dt} = n v_x A \tag{2.5}$$

Bringing it together

- We can now combine our two results to get the force we need to apply to hold the piston in place:

$$F = \frac{dp}{dn_c}\frac{dn_c}{dt} = 2mv_x \times nv_x A = 2mnAv_x{}^2 \tag{2.6}$$

- But the force isn't that useful because as we change the area *A*, then the force also changes. The sensible thing to do here is choose the ratio *F*/*A*, which is then independent of the size of the system. We call this the pressure *P*:

$$P = \frac{F}{A} = 2mnv_x{}^2 \tag{2.7}$$

which now depends only on the mass of the particles *m*, their number per unit volume *n* and their *x*-component velocity v_x. The latter is something we haven't really got any control of, because it could range from 0 right through to the largest *v* of any particle in the system!

Bringing statistics into play

- The most obvious thing to do about v_x is to take the average, but we need to be rather careful about how we do this. Considering Eqn. 2.7:

$$P = 2mnv_x^{\ 2} \tag{2.7}$$

we have a two options – we can take $\langle v_x \rangle^2$ or $\langle v_x^{\ 2} \rangle$.

- It turns our we need to use the latter. As an example, lets consider 7 atoms which have v_x values –3, –2, –1, 0, 1, 2 and 3 m/s. In this case let's consider both cases.

The direct average $\langle v_x \rangle = (\Sigma v_x)/n = (-6 + 0 + 6) / 7 = 0$.

The root mean square average $\langle v_x^{\ 2} \rangle^{½} = [(\Sigma v_x^{\ 2})/n]^{½} = [\ (9 + 4 + 1 + 0 + 1 + 4 + 9) / 7]^{½} = 2$

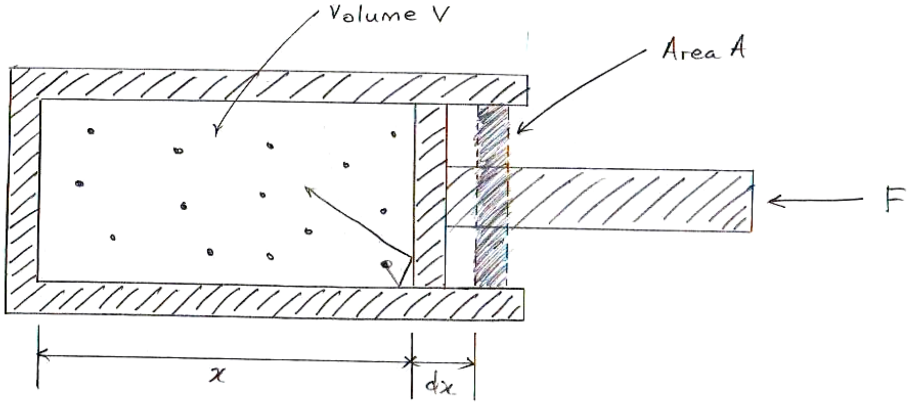
So then its pretty clear that we should make the transformation $v_x^{\ 2} \rightarrow \langle v_x^{\ 2} \rangle$.

- But its not over yet. We're missing one last detail. In our cylinder, half of the particles will have a positive v_x and contribute to P, the other half will have negative v_x and not strike the piston and contribute to P. So our pressure P is actually too large by a factor of 2, so finally:

$$\boxed{P = mn\left\langle v_x^{\ 2} \right\rangle} \tag{2.8}$$

Generalizing this problem to 3D

- **If we go back to our cylinder (imagine its roughly cubic for convenience if you like, but this argument works for *any* geometry) our pressure is only accounting for one wall, but we can easily generalise to 3D.**



- **The trick is to realise that there's nothing special about *x*, *y* and *z* should be the same, so we'd expect that $\langle v_x^{\,2}\rangle^{1/2} = \langle v_y^{\,2}\rangle^{1/2} = \langle v_z^{\,2}\rangle^{1/2}$, and we can show that:**

$$\langle v_x^{\,2}\rangle = \frac{1}{3}\langle v_x^{\,2} + v_x^{\,2} + v_x^{\,2}\rangle = \frac{1}{3}\langle v_x^{\,2} + v_y^{\,2} + v_z^{\,2}\rangle = \langle v^2\rangle/3 \tag{2.9}$$

- **We no longer need to care about direction, so we can rewrite Eqn. 2.8:**

$$P = mn\langle v_x^{\,2}\rangle = \frac{mn\langle v^2\rangle}{3} = \frac{2}{3}\frac{1}{2}mn\langle v^2\rangle = \frac{2}{3}n\left\langle \frac{1}{2}mv^2\right\rangle = \frac{2}{3}\frac{N}{V}\left\langle \frac{1}{2}mv^2\right\rangle \tag{2.10}$$

Introducing the internal energy *U*

$$P = \frac{2}{3}\frac{N}{V}\left\langle \frac{1}{2}mv^2 \right\rangle \qquad \textbf{(2.10)}$$

- If we look closely at Eqn. 2.10, the final component is just the average kinetic energy of a particle. But we need to be careful that the mathematics is making sense here.
- For a gas consisting of single atoms, for example a noble gas like He or Ar, then we should be fine. But if we have something more complex, like N_2 or H_2O or acetylene, then we might be missing something because the particle can also rotate and stretch along the chemical bonds, as we'll discuss in Lecture 5.
- For now, lets consider the simple case of monatomic atoms, where the kinetic energy of motion is all the energy the particles can have. We can define the internal energy *U* as the total energy of the gas $U = N\langle \frac{1}{2}mv^2 \rangle$, and thus arrive at our final result:

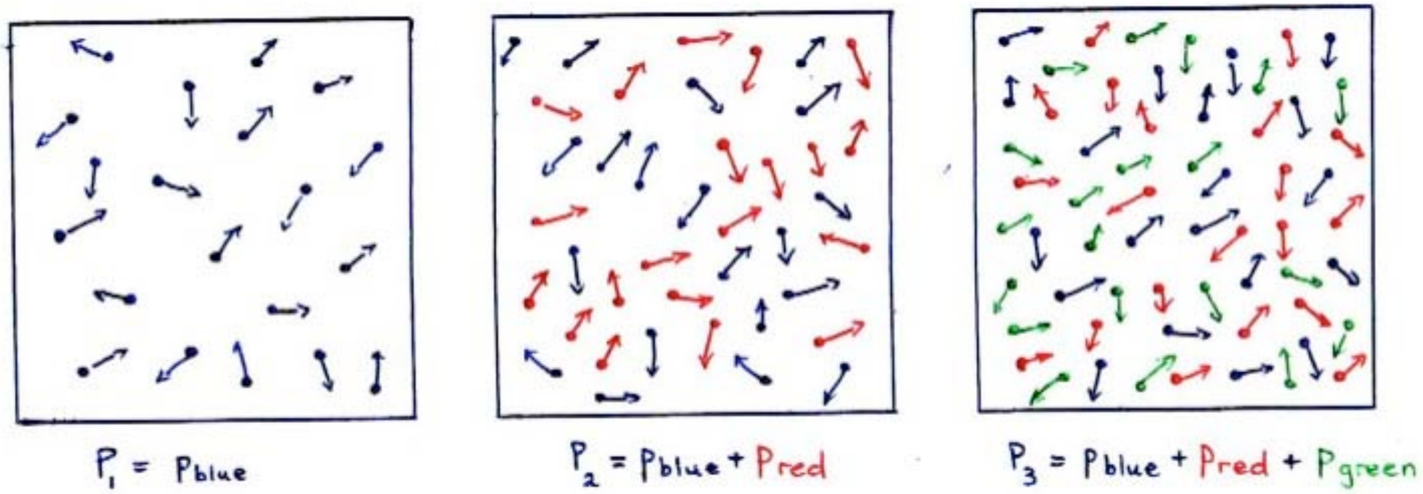
$$\boxed{PV = \frac{2}{3}U} \qquad \textbf{(2.11)}$$

n.b., holds for a monatomic gas only!

we will take this further to link *U* to temperature *T*, and make it universal in coming lectures.

Dalton’s law of partial pressures

- Finally, Dalton’s law, which you may have seen in chemistry, makes great sense from a kinetic theory perspective.



- Dalton’s theory says ‘if one has a mixture of gases in thermal equilibrium, then the total pressure is simply the sum of the pressures due to each component of the mixture’.

But you’d expect this in the figure above. For example in the middle one, you get the same pressure as in the left one due to the blue molecules colliding with the walls, but an added pressure component due to the red molecules as well. In the case above where $n_{blue} = n_{red} = n_{green}$, if all three species have the same mass, then $P_2 = 2P_1$ and $P_3 = 3P_1$.

Radiation pressure

- As a final example, lets consider the ‘pressure’ due to radiation. After all, photons are particles that carry momentum too…

The Earth gets bombarded day & night by sunlight, and this should exert a force of repulsion between the Earth and sun – how big is this force?

The radiation striking the Earth from the sun is about 1300 W/m^2, and the spectral peak wavelength λ = 500nm corresponds to a photon energy of 4×10^{-19}J or 2.5eV, and a momentum per photon of 1.3×10^{-27} kgm/s.

This means that the number of photons striking the Earth per m^2 per second is $1300 / 4 \times 10^{-19} = 3 \times 10^{21}$ photons/m^{2}s.

Hence the total pressure (assuming total absorption, so $\Delta p \sim p$) is $3 \times 10^{21} \times 1.3 \times 10^{-27} \sim 4 \times 10^{-6}$ N/m^2, which doesn’t seem like much. But if we model the Earth as a flat disk with radius 6.4×10^6 m (a sphere looks like a circle after all), then the force exerted by the sunlight is:

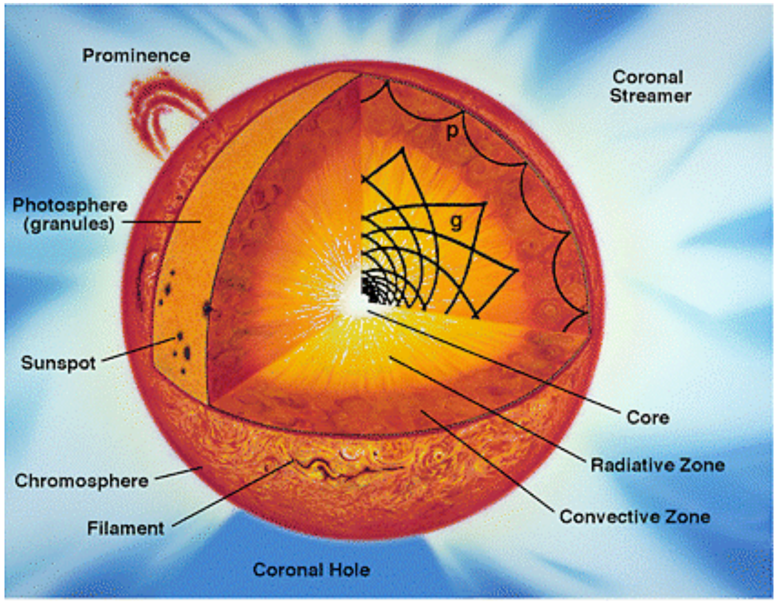
$$F = 4 \times 10^{-6} \times \pi \times (6.4 \times 10^6)^2 = 5 \times 10^8 \text{ N!}$$

So why doesn’t this push the Earth off its orbit?

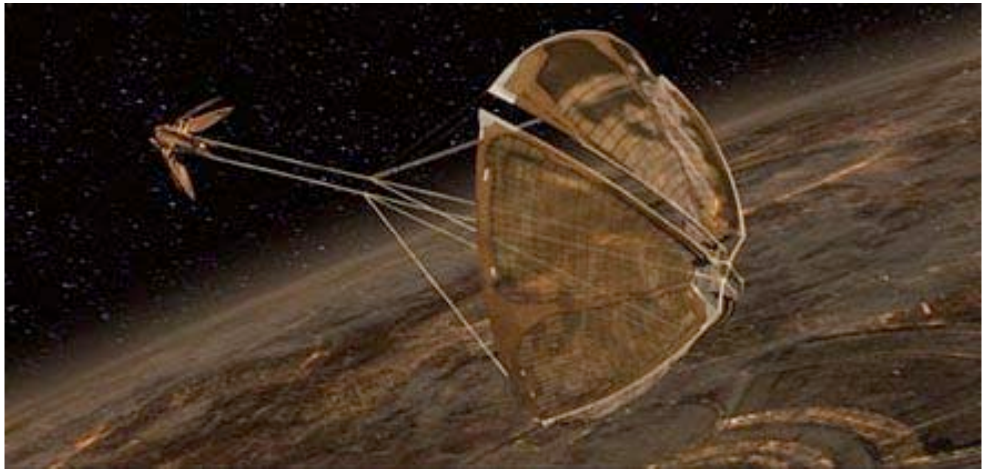
Because the force of gravity is much stronger $F_{grav} = GmM/r^2 = (6.7 \times 10^{-11} \times 6 \times 10^{24} \times 2 \times 10^{30})/(1.5 \times 10^{11})^2 = 3 \times 10^{22}$ N.

Example of radiation pressure

- That might have seemed like a slightly contrived example, but there are some cases where radiation pressure is important/useful.



Radiation pressure is what stops stars from collapsing due to their own gravity, particularly in the radiative zone.



In Star Wars II – Attack of the clones, Count Dooku flys around in a spaceship powered by a solar sail. NASA are also considering this process for real space travel. Can you think of a reason why it might not be very helpful for long distance travel?

Summary

- Pressure in a container is the force per unit area on a surface due to the gas particles colliding with the walls. It depends on the mass & number density of the particles and their velocity component perpendicular to the surface.

- In the thermodynamic limit, the pressure depends on the average velocity of the particles. This average needs to be taken as a root-mean-square average to prevent getting $\langle v_x \rangle = 0$.

- For a monatomic gas, the internal energy U of the gas is the total kinetic energy of the gas. For other gases, U is higher due to energy contributions from other degrees of freedom in the gas particles (e.g., rotation, vibration, etc.)

- Dalton's law of partial pressures says 'if one has a mixture of gases then the total pressure is simply the sum of the pressures due to each component of the mixture'.

- Pressure isn't just restricted to a gas of particles (e.g., air), the same ideas can be adapted to other situations such as a gas of photons, for example.

In the next lecture we will discuss the zeroth law of thermodynamics, how this allows the concept of temperature to be defined, and how temperature is linked to the microscopic properties of a gas.