

11/15 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

$$\overline{v^n} = \int (\vec{v} \cdot \vec{v})^{n/2} F(\vec{v})d^3\vec{v} = \int_0^\infty v^n f(v)dv.$$

- 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

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

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.

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

We thus have

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

where  $\bar{U} = N\frac{1}{2}m\bar{v}^2$  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

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

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

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

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  $v_{rms} \approx 480 m/s$ . Pretty fast! Note  $v_{sound} \approx 340 m/s$ . Makes sense: sound waves can't travel faster than the molecules themselves.