Problem 1: Derivation of a 2-dimensional gas that can't escape a surface

a) Derive the maxwell-Boltzmann speed distribution for a 2-dimensional gas

$$in\ a\ one - dimensional\ plane\ we\ know\ that$$

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

$$From\ a\ cartesian\ coordinate, we\ have$$

$$v^2 = v_x^2 + v_y^2$$

$$P(v_x, v_y)\ dv_x dv_y = P(v_x)P(v_y)\ dv_x dv_y = \frac{m}{2\pi kT} * exp\left(-m * \frac{v_x^2 + v_y^2}{2KT}\right)\ dv_x\ dv_y$$

$$We\ convert\ to\ a\ polar\ coordinate, recall\ dv_x dv_y = v\ dv\ d\theta$$

$$P(\mathrm{v}) = \int_0^{2\pi} \frac{mv}{2 * \pi * k * T} * exp\left(-\frac{mv^2}{2KT}\right)\ \ d\theta$$

$$= 2\pi * v * \frac{m}{2 * \pi kT} * exp\ (-\frac{mv^2}{2KT})$$

$$= \frac{mv}{kT} * exp\ (-\frac{mv^2}{2KT})$$

b) Plot this 2-dimensional speed distribution for O2 molecule at 200, 400, and 600 K
See code in ipynb

```
m = 32*1.6605e-27 # kg k = 1.38e-23 # j/K
k = 1.38e-23 # j/K


## Making a function as defined p(v)
def Probability(v,T):
    return v*m/(T*k)*np.exp(-m*v*v/(2*k*T))

plt.figure()

v = np.linspace(0,1500,1000)
for T in [200,400,600]:
  Prol = Probability(v,T)
  plt.plot(v,Prol,label = '{} K'.format(T))

legend = plt.legend()
plt.xlabel('Speed (m/s)')
plt.ylabel('Probability')
```

c) Calculate the mean speed of a 2-dimensional gas of molecules. How does your answer compare to a one and 3-dimensional gas?

$$From\ class, we\ have < v > = \int_0^\infty P(v) * v\ dv$$

$$we\ plug\ into\ the\ equation\ to\ get < v_z >, which\ is\ the\ mean\ velocity$$

$$< v > = \int_0^\infty \frac{v^2 * m}{kT} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$$using\ a\ u\ sub$$

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

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

$$dv = \frac{kT}{mv} * 2\ u * du$$

$$< v > = \int_0^\infty \frac{v^2 m}{kT} \exp(-u^2)\ \frac{kT}{mv}\ 2\ u\ du$$

$$simplifying, it\ becomes$$

$$< v > = \int_0^\infty 2 * v * u * \exp(-u^2)\, du$$

$$v = \ u * \left(\frac{2 * k * T}{m}\right)^{\frac{1}{2}}$$

$$< v > = \left(\frac{2 * k * T}{m}\right)^{1/2} \int_0^\infty 2\ u^2 * \exp(-u^2)\, du$$

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

$$< v > = \left(\frac{\pi\ k\ T}{2\ m}\right)^{\frac{1}{2}}$$

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

d) Calculate the mean kinetic energy of the particle

$$< v^2 > = \int_0^\infty \frac{v^2 * m}{kT} \exp\left(-\frac{mv^2}{2kT}\right) * v\, dv$$

$$< \epsilon > =< \frac{1}{2} mv^2 > = \frac{1}{2}\, m < v^2 > = \frac{1}{2}\, m \int_0^\infty \frac{v^3 * m}{kT} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$$< \epsilon > = \frac{1}{2} \int_0^\infty \frac{v^3 * m^2}{kT} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

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

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

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

$$< \epsilon > \; = \frac{1}{2} \int_0^\infty \frac{v^3 * m^2}{kT} \exp(-\, u^2)\, \frac{kT}{mv} * 2u * du$$

$$< \epsilon > \; = \; m \int_0^\infty v^2 \;\exp(-u^2) * u * du$$

$$< \epsilon > \; = m \int_0^\infty \frac{u^2 2kT}{m} \;\exp(-u^2) * u * du$$

$$< \epsilon > = 2\, kT \int_0^\infty u^2 \;\exp(-u^2) * u * du$$

$$\int_0^\infty u^2 \;\exp(-u^2) * u * du = 1/2$$

$$< \epsilon > = 1.0\, k\, T$$

1 dimensional gas, the mean kinetic energy is 0.5 kT, 3D is 1.5 kT; 2 dimensional is 1.0 kT. The mean kinetic energy degree of freedom cost is 0.5 kT

HW#2

Problem 2. (Kinetics and Transport)

5. What does gas kinetic theory predict for the gas self-diffusion constant D_{11} of CO_2 gas in the cell, in $cm^2 s^{-1}$?

Solution:

Lets gather the data we need first:

CO_2: Carbon: 12.01 amu
Oxygen: 15.99 amu

CO_2: 44 amu

$$44 \text{ amu} \times \frac{1.66 \times 10^{-27} \text{ Kg}}{1 \text{ amu}} = 7.30 \times 10^{-26} \text{ Kg}$$

$K_B = 1.38 \times 10^{-23}$ J/K
$T = 298$ K
$\sigma_{collision} = 0.40$ nm ; 1 nanometer $= 1 \times 10^{-9}$ m

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Next, going back to what was seen in class we know that:

$$\langle v \rangle = \left(\frac{8 K_B T}{\pi m} \right)^{1/2}$$

mean speed is the expected value of the speed distribution

According to the problem, we have CO_2 at 298K

After calculating the mean speed, we can calculate the collision cross section:

$A = \pi d^2$; In lecture notes A was called sigma σ.
d is the collision diameter.

The following step is to calculate the mean free path: distance between collisions

$$l = \frac{K_B T}{p} \cdot \frac{1}{\sqrt{2} A}$$; Pressure is 1 bar or 1×10^5 Pascal.

Lastly, calculating the self-diffusion constant:

$$D_{11} = \underbrace{\frac{1}{3}}_{\text{dimensionality of the space in which diffusion occurs}} \cdot l \cdot \langle v \rangle$$ In 3-D

Calculations are in jupyter notebook. The gas self-diffusion constant is 0.07 cm^2/s approximately.

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6. Use the Stokes-Einstein relationship to estimate the diffusion constant of CO_2 in the Stoddard solvent. How does this compare with the diffusion constant in the gas phase? Why?

Solution:

For stick boundary, as seen in class we have

$$D = \frac{K_B T}{4\pi \eta r}$$

; appropiate to things of size comparable to liquid

; η represents the viscosity of the fluid in Stokes-Einstein relationship in which the particles are diffusing

1 nanometer $= 1 \times 10^{-9}$ m

Collision radius $= 0.2 \times 10^{-9}$ m

η viscosity = this can be in a range of .74 to 1.65 mPa·s

$$\eta = 1e^{-3} \frac{Kg}{m \cdot s} \quad ; \quad 1 Pa = 1 \frac{Kg}{ms^2}$$

and 0.001 Pa·s $= 1$ mPa·s

Calculations are in jupyter notebook. The diffusion constant of CO_2 in the Stoddard solvent is approximately 1.63×10^{-5} cm^2/s.

The diffusion constant of CO_2 in the Stoddard solvent is lower compared to the diffusion constant in the gas phase. The solvent introduces additional interactions that impedes the movement of solute particles.

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PChem: HW#2

Problem 2. (Kinetics and Transport)

5. What does gas kinetic theory predict for the gas self-diffusion constant D11 of CO2 gas in the cell, in cm^2 s^-1 ?

Solution:

In [72]:
```
import numpy as np
```

Let's gather the data we need first:

In [85]:
```
m = 44*1.66e-27 #kg/atomic mass unit; 1 atomic mass unit = 1.66e-27 kg
kB = 1.38e-23 #J/K
T = 298 #K
d = 0.4e-9 #collision diameter (m)
P = 1e5 #Pa
```

Next, calculating the mean speed and plugging in the data we obtain:

In [86]:
```
v = (8*kB*T/(np.pi*m))**0.5 # mean speed (m/s)
print("The mean speed is {:.2f} m/s".format(v))
```

```
The mean speed is 378.65 m/s
```

Third, calculate collision cross section:

In [87]:
```
A = np.pi*d**2 # collision cross section (m^2)
print(A)
```

```
5.02654824574367e-19
```

The following step is to calculate the mean free path:

In [88]:
```
l = kB*T/p*(1/(2**0.5*A)) # mean free path (m)
print(l)
```

```
5.785095029007004e-08
```

Lastly, calculating the self-diffusion constant:

In [89]:
```
D11 = 1/3*l*v*10000 # self-diffusion constant (cm^2/s); Extra factor 10000 to convert to cm^2/s
print("The gas self-diffusion constant is {:.2f} cm^2/s".format(D11))
```

```
The gas self-diffusion constant is 0.07 cm^2/s
```

6. Use the Stokes-Einstein relationship to estimate the diffusion constant of CO2 in the Stoddard solvent. How does this compare with the diffusion constant in the gas phase? Why?

Solution:

Defining constants

In [90]:
```
r = 0.2e-9 # defining collision  radius (meters)
eta = 1e-3 #units:kg/(meters * seconds);
#eta represents the viscosity of the fluid in Stokes-Einstein relationship in which the particles are di

kB = 1.38e-23 #J/K
T = 298 #K
```

Then calculating the diffusion constant:

In [91]:
```
D_stoddard = kB*T/(4*np.pi*eta*r)*10000 # slip boundary (cm^2/s); Extra factor 10000 to convert to cm^2/s
print ('The diffusion constant of CO2 in the Stoddard solvent is {:.5E} cm^2/s.'.format(D_stoddard))
```

```
The diffusion constant of CO2 in the Stoddard solvent is 1.63627E-05 cm^2/s.
```

The diffusion constant of CO2 in the Stoddard solvent is lower compared to the diffusion constant in the gas phase. There is a solvent in this case compared to the one before. The solvent introduces additional interactions that impedes the movement of solute particles.

7. About how long for 1/3 of molecules in the center of the gas to diffuse to the surface of the liquid?

$\sigma = \sqrt{2D_{\parallel} t}$

use percent point function to find a pt where ~~P(x)~~ probability from $-\infty \rightarrow pt = 2/3$

leftover bit is 1/3 that goes farther

function works with a standard normal distribution, we need to scale.

$x = 1$ cm

$x = \sqrt{2D_{\parallel} t} \cdot y$

$x = \sigma y$

$\sigma = \frac{1}{y}$

$\sigma^2 = \sqrt{2D_{\parallel} t}^{\,2}$

$\sigma^2 = 2D_{\parallel} t$

$\frac{\sigma^2}{2D_{\parallel}} = t$

solve using ~~approxim~~ value from #5 (gas phase) answer I get is 36.889

$\boxed{\sim 36 \text{ seconds}}$

Can also set $\int_{1}^{\infty} P(x) = 1/3$, then solve for t

8. How many average collisions on that trip?

$\lambda = \frac{\langle v \rangle}{z} \rightarrow z = \frac{\langle v \rangle}{\lambda}$ ↑ per unit time, ~~per unit area~~ collision frequency

$\# \text{ collisions} = \frac{\langle v \rangle}{\lambda} \cdot t$

Unit analysis $\frac{m/s}{m} \cdot s$

already have $\langle v \rangle$ and λ, t from #7

Number of collisions $\approx$ $\boxed{2.41 \times 10^{11} \text{ collisions}}$

9. How far does it travel?

Two approaches could work, basically $x = v \cdot t$

$\langle v \rangle \cdot t$ ↑ from #7 or $\lambda \cdot$ # collisions

average # of collisions times average distance between collisions

$\boxed{\approx 14{,}000 \text{ m}}$ exact value in code, along with proof the two methods are equal.

10. How many CO_2 molecules hit solvent surface in one second?

$P = \frac{N k_B T}{V}$

$\frac{P}{k_B T} = \frac{N}{V}$

Think of this boundary as a "wall", can use equation for wall collision frequency

$J_w = \frac{1}{4} \frac{N}{V} \cdot \langle v \rangle = \frac{1}{4} \frac{P}{k_B T} \cdot \langle v \rangle$

↑ per unit time, per unit area

$\# CO_2 = J_w \cdot t \cdot A$

1 second ↓ area of interface ↙

$\boxed{\approx 2.89 \times 10^{24} \text{ molecules}}$

11. How long for 1/3 of the molecules in the liquid to diffuse 1 cm?

Same approach as #7, just use $D_{\parallel}$ from #6

$\boxed{\sim 165{,}000 \text{ seconds}}$

12. Is CO_2 that goes into the solvent replaced?

Gas phase CO_2 is moving much faster than in the solvent, so CO_2 that moves into the solvent should be replaced quickly.

13. What is the final pressure?

$V = 100\ cm^3$ pinhole is $1\ \mu m^2$

$P_0 = 1.1$ atm $t = 4$ hours

Referencing Lecture 3 Notes: $P = P_0 e^{-t/\tau}$

$\frac{1}{\tau} = \frac{A}{V} \cdot \frac{1}{4}\langle v \rangle$ $\quad \tau = \frac{1}{\langle v \rangle} = 4\frac{V}{A}\sqrt{\frac{\pi m}{8 k_B T}}$

$4\sqrt{\frac{\pi m}{8 k_B T}} = \sqrt{\frac{16\pi m}{8 k_B T}} = \sqrt{\frac{2\pi m}{k_B T}}$

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

$\boxed{P = \sim 110{,}000 \text{ Pa or } 1.085 \text{ atm}}$