Chem 30324, Spring 2025, Homework 2

Due: January 31, 2025

Problem 1. Gases on a table top

In class we derived the properties of a 3-dimensional gas from the Boltzmann distribution and three postulates, and you studied a 1-dimensional gas in Homework 1. Suppose you were interested instead in a 2-dimensional gas, for example gas molecules able to freely skate around on a surface but that couldn't escape the surface.

1. Derive the Maxwell-Boltzman speed distribution for a 2-dimensional gas. (*Hint*: Think polar coordinates.)

In a one-dimensional plane, we know that

$$P(v_x)\, dv_x = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{1}{2}m\frac{v_x^2}{kT}\right) dv_x \tag{1}$$

From a Cartesian coordinate system, we have

$$v^2 = v_x^2 + v_y^2 \tag{2}$$

Thus, the joint probability distribution is given by:

$$P(v_x, v_y)\, dv_x dv_y = P(v_x)P(v_y)\, dv_x dv_y \tag{3}$$

$$= \frac{m}{\pi kT}\exp\left(-m\frac{v_x^2 + v_y^2}{2kT}\right) dv_x dv_y \tag{4}$$

We convert to a polar coordinate system (dv(x)dv(y) = v dv d(theta)):

$$P(v) = \int_0^{2\pi} \frac{mv}{2\pi kT}\exp\left(-\frac{mv^2}{2kT}\right) d\theta \tag{5}$$

$$= 2\pi v \times \frac{m}{2\pi kT}\exp\left(-\frac{mv^2}{2kT}\right) \tag{6}$$

$$= \frac{mv}{kT}\exp\left(-\frac{mv^2}{2kT}\right) \tag{7}$$

2. Plot this 2-dimensional speed distribution for O_2 molecules at 200, 400 and 600 K.

In [ ]:
```python
# Constants
m = 32 * 1.6605e-27  # kg (assuming Oxygen molecule O2)
k = 1.38e-23  # J/K

# Function defining Maxwell-Boltzmann speed distribution in 2D
def Probability(v, T):
    return v * (m / (T * k)) * np.exp(-m * v * v / (2 * k * T))

# Generate velocity values
v = np.linspace(0, 1500, 1000)

# Plot for different temperatures
plt.figure()
for T in [200, 400, 600]:
    Prol = Probability(v, T)
    plt.plot(v, Prol, label='{} K'.format(T))

# Labels and legend
plt.legend()
plt.xlabel('Speed (m/s)')
plt.ylabel('Probability')
plt.title('Maxwell-Boltzmann Speed Distribution in 2D')

plt.show()
```
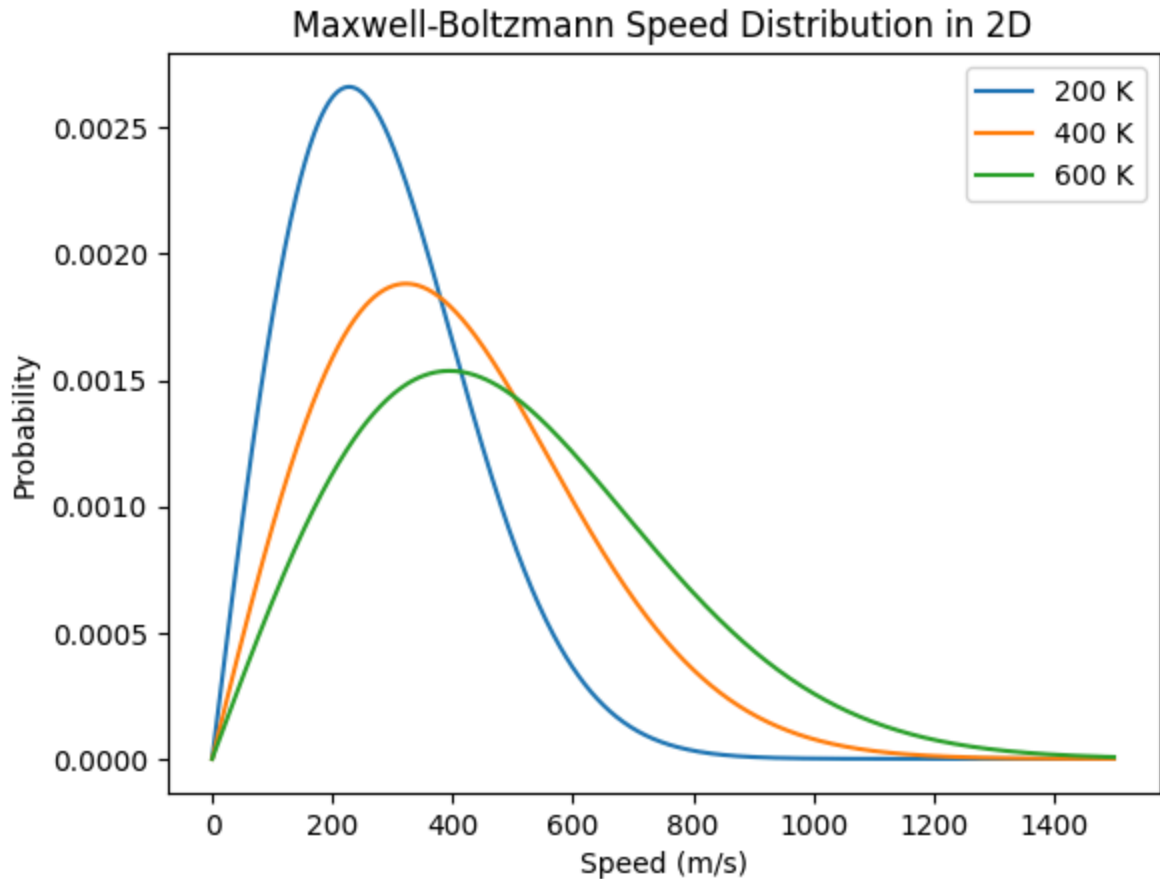
Maxwell-Boltzmann Speed Distribution in 2D

3. Calculate the mean (expected value) of the speed of a 2-dimensional gas of molecules. How does your answer compare to a 3-dimensional gas?

From class, we have

$$\langle v \rangle = \int_0^\infty P(v) \cdot v \, dv \qquad (8)$$

We plug into the equation to get (\langle v \rangle), which is the mean velocity:

$$\langle v \rangle = \int_0^\infty \frac{v^2 m}{kT} \exp\left(-\frac{mv^2}{2kT}\right) dv \qquad (9)$$

Using a substitution,

$$u^2 = \frac{mv^2}{2kT} \qquad (10)$$

$$2u \, du = \frac{mv}{kT} dv \qquad (11)$$

$$dv = \frac{kT}{mv} \cdot 2u \, du \qquad (12)$$

Substituting, we obtain:

$$\langle v \rangle = \int_0^\infty \frac{v^2 m}{kT} \exp(-u^2) \cdot \frac{kT}{mv} \cdot 2u \, du \tag{13}$$

Simplifying, it becomes:

$$\langle v \rangle = \int_0^\infty 2uv \cdot u \exp(-u^2) \, du \tag{14}$$

Since

$$v = u \left(\frac{2kT}{m} \right)^{\frac{1}{2}} \tag{15}$$

we substitute:

$$\langle v \rangle = \left(\frac{2kT}{m} \right)^{\frac{1}{2}} \int_0^\infty 2u^2 \exp(-u^2) \, du \tag{16}$$

Since

$$\int_0^\infty 2u^2 \exp(-u^2) \, du = \frac{\sqrt{\pi}}{2} \tag{17}$$

we obtain:

$$\langle v \rangle = \left(\frac{\pi kT}{2m} \right)^{\frac{1}{2}} \tag{18}$$

compared to the square root of the 3-D gas, they are all dependent on the square root of T/m. it's expected to be bigger in 3-dimensions

4. Calculate the mean kinetic energy of a 2-dimensional gas. How does your answer compare to a one and 3-dimensional gas?

$$\langle v^2 \rangle = \int_0^\infty \frac{v^2 m}{kT} \exp\left(-\frac{mv^2}{2kT} \right) v \, dv \tag{19}$$

$$\langle \epsilon \rangle = \left\langle \frac{1}{2} mv^2 \right\rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \int_0^\infty \frac{v^3 m}{kT} \exp\left(-\frac{mv^2}{2kT} \right) dv \tag{20}$$

$$\langle \epsilon \rangle = \frac{1}{2} \int_0^\infty \frac{v^3 m^2}{kT} \exp\left(-\frac{mv^2}{2kT} \right) dv \tag{21}$$

Using a substitution,

$$u^2 = \frac{mv^2}{2kT} \tag{22}$$

$$2u\,du = \frac{mv}{kT}dv \tag{23}$$

$$dv = \frac{kT}{mv} \cdot 2u\,du \tag{24}$$

Substituting, we obtain:

$$\langle \epsilon \rangle = \frac{1}{2}\int_0^\infty \frac{v^3 m^2}{kT}\exp(-u^2)\frac{kT}{mv} \cdot 2u\,du \tag{25}$$

$$\langle \epsilon \rangle = m\int_0^\infty v^2 \exp(-u^2) \cdot u\,du \tag{26}$$

$$\langle \epsilon \rangle = m\int_0^\infty \frac{u^2 2kT}{m}\exp(-u^2) \cdot u\,du \tag{27}$$

$$\langle \epsilon \rangle = 2kT\int_0^\infty u^2 \exp(-u^2) \cdot u\,du \tag{28}$$

$$\int_0^\infty u^2 \exp(-u^2) \cdot u\,du = \frac{1}{2} \tag{29}$$

$$\langle \epsilon \rangle = 1.0\,kT \tag{30}$$

Problem 2. (Kinetics and Transport)

In junior Chemical Engineering laboratory, you might study the diffusion and solubility of CO_2 in an organic solvent using a diffusion cell like the one sketched here. No description has been provided for this imageLet's suppose that the gas space at the top of the diffusion cell is approximately 2 cm high and 4 cm in diameter. Further suppose that the gas in the head of the cell is pure CO_2 at 298 K and 1 bar pressure. Note that CO_2 has a collision diameter d of 0.40 nm.

```
In [ ]:  import numpy as np
         m = 44*1.6605e-27 # [=] kg
         k = 1.38065e-23 # [=] J/K
         T = 298 # [=] K
         d = 0.4e-9 # [=]
         p = 1e5 # [=] Pa
```

5. What does gas kinetic theory predict for the gas self-diffusion constant

D_{11} of CO_2 gas in the cell, in cm^2s^{-1}?

```python
In [ ]: # first, we need to get mean speed
        v = (8*k*T/(np.pi*m))**0.5 # [=] m/s
        sigma = np.pi*d**2
        # mean free path
        l = k*T/p*(1/(2**0.5*sigma))
        D11 = 1/3*l*v*10000 # [=] cm^2/s (10000 is factor to convert m^2 to cm^2)
        print(f'The self diffustion constant in a gas phase is: {D11:.3} cm^2/s')
```

```
The self diffustion constant in a gas phase is: 0.0731 cm^2/s
```

6. Use the Stokes-Einstein relationship to estimate the diffusion constant of CO_2 in the organic solvent (take it to be Stoddard solvent, a relatively high molecular weight petroleum distillate). How does this compare with the diffusion constant in the gas phase? Why?

```python
In [ ]: r = d/2
        eta = 1e-3
        D_stoddard = k*T/(4*np.pi*eta*r)*10000
        print(f'The diffusion constant in the organic solvent is: {D_stoddard:.3} cm
        print('The diffusion constant in the solvent is much smaller than the self c
```

```
The diffusion constant in the organic solvent is: 1.64e-05 cm^2/s
The diffusion constant in the solvent is much smaller than the self diffusio
n constant in a gas phase
because there are additional interactions hindering the movement of solute p
articles.
```

7. We found in class that the probability for a molecule to diffuse a distance x in time t is Gaussian with mean 0 and standard deviation $\sigma = \sqrt{2D_{11}t}$. About how long will it take for 1/3 of the molecules starting at the center of the gas space to diffuse all the way to the surface of the liquid, i.e., > 1 cm?

```python
In [ ]: from scipy.stats import norm

        y = norm.ppf(1/3) # ppf is the probability density function. either of 1/3 a

        sigma = 1/y
        lamb = (k*T)/(p*np.sqrt(2)*np.pi*(d)**2)
        v = np.sqrt((8*k*T)/(np.pi*m))
        # The equation below is demonstrated in Lecture 3. Transport - Fick's first
        D11 = (1/3)*v*lamb*10000 #Extra factor to convert to cm^2/s
```

```
t = (sigma**2)/(2*D11)
print(t)
```

36.889030826299674

8. How many collisions on average does one of these diffusing CO_2 molecule make with other gas molecules on the way from the middle of the vapor space to the surface of the solvent?

In [ ]:
```
Num = (v/lamb)*t
print("{:e}".format(Num))
```

2.413551e+11

9. How far in total distance does this typical CO_2 molecule travel in the time it takes to reach the solvent surface from the middle of the cell?

You can look at either the average velocity times t

$$<v>t \tag{31}$$

or the average distance between collisions times the total number of collisions

$$\lambda N_{col} \tag{32}$$

(Use dimensional analysis to make sure your units make sense)

In [ ]:
```
#The first equation gives you:
distance1a = v*t
print(distance1a, "m")
#Second equation gives you:
distance1b = lamb*Num
print(distance1b, "m")
```

13969.197414242582 m
13969.197414242582 m

10. How many CO_2 molecules impinge on the surface of the Stoddard solvent in one second?

This is outlined further in the Kinetic Theory Notes

Think of the boundary as a "wall" and use the equation for wall collision frequency. And reorganize the equation using ideal gas law

$$J_w = \frac{1}{4} \frac{N}{V} <v> \tag{33}$$

$$J_w = \frac{1}{4}\frac{P}{k_B T} <v>$$ (34)

Number of CO2

$$N_{CO_2} = J_w t A$$ (35)

```
In [ ]:  #Calculate the Flux First
         #p is in Pa, which is 1kg/(m s^2)
         #v is in m/s
         #k is J/K, kg m^2/K s^2
         #t is K
         #J is in units of per m^2s,which makes sense as its dependent on area of the
         J = .25*p*v/(k*T)

         #t for this problem is 1 second
         t2=1
         #r is in m

         N=J*t2*np.pi*r**2
         print(N, "CO_2 Molecules")
```

289150681.9965662 CO_2 Molecules

11. Using your estimate of the diffusion constant in the solvent, how long does it take the same fraction CO_2 molecules to diffuse a similar distance in 1-dimension in the liquid phase?

We use the same approach for the gaseous diffusion in number 7, however we utilize the liquid phase diffusion constant we calculated for problem 6.

```
In [ ]:  #Our diffusion constant in 6 is D_stoddard
         t3 = (sigma**2)/(2*D_stoddard)
         print(t3, "seconds")
```

164628.57032240854 s

12. Is it safe to assume that any CO_2 that travels from the surface into the bulk of the solvent is rapidly replaced from the gas phase?

Yes because of the differences in diffusion seen in problem 6. The Gas phase CO2 is moving much more rapidly than the liquid phase CO2. Any liquid CO2 that moves away from the interface should be replaced by gas phase CO2.

13. Suppose the volume of the gas-handling manifold is 100 cm^3 and is pressurized with CO_2 in the morning to 1.1 atm. What will the pressure in the manifold be four

hours later, when lab starts, if the manifold has a pinhole of 1 μm^2?

We have initial pressure, volume, and time we just need to solve for tau

$$P = P_0 e^{-\frac{t}{\tau}} \tag{36}$$

$$\frac{1}{\tau} = \frac{1}{4}\frac{A}{V} <v> \tag{37}$$

Rearrange the above equation, and use definition of to simplify

$$\tau = \frac{V}{A}\sqrt{\frac{2\pi m}{k_B T}} \tag{38}$$

```
In [ ]:  #Pressure is given in atm, convert to Pa
         P0=1.1*101325
         #Time is given in hours, convert to seconds
         t4=4*60*60
         #given volume is in cm^3, convert that to m
         vol=100/(100**3)
         #given pinhole area is in um^2, convert to m^2
         A=1/(1e6**2)
         #m is in kg, and we use kb and T in standard units
         tau = vol/A*np.sqrt(2*np.pi*m/(k*T))
         P = P0*np.exp(-t4/tau)
         print(P,"Pa")
```

109948.36148499705 Pa