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

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

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

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

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

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

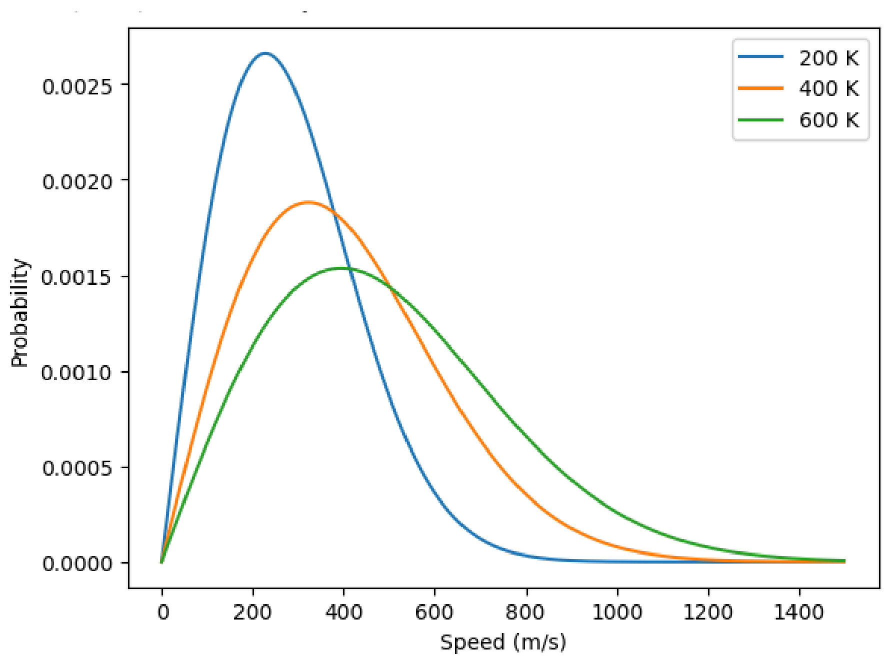
$$We\ convert\ to\ a\ polar\ coordinate,\ recall\ dv_x dv_y = v\, dv\, d\theta$$

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

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

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

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




```python
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?

$$From\ class,\ we\ have\ < v > \ = \int_{0}^{\infty} P(v) * \ v\, dv$$

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

$$< v > \ = \int_{0}^{\infty} \frac{v^2 * m}{kT} \exp exp\left(- \frac{mv^2}{2kT}\right) dv$$

$$using\ a\ u\ sub$$

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

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

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

$$< v > \ = \int_{0}^{\infty} \frac{v^2 m}{kT} \exp exp\left(- u^2\right) \frac{kT}{mv}\, 2\, u\, du$$

$$simplifying,\ it\ becomes$$

$$< v > \ = \int_{0}^{\infty} 2 * v * u * \exp exp\left(- u^2\right) du$$

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

$$< v > \ = \left(\frac{2*k*T}{m}\right)^{1/2} \int_{0}^{\infty} 2\, u^2 * \exp exp\left(- u^2\right) du$$

$$\int_{0}^{\infty} 2\, u^2 * \exp exp\left(- u^2\right)\, du = \frac{\sqrt{\pi}}{2}$$

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

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

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

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

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

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

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

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

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

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

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

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

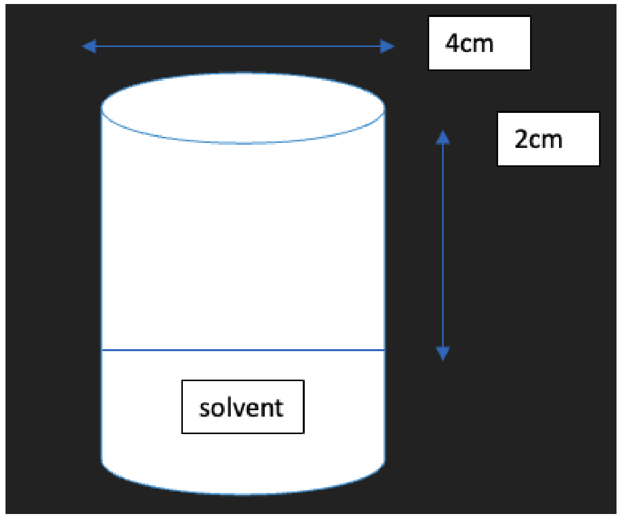
$$\int_0^\infty u^2 \; \exp exp \left(- \, u^2\right) \; * \; u \; * \; du \; = \; 1/2$$

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

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

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 [22]:
```
import numpy as np
```

Let's gather the data we need first:

In [41]:
```
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 = 4e-10 #m
P = 1e5 #Pa
```

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

In [42]:
```
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 [50]:
```
A = np.pi*d**2 # collision cross section (m^2)
```

The following step is to calculate the mean free path:

In [54]:
```
l = kB*T/p*(1/(2**0.5*A)) # mean free path (m)
```

Lastly, calculating the self-diffusion constant:

In [56]:
```
D11 = 1/3*l*v*10000 # self-diffusion constant (cm^2/s); Extra factor 10000 to convert to cm^2/
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 [37]:
```
r = 0.02 # defining radius (m)
eta = 1e-5 #viscosity of the fluid in which the particles are diffusing
```

Then calculating the diffusion constant:

In [38]:
```
D_stoddard = kB*T/(4*np.pi*eta*r)*10000 # slip boundary (cm^2/s); Extra factor 10000 to conver
#The equation above is used because of diffusion in three dimensions and Stokes'Law
print ("The diffusion constant of CO2 in the Stoddard solvent is", D_stoddard, "cm^2/s")
```

```
The diffusion constant of CO2 in the Stoddard solvent is 1.6362719699277757e-13 cm^2/s
```

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

$\sigma = \sqrt{2D_{11}t}$

use percent point function to find a pt where 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

$$X = \sqrt{2D_{11}t} \cdot y$$

$$X = \sigma y$$

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

$$\sigma^2 = \sqrt{2D_{11}t}^{\,2}$$

$$\sigma^2 = 2D_{11}t$$

$$\frac{\sigma^2}{2D_{11}} = t$$

solve using approximate 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

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

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

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 $x = v \cdot t$

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

from #7

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

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

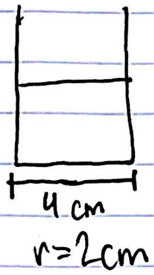
per unit time, per unit area

1 second

area of interface

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

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



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

Same approach as #7, just use D_{11} 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: $P = P_0 e^{-t/\tau}$

$\frac{1}{\langle v \rangle}$

$\frac{1}{\tau} = \frac{A}{V} \cdot \frac{1}{4} \langle v \rangle$ $\tau = 4 \frac{V}{A} \sqrt{\frac{\pi m}{8 k_B T}} = \frac{V}{A} \sqrt{\frac{2\pi m}{k_B T}}$

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

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

HW2

February 2, 2024

[31]:
```
from scipy.stats import norm
import numpy
```

[46]:
```
#Number 7
k = 1.38065e-23
T = 298
d = 0.4e-9
p = 1e5
m = 44*1.6605e-27

y = norm.ppf(2/3)

sigma = 1/y
lamb = (k*T)/(p*numpy.sqrt(2)*numpy.pi*(d)**2)
v = numpy.sqrt((8*k*T)/(numpy.pi*m))
D11 = (1/3)*v*lamb*10000

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

```
36.889030826299695
```

[33]:
```
#Problem 8
Num = (v/lamb)*t
print("{:e}".format(Num))
```

```
2.413551e+11
```

[34]:
```
#Problem 9
dist_1 = v*t
dist_2 = (lamb*Num)

print(dist_1)

print(dist_1 == dist_2)
```

```
13969.19741424259
True
```

[35]:
```
#Problem 10
Jw = (1/4)*(p/(k*T))*v
A = .02**2*numpy.pi
time = 1
num = Jw*A*time
print(num)
```

```
2.891506819965661e+24
```

[42]:
```
#Problem 11
eta = 1e-3
D_2 = (k*T)/(4*numpy.pi*(d/2)*eta)*10000
t2 = (sigma**2)/(2*D_2)
print(t2)
```

```
164628.57032240863
```

[45]:
```
#Problem 13
#Starts by getting numbers in consistent units
V = 100/(100**3) #cm^3 to m^3
P_0 = 1.1*101325 #atm to Pa
a = 1*(1e-6)**2 #um^2 to m^2
Time = 4*3600 #hours to seconds

tau = V/a*(2*numpy.pi*m/(k*T))**0.5

P_f = P_0*numpy.exp(-Time/tau)
Pf_atm = P_f/101325

print(P_f)
print(Pf_atm)
```

```
109948.36148499705
1.0851059608684632
```