11/2 Lecture outline

• Gas has lots of particles. Typical densities: $N/V \sim 6\times 10^{26}/22m^3 \sim 3\times 10^{25} m^{-3}$. Inter-particle distance $\sim (V/N)^{1/3} \sim 10^{-8}m$, big compared with molecular sizes – approximately non-interacting point particles.

• Velocity distribution $F(\vec{v})$, with

$$\int F(\vec{v})d^3\vec{v} = 1.$$

$F(\vec{v})d^3\vec{v}$ gives the fraction of particles with velocity in the range between $\vec{v}$ and $\vec{v}+d\vec{v}$. Suppose isotropically random distribution, $F(\vec{v}) = F(v)$, depends only on *speed*, $v = |\vec{v}|$ not on direction of motion. Use spherical coordinates, where $d^3\vec{v} = v^2 \sin\theta d\theta d\phi dv$. Recall $\int \sin\theta d\theta d\phi = 4\pi$. Then fraction of particles with *speed* in range between v and $v + dv$ is $f(v) = F(v)4\pi v^2$. Satisfies $\int_0^\infty f(v)dv = 1$. Use to compute averages

$$\overline{v^n} = \int (\vec{v}\cdot\vec{v})^{n/2} F(\vec{v})d^2\vec{v} = \int_0^\infty v^n f(v)dv.$$

• Consider the flux of particles through a tiny surface, with area element $d\vec{a} = da\hat{n}$. The flux of particles, per area da, per time, passing through this element is given by

$$\frac{N}{V}\int_{\hat{n}\cdot v>0} d^3\vec{v}F(\vec{v})\hat{n}\cdot\vec{v} = \frac{N}{4\pi V}\int_0^\infty dv\int_0^1 dx\int_0^{2\pi} d\phi(xvf(v)) = \frac{1}{4}\frac{N}{V}\overline{v}.$$

In the first expression, we use the fact that only particles with $\hat{n}\cdot v > 0$ pass through the area element – the others travel away. In the 2nd expression, we define $x \equiv \cos\theta = \hat{v}\cdot\hat{n}$ (where $\vec{v} = v\hat{v}$), and the fact that only particles with $x > 0$ pass through the area element (which is why the x integral doesn't go from -1 to $+1$) – the particles with $x > 0$ travel toward the area element, and those with $x < 0$ travel away.

• The momentum imparted to area da, per unit area, per unit time – i.e. the normal outward pressure – is similar to the flux, but with an extra factor of $(2m\vec{v}\cdot\hat{n})$, coming from the fact that a particle which bounces off a wall reverses its normal momentum, and thus imparts this momentum transfer or impulse to the wall.

$$P = \frac{N}{V}\int_{\hat{n}\cdot v>0} d^3\vec{v}F(\vec{v})2m(\hat{n}\cdot\vec{v})^2 = \frac{N}{2\pi mV}\int_0^\infty dv\int_0^1 dx\int_0^{2\pi} d\phi(x^2v^2f(v)) = \frac{1}{3}\frac{N}{V}m\overline{v^2}.$$

We thus have

$$PV = \frac{2}{3}\overline{U},$$

where $\overline{U} = N\frac{1}{2}m\overline{v^2}$ is the average total kinetic energy. Hey, we've seen this before! Ideal monatomic gas: $PV = nRT$, $U = C_V T = \frac{3}{2}nRT$. If we eliminate T, we get $PV = \frac{2}{3}U$. To complete the connection, we need to understand why

$$\overline{U} = N\tfrac{1}{2}m\overline{v^2} = \frac{3}{2}nRT \qquad \text{i.e. why} \quad \tfrac{1}{2}m\overline{v^2} = \frac{3}{2}kT,$$

where we use $n = N/N_A$ and $k = R/N_A$, with $N_A = 6.02 \times 10^{26}$ particles per kilomole. We can extend this to diatomic and other ideal gases - then we have seen that

$$\overline{U} = N\frac{f}{2}kT,$$

where f is the number of degrees of freedom. This last expression is called equipartition of energy.

• Plug in some numbers: at room temperature, $\frac{3}{2}kT \approx 6 \times 10^{-21}J$. Mass of e.g. O_2 molecule is $m = 32 \times 1.66 \times 10^{-27}kg$, so $v_{rms} \approx 480m/s$. Pretty fast! Note $v_{sound} \approx 340m/s$. Makes sense: sound waves can't travel faster than the molecules themselves.

• Now let's figure out what $F(\vec{v})$ is. Argue it should be of the gaussian normal distribution form:

$$F(\vec{v}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha\vec{v}^2),$$

where α is a constant, and the normalization factor ensures $\int F(\vec{v})d^3\vec{v} = 1$. With this distribution, we easily compute $\overline{v^2} = 3/2\alpha$ - this sets the size of the standard deviation of the probability distribution. To get our desired relation, $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$, we see that we need the probability distribution to have $\alpha = m/2kT$, i.e.

$$F(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-\tfrac{1}{2}m\vec{v}^2/kT),$$

This is the Maxwell-Boltzman velocity distribution. It is sharply peaked around $\vec{v}$ when T is small, and becomes a very broad distribution when T is large. This fits with our intuition: larger T means more jiggling of the molecules.

• Mean speed: $\overline{v} = \int_0^\infty vf(v)dv = \sqrt{8kT/\pi m}$. $\overline{v}^2 = \int_0^\infty v^2 f(v)dv = 3kT/m$, so $v_{RMS} = \sqrt{3kT/m}$. Most probable speed: $f(v)$ is a maximum at $v_{m.p.} = \sqrt{2kT/m}$.