Contents

1 Chem 30324, Spring 2018, Homework 2 Solution

1.1 Problem 1. Gases on a table top

1.1.1 Derive the Maxwell-Boltzmann speed distribution for a 2-dimensional gas.

The Maxwell-Bolzmann distribution for 2 dimensions can be derived by considering each dimension as independent.

In cartesian coordinates, the distribution looks like

$$P(v)dv_x dv_y = \frac{m}{2\pi k_B T} e^{\frac{m(v_x^2 + v_y^2)}{2k_B T}}$$

When converted to polar coordinates, the distribution is

$$P(v)dv = \int_0^{2\pi} \frac{m}{2\pi k_B T} e^{\frac{mv^2}{2k_B T}} v\, dv\, d\theta$$

which finally gives:

$$P(v)dv = \frac{mv}{k_B T} e^{\frac{mv^2}{2k_B T}} dv$$

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

The speed distribution looks like:

2-D Maxwell-Boltzmann speed distribution of O_2 gas
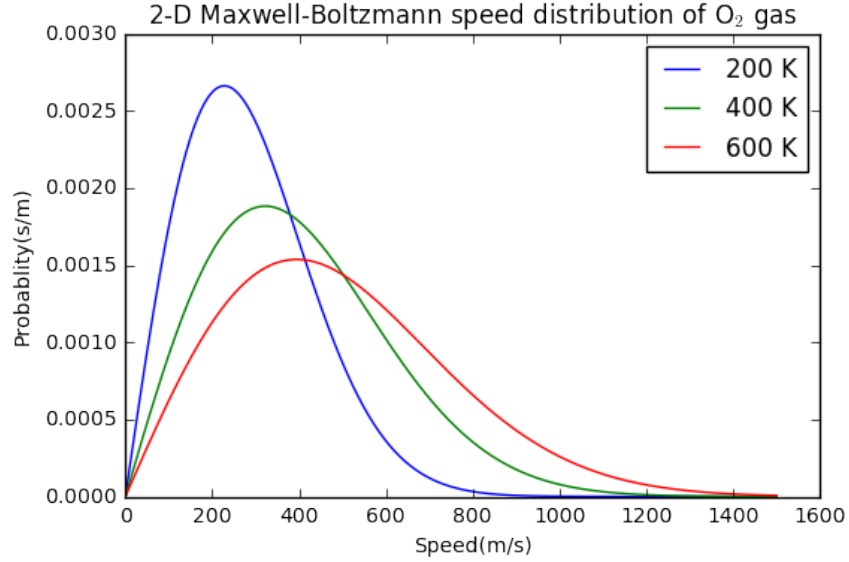
1.1.3 Calculate the mean (expected value) of the speed of a 2-dimensional gas of molecules. How does your answer compare to a 2-dimensional gas?

The mean value of speed can be calculated through:

$$< v >= \int_0^{inf} vP(v)dv$$

The mean value comes out to be :

$$< v >= \sqrt{\frac{\pi k_B T}{2m}}$$

This value is different from that of a 3-dimensional gas where

$$< v >= \sqrt{\frac{8k_B T}{\pi m}}$$

Both results are dependent on (T/m)^0.5

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

The mean value of kinetic energy can be calculated through:

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$$< K >= \int_0^{inf} \frac{mv^2}{2} P(v)dv$$

The mean value comes out to be k_BT
Mean value of 1-D gas : $0.5k_BT$
Mean value of 3-D gas : $1.5k_BT$
They are all multiples of $0.5k_BT$ since the velocity components in different directions are assumed independent of each other.

1.2 Problem 2. (Kinetics and Transport)

1.2.1 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 ?

Taking m = $44*m_p$= $44*1.6605*10^{-27}$ = $73.062*10^{-27}$
k = $1.38*10^{-23}$ J/K
T = 298 K
d = $0.4*10^{-9}$ m
p = 10^5 Pa
The mean speed is calculated as :

$$< v >= \sqrt{\frac{8k_BT}{\pi m}} = 378.592 m/s$$

Collision cross section is given by:

$$A = \pi * d^2 = 5.0265 * 10^{-19} m^2$$

Mean free path is given by :

$$l = kT/\sqrt{2}Ap = 5.785 * 10^{-8} m$$

Self diffusion constant is given by:

$$D_{11} = 1/3 < v > l * 10000 = 7.30064 * 10^{-2} cm^2/s$$

1.2.2 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?

r = d/2 = 0.2*10^-9 m

Viscosity, $\eta = 1*10^{-3}$ kg/m.s
The diffusion constant in Stoddard solvent is:

$$D_2 = kT/(4\pi\eta r) * 10000 = 1.63627 * 10^{-5} cm^2/s$$

It's less than that of the gas phase by 3 orders of magnitude.
That's because mean free path length in liquid phase is less
than for the gas phase.

1.2.3 **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 $= 2\,D_{11}t$. 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?**

To get the time for 1/3 of molecules to diffuse
We use the Guassian probability distribution for diffusion

$$P(x,t) = \frac{e^{\frac{-x^2}{4D_{11}t}}}{2\sqrt{\pi D_{11}T}}$$

To get the time of 1/3 molecules to diffuse,
we set the integral of distribution from 1 cm to infinty as 1/3:

$$\int_1^{\text{inf}} P(x,t)dx = 1/3$$

After integration, the solution is 36.915 s
(Another way to go about it is given in the python notebook)

1.2.4 **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?**

Total distance travelled by molecules in the above time:
= mean speed * time
= 378.592*36.915 = 13975.723 m
Number of collisions = Total distance/mean free path
$= 2.41582*10^{11}$

1.2.5 **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?**

Total distance = Mean free path*Number of collisons
$= 1.3975*10^4$ m

1.2.6 **How many CO$_2$ molecules impinge on the surface of the Stoddard solvent in one second?**

Total wall collision frequency J$_w$ is given as:

$$J_w = \frac{N<v>}{4V} = \frac{p<v>}{4kT} = 2.3015*10^{27} coll/m^2s$$

Area of surface = π 0.02^2 = 1.2566*10^{-3} m^2
Time = 1s
Number of molecules = J$_w$*Area*Time = 2.8921*10^{24}

1.2.7 **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?**

Taking D$_2$ = 1.63627*10^{-5} cm^2/s in

$$P(x,t) = \frac{e^{\frac{-x^2}{4Dt}}}{2\sqrt{\pi D_{11}T}}$$

We do the same procedure as before
To get the time of 1/3 molecules to diffuse,
we set the integral of distribution from 1 cm to infinty as 1/3:

$$\int_1^{inf} P(x,t)dx = 1/3$$

After integration, the solution is 164706.113s
(Another way to go about it is given in the python notebook)

1.2.8 **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?**

By looking at the answers obtained in part 5 and 6 (or even 7 and

11)It is clear that CO_2 molecules travel faster in gas phase.
So it is safe to assume that the diffusing molecules are rapidly re placed.

1.2.9 **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 μ m^2 ?**

V = 100 cm^3 = 10^-4 m^2
P_0 = 1.1*101325 = 111457.5 Pa
A = 1 μ m^2 = 10^{-12} m^2
Given time = 4 hr = 14400 s
Time constant is given by:

$$\tau = \frac{V}{A}\sqrt{\frac{2\pi m}{k_B T}} = 1.0565 * 10^6 s$$

Pressure P = P$_0$ e$^{\frac{-time}{\tau}}$ = 109948.71 Pa (1.085 atm)