Assignment #3 - Solutions

1. (6.5 in text)

a) We let $g(\theta) = \cos\theta \sin\theta$. Now, the average of $\cos\theta$ is thus,

$$\langle\cos\theta\rangle = \frac{\int_0^{\pi/2} \cos\theta\, g(\theta)d\theta}{\int_0^{\pi/2} g(\theta)d\theta} = \frac{\int_0^{\pi/2} \cos^2\theta \sin\theta d\theta}{\int_0^{\pi/2} \cos\theta\sin\theta d\theta}$$

Let $u = \cos\theta$, $du = -\sin\theta d\theta$, and our integration range changes from $[0, \pi/2]$ to $[1, 0]$, so,

$$\langle\cos\theta\rangle = \frac{\int_0^1 u^2 du}{\int_0^1 u du} = \frac{u^3/3|_0^1}{u^2/2|_0^1} = \frac{2}{3}$$

b) The kinetic energy is,

$$E_K = \frac{1}{2} m v^2$$

and we know that,

$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_BT}}$$

The average kinetic energy of all molecules is then,

$$\langle E_K\rangle_{TOT} = \langle\tfrac{1}{2}mv^2\rangle = \int_0^\infty \frac{1}{2}mv^2 f(v)dv = \frac{1}{2}m\langle v^2\rangle = \frac{m}{2}v_{rms}^2$$

We already know that $v_{rms} = \sqrt{3k_BT/m}$ so,

$$\langle E_k\rangle_{TOT} = \frac{m}{2}v_{rms}^2 = \frac{3}{2}k_BT$$

For the molecules that hit the surface we have,

$$\langle E_k\rangle_{surf} = N\int_0^\infty E_k\, v f(v)dv$$, extra factor of v is from part a)

The factor of N appears as we now have to renormalize for the distribution $vf(v)$ instead of v. N is easy to find, since,

$$\frac{1}{N} = \int_0^\infty v f(v) dv = \langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}}$$

Thus,

$$\begin{aligned}\langle E_K \rangle_{surf} &= \sqrt{\frac{\pi m}{8k_BT}} \int_0^\infty E_K v f(v) dv \\ &= \sqrt{\frac{\pi m}{8k_BT}} \cdot \frac{1}{2} m \cdot \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_BT}\right)^{3/2} \int_0^\infty v^5 e^{-mv^2/2k_BT} dv \\ &= m\left(\frac{m}{2k_BT}\right)^2 \int_0^\infty v^5 e^{-mv^2/2k_BT} dv\end{aligned}$$

To solve this use the following result from Appendix C,

$$\int_0^\infty v^{2n+1} e^{-\alpha v^2} dv = \frac{n!}{2\alpha^{n+1}}$$

Here $n=2$, and $\alpha = m/2k_BT$ so,

$$\langle E_K \rangle_{surf} = m\left(\frac{m}{2k_BT}\right)^2 \cdot \left(\frac{m}{2k_BT}\right)^{-3} = 2k_BT$$

Thus we have:

$$\langle E_K \rangle_{TOT} = \frac{3}{2} k_BT$$

$$\langle E_K \rangle_{surf} = 2k_BT$$

2. (7.1 in text)

We want to calculate the pressure needed for a one mono-layer coverage in an hour. The flux needed is thus,

$$\Phi = \frac{10^{19}\ \frac{\text{atoms}}{m^2}}{3600\,s}$$

$$= 2.78\times10^{15}\ m^{-2}s^{-1}$$

Now, the flux is related to pressure via,

$$\Phi = \frac{P}{\sqrt{2\pi m k_B T}}$$

Rearranging for P gives,

$$P = \Phi\sqrt{2\pi m k_B T}$$

We assume the residual gas is N_2 so that,

$$m = \frac{28\ g/mol}{6.02\times10^{23}\ mol^{-1}} = 4.65\times10^{-26}\ kg$$

and, with $T = 25°C = 298K$ we get,

$$P = (2.78\times10^{15} m^{-2}s^{-1})\sqrt{2\pi(4.65\times10^{-26}kg)(1.381\times10^{-23}JK^{-1})(298K)}$$

$$= 3\times10^{-7}\ Pa$$

$$= 3\times10^{-9}\ mbar$$

So the pressure must be kept below 3×10^{-9} mbar.

3. (7.4 in text)

The distribution of molecules effusing through the hole is given by,

$$f_E(v) = N v f(v)$$

We calculated N in the first problem to be,

$$N = 1/\langle v \rangle = \sqrt{\frac{\pi m}{8 k_B T}}$$

So,

$$f_E(v) = \sqrt{\frac{\pi m}{8 k_B T}} \cdot \frac{4}{\sqrt{\pi}} \left(\frac{m}{2 k_B T}\right)^{3/2} v^3 e^{-mv^2/2k_BT}$$

$$= 2\left(\frac{m}{2k_BT}\right)^2 v^3 e^{-mv^2/2k_BT}$$

The mean speed for these molecules is then,

$$\langle v \rangle_E = \int_0^\infty v f_E(v) = 2\left(\frac{m}{2k_BT}\right)^2 \int_0^\infty v^4 e^{-mv^2/2k_BT}$$

We use the result from Appendix C,

$$\int_0^\infty v^{2n} e^{-\alpha v^2} dv = \frac{(2n)!}{n!\, 2^{2n+1}} \sqrt{\frac{\pi}{\alpha^{2n+1}}}$$

Here $n=2$ and $\alpha = m/2k_BT$ so,

$$\langle v \rangle_E = 2\left(\frac{m}{2k_BT}\right)^2 \cdot \frac{4!}{2!\, 2^5} \sqrt{\frac{\pi}{(m/2k_BT)^5}}$$

$$= \frac{3}{4}\sqrt{\pi}\left(\frac{m}{2k_BT}\right)^2\left(\frac{m}{2k_BT}\right)^{-5/2}$$

$$= \frac{3}{4}\sqrt{\frac{2\pi k_BT}{m}}$$

$$= 1.88\sqrt{k_BT/m}$$

The most probable speed is found by setting $dF_E/dv = 0$,

$$0 = \left.\frac{dF_E}{dv}\right|_{v_{mp}} = 2\left(\frac{m}{2k_BT}\right)^2\left[\frac{d}{dv}v^3 e^{-mv^2/2k_BT}\right]\Bigg|_{v=v_{mp}}$$

$$= 2\left(\frac{m}{2k_BT}\right)^2\left[3v^2 e^{-mv^2/2k_BT} + v^3\left(\frac{-2mv}{2k_BT}\right)e^{-mv^2/2k_BT}\right]\Bigg|_{v=v_{mp}}$$

$$= 2\left(\frac{m}{2k_BT}\right)^2 e^{-mv^2/2k_BT}\left[3v^2 - \frac{mv^4}{k_BT}\right]\Bigg|_{v=v_{mp}}$$

Divide each side by $2\left(\frac{m}{2k_BT}\right)^2 e^{-mv^2/2k_BT}\, v^2$ to get,

$$0 = 3 - \frac{mv_{mp}^2}{k_BT}$$

or,

$$v_{mp} = \sqrt{\frac{3k_BT}{m}}$$

$$= 1.73\sqrt{\frac{k_BT}{m}}$$

Thus we have found for molecules effusing through a hole,

$$\langle v \rangle_E = \sqrt{\frac{9\pi}{8}} \cdot \sqrt{\frac{k_BT}{m}} = 1.88\sqrt{\frac{k_BT}{m}}$$

$$v_{mp} = \sqrt{3}\sqrt{\frac{k_BT}{m}} = 1.73\sqrt{\frac{k_BT}{m}}$$

Obviously $\langle v \rangle$ is the larger of the two.

4. (8.1 in text)

For N_2 we have,

$$m = \frac{28\,g/mol}{6.02\times10^{23}\,mol^{-1}} = 4.65\times10^{-26}\,kg$$

$$d = 0.37\,nm$$

$$\sigma = \pi d^2 = 0.43\,nm^2 = 0.43\times10^{-18}\,m^2$$

The mean speed is (assuming room temp.),

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8(1.381\times10^{-23}\,J/K)(298K)}{\pi(4.65\times10^{-26}\,kg)}} = 475\,m/s$$

The number density of molecules is given by IGL,

$$n = \frac{P}{k_BT}$$

So, we have the mean free path as,

$$\lambda = \frac{1}{\sqrt{2}\,n\sigma} = \frac{k_BT}{\sqrt{2}\,P\sigma} = \frac{(1.381\times10^{-23}\,J/K)(298K)}{\sqrt{2}\,(1\times10^{-8}\,Pa)(0.43\times10^{-18}\,m^2)} = 6.8\times10^5\,m$$

The collision time is,

$$\tau = \frac{\lambda}{\langle v\rangle} = \frac{6.8\times10^5\,m}{475\,m/s} = 1.4\times10^3\,s = 24\,min$$

The mean free path is $6.8\times10^5\,m / 0.5\,m \approx 10^6$ times bigger than the chamber dimensions, so, on average the molecules will collide about 10^6 more times with the walls than other atoms.

Since λ and τ are inversely proportional to P, increasing P by 10^4 decreases λ and τ by 10^4.

5. (8.2 in text)

The probability of a molecule travelling a distance x is given by,
$$P(x) = \frac{1}{\lambda} e^{-x/\lambda}$$
a)
The rms free path is given by,
$$\langle x^2 \rangle = \int_0^\infty \frac{x^2}{\lambda} e^{-x/\lambda} dx = \frac{1}{\lambda} \int_0^\infty x^2 e^{-x/\lambda} dx$$
$$= \cancel{-x^2 e^{-x/\lambda} \Big|_0^\infty} + 2 \int_0^\infty x e^{-x/\lambda} dx$$
$$= \cancel{-2x\lambda e^{-x/\lambda} \Big|_0^\infty} + 2\lambda \int_0^\infty e^{-x/\lambda} dx$$
$$= -2\lambda^2 e^{-x/\lambda} \Big|_0^\infty$$
$$= 2\lambda^2$$

So,
$$x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{2}\,\lambda$$

b) Normally, we would set $dP/dx = 0$, however, since $e^{-x/\lambda}$ decreases as x increases, the most probable value of x is clearly 0.

c) The percentage of molecules travelling greater than y is,
$$P(x>y) = \int_y^\infty P(x) dx = \frac{1}{\lambda} \int_y^\infty e^{-x/\lambda} dx = -e^{-x/\lambda} \Big|_y^\infty$$
$$= e^{-y/\lambda}$$
So, the probabilities are,

i) $P(x>\lambda) = e^{-1} = 37\%$

ii) $P(x>2\lambda) = e^{-2} = 14\%$

iii) $P(x>3\lambda) = e^{-3} = 5\%$

6.

We have the following:

\# density, $n = 1\ \text{cm}^{-3} = 10^6\ \text{m}^{-3}$

molecular diameter, $d = 10^{-10}\ \text{m}$

Temperature, $T = 10\ \text{K}$

a) The mean free path is,

$$\lambda = \frac{1}{\sqrt{2}\, n\sigma} = \frac{1}{\sqrt{2}\, n \pi d^2} = \frac{1}{\sqrt{2}\,(10^6\ \text{m}^{-3})\,\pi\,(10^{-10}\ \text{m})^2}$$
$$= 2.3\times 10^{13}\ \text{m}$$

b) The mass of H_2 is $m = 2\ \text{g/mol} / 6.02\times10^{23}\ \text{mol}^{-1} = 3.3\times10^{-27}\ \text{kg}$
so,

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8(1.381\times10^{-23}\ \text{J/K})(10\ \text{K})}{\pi\,(3.3\times10^{-27}\ \text{kg})}}$$
$$= 325\ \text{m/s}$$

The mean collision time is,

$$\tau = \frac{\lambda}{\langle v\rangle} = 7.1\times10^{10}\ \text{s}$$
$$\approx 2000\ \text{yrs}$$

The collision frequency is thus,

$$f = \frac{1}{\tau} = \frac{1}{2000\ \text{yrs}} = 5\times10^{-4}\ \text{yr}^{-1}$$