11/20 Lecture outline

• Last time: 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 $\overline{v^2} = \frac{3}{2}\alpha$ - 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 $v_{m.p.} = \sqrt{2kT/m}$.

• Review gaussian distribution:

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp(-(x-\overline{x})^2/2\sigma^2),$$

where $\overline{x}$ is the mean and σ is the standard deviation. This distribution is common when there are large numbers in the sample. Note that

$$\int_{-\infty}^{\infty}(x-\overline{x})^n p(x) = \begin{cases} \frac{1}{\sqrt{\pi}}2^{n/2}\sigma^n\Gamma(\frac{1}{2}(1+n)) & \text{for } n \text{ even} \\ 0 & \text{for } n \text{ odd} \end{cases} \tag{1}$$

Here $\Gamma(z) \equiv \int_0^\infty t^{z-1}e^{-t}dt$ is the gamma function. By an integration by parts (with $u = t^z$ and $dv = e^{-t}dt$), you can show the gamma function satisfies the interesting property: $\Gamma(z+1) = z\Gamma(z)$. From this, it follows that $\Gamma(n) = (n-1)!$ for integer n, so the gamma function is sometimes called the factorial function. Also, find $\Gamma(1/2) = \sqrt{\pi}$ (and then $\Gamma(z+1) = z\Gamma(z)$ gives e.g. $\Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$). The above Eqn. (1) follows upon setting $t = (x-\overline{x})^2/2\sigma^2$ for n even (the integral clearly vanishes for n odd, since it's then an odd function of $\Delta x \equiv x - \overline{x}$, integrated over a range symmetric around $\Delta x = 0$).

In particular, the $n = 0$ case of Eqn. (1) gives $\int_{-\infty}^{\infty} p(x)dx = 1$, so $p(x)$ is correctly normalized. The $n = 1$ case of Eqn. (1) shows that $\int_{-\infty}^{\infty} xp(x) = \overline{x}$, so the $\overline{x}$ in $p(x)$ is indeed the mean value of x. The $n = 2$ case of (1) gives, upon defining $\Delta x \equiv x - \overline{x}$, $\overline{\Delta x^2} = \overline{x^2} - (\overline{x})^2 = \sigma^2$. This shows how σ, which is the "standard deviation" sets the width of the gaussian distribution. We can write $\Delta x_{RMS} \equiv \sqrt{\overline{\Delta x^2}} = \sigma$.

• The Maxwell-Boltzmann velocity distribution

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

is a product of gaussian distributions $F(\vec{v}) = p(v_x)p(v_y)p(v_z)$, each with zero mean, $\overline{v_x} = \overline{v_y} = \overline{v_z} = 0$ and standard deviation $\sigma = \sqrt{kT/m}$, so $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = kT/m$, which is the average energy equi-partition statement, $\overline{\frac{1}{2}mv_x^2} = \frac{1}{2}kT$ etc. So $v_{RMS} = \sqrt{\overline{v^2} - \overline{v}^2} = \sqrt{3kT/m}$. Also mean speed $\overline{v} = \int_0^\infty v(4\pi v^2)F(v)dv = \sqrt{8kT/\pi m}$. Most probable speed: $F(v)4\pi v^2$ is a maximum at $f(v)$ is a maximum at $v_{m.p.} = \sqrt{2kT/m}$.

• Write the Maxwell-Boltzman velocity distribution as an energy distribution: define $\epsilon \equiv \frac{1}{2}mv^2$ and define $p(\epsilon)d\epsilon = p(v)dv = 4\pi F(v)v^2dv$. Using $d\epsilon = mvdv$ and our expression for $F(v)$, and then writing v in terms of ϵ, this gives the energy distribution

$$p(\epsilon)d\epsilon = 2\pi^{-1/2}(kT)^{-3/2}\exp(-\epsilon/kT)\epsilon^{1/2}d\epsilon$$

which is the fraction of particles with energy in the range from ϵ to $\epsilon + d\epsilon$. It is properly normalized, as $\int_0^\infty p(\epsilon)d\epsilon = 1$.

- Effusion out of a hole in a box. Replace

$$f(v_z) \to \tilde{f}(v_z) = \begin{cases} const.p(v_z)v_z & \text{for } v_z > 0 \\ 0 & \text{for } v_z < 0 \end{cases} .$$

Gives

$$\begin{aligned} \overline{v_z^2} &= \int_0^\infty v_z^2 \exp(-\tfrac{1}{2}mv_z^2/kT)v_z dv_z / \int_0^\infty \exp(-\tfrac{1}{2}mv_z^2/kT)v_z dv_z \\ &= \tfrac{1}{2}(2kT/m)^2/\tfrac{1}{2}(2kT/m) = 2kT/m \end{aligned},$$

(using $\int_0^\infty \exp(-ax^2)x^n dx = \frac{1}{2}a^{-(n+1)/2}\Gamma(\frac{1}{2}(n+1))$), vs. $\overline{v_x^2} = \overline{v_y^2} = kT/m$. Doesn't satisfy equi-partition, and now $\overline{\epsilon} = 2kT$ - it's increased. Eventually recover equipartition, thanks to interactions. Equipartition is the most likely state. Effusion can be used to separate molecules of different masses, as lighter ones are more likely to effuse out the hole, as seen from the flux $\Phi = N\overline{v}/4V = P/\sqrt{2\pi mkT}$.