Week 3, Meeting 1 Solutions

GSI: Caleb Eades

9/6

1 More Statistics

1.1 Continuous vs Discrete

(a) First, we solve for A:

$$\begin{aligned}\int_0^\infty f(v)dv &= \int_0^1 f(v)dv \\ &= A\int_0^1 sin(\pi v)|_0^1 \\ &= \frac{-A}{\pi}cos(\pi v)|_0^1 \\ &= \frac{2A}{\pi}\end{aligned}$$

We mush have $\int_0^\infty f(v)dv = 1$, so $A = \frac{\pi}{2}$. Now, solving for B:

$$\begin{aligned}P(v = 0) + P(v = 1/4) + P(v = 1/2) + P(v = 3/4) + P(v = 1) &= 1 \\ 0 + B/\sqrt{2} + B + B/\sqrt{2} + 0 &= 1 \\ B(1 + \sqrt{2}) &= 1 \\ B &= \frac{1}{1+\sqrt{2}}\end{aligned}$$

For the quesiton of units, A has units of seconds/meter, B is unitless, and π has units of seconds/meter. If this last one confuses you, you could equivalently have a "ghost" one in there with units of seconds/meter and let π be unitless.

(b) For each distribution, we calculate $< v >= \bar{v}$, v_{rms}, σ, and v_p. Starting with A:

$$\begin{aligned}
< v > &= \int_0^\infty vf(v)dv \\
&= \int_0^1 \frac{\pi}{2} vsin(\pi v)dv \\
&= \frac{\pi}{2}\left[\frac{-v}{\pi}cos(\pi v)|_0^1 + \int_0^1 \frac{1}{\pi}cos(\pi v)dv\right] \\
&= \frac{1}{2}\left[-vcos(\pi v) + \frac{1}{\pi}sin(\pi v)|0^1\right] \\
&= \frac{1}{2}m/s
\end{aligned}$$

$$\begin{aligned}
< v^2 > &= \int_0^\infty v^2 f(v)dv \\
&= \int_0^1 \frac{\pi}{2} v^2 sin(\pi v)dv \\
&= \frac{\pi}{2}\left[\frac{-v^2}{\pi}cos(\pi v)|_0^1 + \int_0^1 \frac{2}{\pi}vcos(\pi v)dv\right] \\
&= \frac{-v^2}{2}cos(\pi v)|_0^1 + \frac{v}{\pi}sin(\pi v) + \frac{1}{\pi^2}cos(\pi v)|_0^1 \\
&= \frac{1}{2} - \frac{2}{\pi^2} \\
&= \frac{\pi^2 - 4}{2\pi^2} \\
&\approx 0.30m^2s^{-2}
\end{aligned}$$

$$\begin{aligned}
\sigma &= \sqrt{< v^2 > - < v >^2} \\
&= \sqrt{\frac{1}{2} - \frac{2}{\pi^2} - \frac{1}{4}} \\
&= \sqrt{\frac{1}{4} - \frac{2}{\pi^2}} \\
&= \frac{1}{2\pi}\sqrt{\pi^2 - 8} \\
&\approx 0.22m/s
\end{aligned}$$

Lastly, taking derivatives and finding the local maximum between 0 and 1:

$$f'(v) = \frac{\pi^2}{2}cos(\pi v) \implies v_p = \frac{1}{2}m/s \tag{1}$$

where this can be verified with a second derivative test if you want. Now, for B, we do the same thing in the discrete case:

$$\begin{aligned} < v > &= \frac{1}{1+\sqrt{2}}\left(\frac{1}{\sqrt{2}}\frac{1}{4} + \frac{1}{\sqrt{2}}\frac{3}{4} + \frac{1}{2}\right) \\ &= \frac{1}{1+\sqrt{2}}\left(\frac{1}{\sqrt{2}} + \frac{1}{2}\right) \\ &= \frac{1}{1+\sqrt{2}}\frac{1+\sqrt{2}}{2} \\ &= \frac{1}{2}m/s \end{aligned}$$

$$\begin{aligned} < v^2 > &= \frac{1}{1+\sqrt{2}}\left(\frac{1}{\sqrt{2}}\frac{1}{16} + \frac{1}{\sqrt{2}}\frac{9}{16} + \frac{1}{4}\right) \\ &= \frac{1}{1+\sqrt{2}}\frac{5+2\sqrt{2}}{8\sqrt{2}} \\ &\approx 0.29m^2s^{-2} \end{aligned}$$

$$\begin{aligned} \sigma &= \sqrt{< v^2 > - < v >^2} \\ &\approx 0.19m/s \end{aligned}$$

Lastly, $v_p = \frac{1}{2}$ m/s since it is simply the speed with the highest probability.

(c) A:

$$\begin{aligned} < v^2 > &= 3\frac{k}{m}T \\ T &= \frac{m}{3k} < v^2 > \\ &\approx \frac{1}{10}\frac{m}{k}(m^2s^{-2}) \end{aligned}$$

B:

$$T = \frac{m}{3k} < v^2 > \approx 0.096\frac{m}{k}(m^2s^{-2}) \tag{2}$$

(d) Even though the discrete distribution was taken from samples of the continuous one, the statistics differe slightly. Nonetheless, for only five samples, the difference are fairly small: $\sigma_A \approx 0.22$ m/s whereas $\sigma_B \approx 0.19$ m/s. Hence, B has a tighter distribution, which makes sense since the tails of A are ignored with the resampling.

In general, you have to be careful with how you resample a continuous distribution to get a discrete spectrum that is more computable (in "real-life" cases where the continuous distribution does not follow a pretty function or is unknown entirely).

1.2 Fun with Maxwell

(1) Method 1 (following pgs. 477-78 of Giancoli): With wall collisions, $\Delta(mv) = 2mv_x$ on the x-direction walls. In a box of dimensions L, the time between collisions in this direction is $\Delta t = 2L/v_x$, so

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{mv_x^2}{L} \tag{3}$$

for the wall's force exerted on a molecule in a collision (averaged). Summing over all the molecules,

$$F_{total} = \frac{m}{L}\left(v_{x1}^2 + \cdot + v_{xN}^2\right) \tag{4}$$

Mulitplying by N/N and noting that $\bar{v_x^2} = \frac{v_{x1}^2 + \cdot + v_{xN}^2}{N}$, we have

$$F = \frac{m}{L} N \bar{v_x^2} \tag{5}$$

Now, $\bar{v^2} = 3\bar{v_x^2}$, so with $P = \frac{F}{A} = \frac{F}{L^2}$, we have

$$P = \frac{1}{3}\frac{Nm\bar{v^2}}{L^3} = \frac{1}{3}\frac{Nm\bar{v^2}}{V} \tag{6}$$

Rearranging, $PV = \frac{2}{3}N\left(\frac{1}{2}m\bar{v^2}\right)$. From the Ideal Gas Law, $PV = NkT$, so

$$\frac{2}{3}E = kT \implies E = <\frac{1}{2}m\bar{v^2}> = \frac{3}{2}kT \tag{7}$$

(2) Method 2 (from the Maxwell distribution): Using $f(v)$ from the Maxwell distribution and $< v^2 > = \int_0^\infty v^2 f(v)dv$, we have

$$< v^2 > = \int_0^\infty Av^4 e^{-Bv^2} dv \tag{8}$$

where $A = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}$ and $B = \frac{1}{2}\frac{m}{kT}$. Observe that

$$v^4 e^{-Bv^2} = \frac{d^2}{dB^2}\left(e^{-Bv^2}\right) \tag{9}$$

So we can use this to rewrite (and using the formula for the integral of a Gaussian on the second step)

$$\begin{aligned}
< v^2 > &= A\frac{d^2}{dB^2}\int_0^\infty e^{-Bv^2} dv \\
&= A\frac{d^2}{dB^2}\left(\frac{1}{2}\sqrt{\frac{\pi}{B}}\right) \\
&= \frac{1}{2}\sqrt{\pi}\frac{-1}{2}\frac{-3}{2}B^{-5/2} \\
&= \frac{3\sqrt{\pi}}{8}AB^{-5/2}
\end{aligned}$$

Plugging in the constants again,

$$\begin{aligned} < v^2 > &= \frac{3\sqrt{\pi}}{8} \times 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \times \left(\frac{1}{2}\frac{m}{kT}\right)^{-5/2} \\ &= 3\left(\frac{m}{kT}\right)^{3/2}\left(\frac{kT}{m}\right)^{5/2} \\ &= 3\frac{kT}{m} \end{aligned}$$

Hence,

$$< \frac{1}{2}mv^2 >= \frac{3}{2}kT \tag{10}$$

2 Gases: Ideal, Real and van der Waals

2.1 Conceptual Questions

(a) Average velocity is zero but speed looks at the magnitude (some move left and some move right, for example). So overall while average speed is nonzero, average velocity will be.

(b) We can infer that there is less inter-molecular bonding since there is a lower "escape velocity" for the alcohol.

2.2 Escape Velocities

First off, in a Maxwell Distribution,

$$\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \approx 1.60\sqrt{\frac{kT}{m}} \tag{11}$$

(a) Solving for T,

$$\begin{aligned} T &= \frac{m\pi}{8k}\bar{v}^2 \\ &= \frac{(2 * 16 * 1.66 \times 10^{-27} kg)\pi}{8(1.38 \times 10^{-23} J/K)}(1.12 \times 10^4 m/s)^2 \\ &\approx 1.9 \times 10^5 K \end{aligned}$$

(b) $m_{He} = \frac{1}{8} m_{O_2}$, so

$$T_{He} = \frac{1}{8} T_{O_2} \approx 2.4 \times 10^4 K \tag{12}$$

(c) At the same temperature, He will go much faster than O_2, so more of it will escape, leaving the O_2 concentration much higher than He.

2.3 Fermi-ish Validation of Ideal Gas Law

Starting with the Ideal Gas Law,

$$\begin{aligned} PV &= nRT \\ n &= \frac{PV}{RT} \\ &\approx \frac{(1 \times 10^5 Pa)(100 m^3)}{(10 J mol^{-1} K^{-1})(300K)} \\ &\approx \frac{1}{3} \times 10^4 mol \\ &\approx 3 \times 10^3 mol \end{aligned}$$

Now, looking at the volume fo the gas,

$$\begin{aligned} V_{gas} &= \frac{4}{3}\pi(1.5 \times 10^{-10}m)^3(3 \times 10^3 mol)(6.022 \times 10^{23}) \\ &\approx 0.03m^3 \end{aligned}$$

Hence, the ratio of the vlume of a gas particle to the volume of the room is

$$\frac{V_{gas}}{V_{room}} \approx \frac{0.03}{10^3} = 3 \times 10^{-5} \tag{13}$$

As we can see, the gas molecules take up less that three parts per hundred thousand in volume. So the Ideal Gas Law is a decent approximation.

2.4 Reformulation of Pressure

From the Ideal Gas Law and the average kinetic energy of a molecule, $PV = NkT$ and $\frac{1}{2}mv^2 = \frac{3}{2}kT$, respectively. Identifying $< v^2 >= v_{rms}^2$,

$$v_{rms}^2 = \frac{3kT}{m} = 3\frac{PV/N}{m} \tag{14}$$

At this point, it is usefull to recall that m is the mass of a single molecule, so $mN = M$ is the total mass of the gas and hence $\frac{mN}{V} = \frac{M}{V} = \rho$, the density. Putting this together,

$$v_{rms}^2 = 3\frac{P}{\rho} \implies v_{rms} = \sqrt{3P/\rho} \tag{15}$$

2.5 Pressure from Other Things

Assuming they collide elastically with the window, the total change in momentum is $2mv_x$, with $v_x = \sqrt{2}v/2$. Then,

$$\begin{aligned} P &= F/A \\ &= \frac{\Delta p}{\Delta t}/A \\ &= \frac{2\sqrt{2}vm}{2} \times \left(30\frac{1}{second}\right)/A \end{aligned}$$

where we have identified $\frac{1}{\Delta t}$ as the number of molecules that hit the window per second. So

$$\begin{aligned} P &= \frac{2 * 15 * 2 \times 10^{-3}}{\sqrt{2}} \times 30/(0.5) \\ &\approx 2.6Nm^{-2} \end{aligned}$$

This is about five orders of magnitude weaker than atmospheric pressure of 1 atm $\approx 1 \times 10^5 Nm^{-2}$.