

Week 3, Meeting 1 Solutions

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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 must 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 question 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 $\langle v \rangle = \bar{v}$, v_{rms} , σ , and v_p . Starting

with A :

$$\begin{aligned}
\langle v \rangle &= \int_0^\infty v f(v) dv \\
&= \int_0^1 \frac{\pi}{2} v \sin(\pi v) dv \\
&= \frac{\pi}{2} \left[\frac{-v}{\pi} \cos(\pi v) \Big|_0^1 + \int_0^1 \frac{1}{\pi} \cos(\pi v) dv \right] \\
&= \frac{1}{2} \left[-v \cos(\pi v) + \frac{1}{\pi} \sin(\pi v) \Big|_0^1 \right] \\
&= \frac{1}{2} m/s
\end{aligned}$$

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

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

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

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

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:

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

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

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

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

(c) A:

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

B:

$$T = \frac{m}{3k} \langle v^2 \rangle \approx 0.096 \frac{m}{k} (m^2 s^{-2}) \quad (2)$$

- (d) Even though the discrete distribution was taken from samples of the continuous one, the statistics differ 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

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

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

$$F_{total} = \frac{m}{L} (v_{x1}^2 + \dots + v_{xN}^2) \quad (4)$$

Multiplying by N/N and noting that $\bar{v}_x^2 = \frac{v_{x1}^2 + \dots + v_{xN}^2}{N}$, we have

$$F = \frac{m}{L} N \bar{v}_x^2 \quad (5)$$

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

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

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

$$\frac{2}{3}E = kT \implies E = \frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT \quad (7)$$

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

$$\langle v^2 \rangle = \int_0^\infty Av^4 \exp -Bv^2 dv \quad (8)$$

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

$$v^4 \exp -Bv^2 = \frac{d^2}{dB^2} (\exp -Bv^2) \quad (9)$$

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

$$\begin{aligned} \langle v^2 \rangle &= A \int_0^\infty v^4 \exp -Bv^2 dv \\ &= A \int_0^\infty \frac{d^2}{dB^2} (\exp -Bv^2) dv \\ &= \frac{1}{2} \sqrt{\pi} \frac{-1}{2} \frac{-3}{2} B^{-5/2} \\ &= \frac{3\sqrt{\pi}}{8} AB^{-5/2} \end{aligned}$$

Plugging in the constants again,

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

Hence,

$$\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} kT \tag{10}$$

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,

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

- (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

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

- (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,

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

Now, looking at the volume for the gas,

$$\begin{aligned} V_{gas} &= \frac{4}{3}\pi(3 \times 10^{-10}m)^3(3 \times 10^3mol)(6.022 \times 10^{23}) \\ &\approx 1 \times 10^{-4}m^3 \end{aligned}$$

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

$$\frac{V_{gas}}{V_{room}} \approx \frac{10^{-4}}{10^3} = 10^{-7} \quad (13)$$

As we can see, the gas molecules take up less than one part per billion 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 $\langle v^2 \rangle = v_{rms}^2$,

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

At this point, it is useful 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,

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

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 $\approx 1 \times 10^5 Nm^{-2}$.