HW2-soln2020

January 31, 2020

1 Chem 30324, Spring 2019, Homework 2

1.1 Due: January 29, 2020

1.2 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.

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

For a 1-dimensional gas,

$$P = (\frac{m}{2\pi kT})^{1/2} \exp(\frac{-mv^2}{2kT})$$

For a 3-dimensional gas,

$$P = 4\pi v^2 (\frac{m}{2\pi kT})^{3/2} \exp(\frac{-mv^2}{2kT})$$

Where $4\pi v^2$ is the number of directions (area of sphere).

In a 2-dimensional space, the number of directions is $2\pi v$ (circumference of circle).

Therefore,

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

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

for a 2-dimensional space.

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

```
[0]: import numpy as np
     import matplotlib.pyplot as plt

     m = 32/1000/(6.022*10**23) #mass of O2 (kg/molecule)
     k = 1.38064852*10**-23 # Boltzmann Constant (m^2 kg s^-2 K^-1)
     v = np.linspace(0,1500,1000) #velocity (m/s)
```
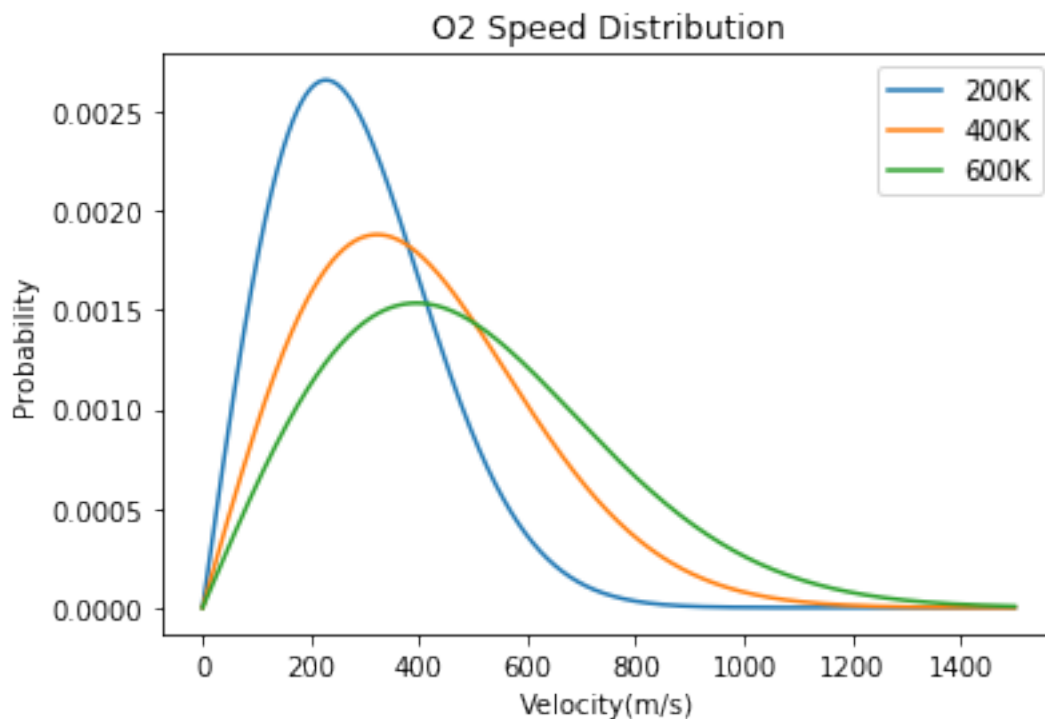
```
for T in [200,400,600]:
    P = (m*v/k/T)*np.exp(-m*v**2/(2*k*T)) #Maxwell-Boltzman speed distribution␣
    ↪for a 2-D gas
    plt.plot(v,P, label = '{0}K'.format(T))

plt.xlabel('Velocity(m/s)')
plt.ylabel('Probability')
plt.legend(loc='best')
plt.title('O2 Speed Distribution')
plt.show()
```


1.2.3 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?

```
[0]: from sympy import *

T = Symbol('T',positive=True)
k = Symbol('k',positive=True)
m = Symbol('m',positive=True)
v = Symbol('v',positive=True)

#2D Gas
```

```
eqn2d = (2*pi*v)*(m/2/pi/k/T)*exp(-m*v**2/2/k/T)
vbar2top = integrate(eqn2d*(v),(v,0,oo))
vbar2bot = integrate(eqn2d,(v,0,oo))
pprint(vbar2top/vbar2bot)
pprint(vbar2top)

#1D Gas
eqn1d = (m/2/pi/k/T)**(0.5)*exp(-m*v**2/2/k/T)
vbar1top = integrate(eqn1d*(v),(v,0,oo))
vbar1bot = integrate(eqn1d,(v,0,oo))
pprint(vbar1top/vbar1bot)

#3D Gas
eqn3d = (4*pi*v**2)*(m/2/pi/k/T)**(1.5)*exp(-m*v**2/2/k/T)
vbar3top = integrate(eqn3d*(v),(v,0,oo))
vbar3bot = integrate(eqn3d,(v,0,oo))
pprint(vbar3top/vbar3bot)
```

√2 √ √T √k
───────────
    2 √m

√2 √ √T √k
───────────
    2 √m
         -0.5 0.5 0.5 -0.5
1.0 √2   T   k   m
         -0.5 0.5 0.5 -0.5
2.0 √2   T   k   m

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

```
[0]: from sympy import *

T = Symbol('T',positive=True)
k = Symbol('k',positive=True)
m = Symbol('m',positive=True)
v = Symbol('v')

#2D Gas
eqn2d = (2*pi*v)*(m/2/pi/k/T)*exp(-m*v**2/2/k/T)
vbar2top = integrate(eqn2d*(v**2/2),(v,0,oo))
vbar2bot = integrate(eqn2d,(v,0,oo))
pprint(vbar2top/vbar2bot)

#1D Gas
eqn1d = (m/2/pi/k/T)**(0.5)*exp(-m*v**2/2/k/T)
```

3

```
vbar1top = integrate(eqn1d*(v**2/2),(v,-oo,oo))
vbar1bot = integrate(eqn1d,(v,-oo,oo))
pprint(vbar1top/vbar1bot)

#3D Gas
eqn3d = (4*pi*v**2)*(m/2/pi/k/T)**(1.5)*exp(-m*v**2/2/k/T)
vbar3top = integrate(eqn3d*(v**2/2),(v,-oo,oo))
vbar3bot = integrate(eqn3d,(v,-oo,oo))
pprint(vbar3top/vbar3bot)
```

T k

 m

0.5 T k

   m

1.5 T k

   m

1.3 Problem 2. (Kinetics and Transport)

In junior Chemical Engineering laboratory, you will study the diffusion and solubility of CO_2 in an organic solvent using a diffusion cell like the one sketched here. Let'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.

1.3.1 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}?

```
[0]: import numpy as np

     #Constants
     T = 298 #K
     P = 100000 #Pa (kg/m/s^2)
     d = 4*10**-10 #m
     MW = 44.01 #g/mol
     Na = 6.022*10**23 #molecules/mol
     kB = 1.38064582*10**-23 #m^2 kg/s^2/K
     m = MW/Na/1000 # kg/molecule

     v = (8*kB*T/np.pi/m)**0.5 #m/s, mean speed
     V = Na*kB*T/P #m^3/mol, volume
     sigma = np.pi*d**2   #m^2, collision cross section
     z = np.sqrt(2)*sigma*Na/V*v #1/s, molecular collision frequency
     lambd = v/z #m, mean free path
     D11 = 1/3*v*lambd #m^2/s, self-diffusion constant
```

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```
print('The self diffusion constant D11 is',round(D11*100**2,5),'cm^2/s')
```

The self diffusion constant D11 is 0.07305 cm^2/s

1.3.2   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?

```
[0]:  r = d/2 #m
      eta = 14.93e-6 # Pa*s, Viscosity of CO2 at 298 K (source from
      ↪engineeringtoolbox.com)
      D12 = kB*T/(4*np.pi*eta*r) #m^2/s

      print('The diffusion constant in the Stoddard solvent is',
      ↪round(D12*100**2,7),'cm^2/s.')
      print('This value is smaller in Stoddard solvent due to greater viscosity.')
```

The diffusion constant in the Stoddard solvent is 0.0010965 cm^2/s.
This value is smaller in Stoddard solvent due to greater viscosity.

1.3.3   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?

```
[0]:  from scipy.stats import norm

      prob = norm.ppf(2/3) #cm
      print('The 66.7% percentile of a normal distribution function lies at x
      ↪=',round(prob,3),'cm.')
      print('However, we already know that x = 1 cm here. Therefore, sigma must be
      ↪greater than one.')
      sigma1 = 1/prob #cm
      print('sigma =',round(sigma1,3),'cm')
      t = sigma1**2/2/D11/(100**2) #s
      print('For 1/3 of the molecules to diffuse all the way to the surface
      ↪is',round(t,2),'seconds.')
```

The 66.7% percentile of a normal distribution function lies at x = 0.431 cm.
However, we already know that x = 1 cm here. Therefore, sigma must be greater
than one.
sigma = 2.322 cm
For 1/3 of the molecules to diffuse all the way to the surface is 36.89 seconds.

1.3.4 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?

```
[0]: print('Average collisons=z*t=',round(z*t,0))
```

```
Average collisons=z*t= 241356542860.0
```

1.3.5 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?

```
[0]: print('Total distance =',round(v*t,1),'m.')
```

```
Total distance = 13969.2 m.
```

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

```
[0]: jw = 1/4*P/kB/T*v #collisions/area/time
     area = np.pi*.02**2 #m^2
     n = jw*area*1
     print('Wall collision frequency =',n)
```

```
Wall collision frequency = 2.891114873231068e+24
```

1.3.7 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?

```
[0]: t2 = sigma1**2/2/(D12*100**2)
     print('Using the diffusion constant from #6, t =',round(t2,0),'s.')
```

```
Using the diffusion constant from #6, t = 164629.0 s.
```

1.3.8 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?

```
[0]: print('Comparing problems 7 and 11, we see that diffusion is order-of-magnitude␣
     ↪greater in gas phase than in liquid phase.')
     print('Therefore, gas molecule dissolved into solvent will be rapidly replaced␣
     ↪by other gas molecules.')
```

```
Comparing problems 7 and 11, we see that diffusion is order-of-magnitude greater
in gas phase than in liquid phase.
Therefore, gas molecule dissolved into solvent will be rapidly replaced by other
gas molecules.
```

1.3.9   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 m^2?

```
[0]: import numpy as np

     V = 100/(100**3) #m^3
     P0 = 1.1*101325 #Pa
     t = 4*3600 #s
     A = 1/(10**12) #m^2
     kB = 1.38064582*10**-23 #m^2 kg/s^2/K



     Tau = V/A*(2*np.pi*m/kB/T)**.5 #s
     P = P0*np.exp(-t/Tau)
     print ('Four hours later, P=',round(P,1),'Pa')
```

```
Four hours later, P= 109948.6 Pa
```

[0]: