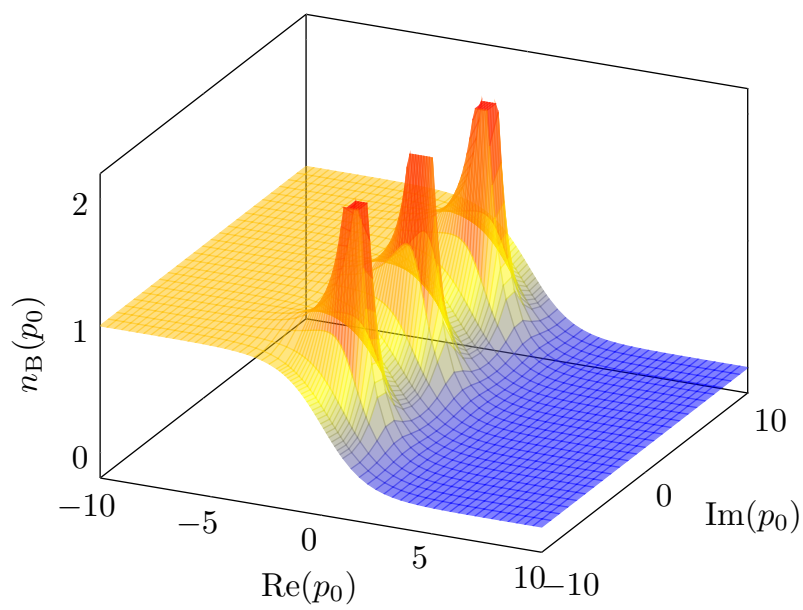


Molecular Effusion & Mean Free Path

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Contents

1	Molecular Effusion	3
1.1	Flux	3
1.2	Effusion	4
1.3	Chapter Summary	5
2	The Mean Free Path & Collisions	6
2.1	The Mean Collision Time	6
2.2	The Collision Cross-Section	7
2.3	The Mean Free Path	8
2.4	Chapter Summary	9

1 Molecular Effusion

Effusion is the process by which gas escapes from a small hole. We begin by first evaluating the flux of particles hitting the inside walls of a container of gas.

1.1 Flux

Of relevance to this section, the molecular flux, Φ , is defined to be the # molecules striking unit area per second.

$$\Phi = \frac{\text{number of molecules}}{\text{area} \times \text{time}}$$

As derived in the previous chapter, the # of molecules hitting unit area of wall in unit time, with speeds between v and $v + dv$ and traveling at angles between θ and $\theta + d\theta$ is given by

$$v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta$$

Therefore, the flux of molecules in a gas can be evaluated by integrating over all v and θ so that

$$\begin{aligned} \Phi &= \int_0^\infty \int_0^{\pi/2} v \cos \theta n f(v) \frac{1}{2} \sin \theta d\theta dv \\ &= \frac{n}{2} \int_0^\infty v f(v) dv \int_0^{\pi/2} \cos \theta \sin \theta d\theta \end{aligned}$$

which yields

$$\boxed{\Phi = \frac{1}{4} n \langle v \rangle}$$

If we define n by rearranging the ideal gas law,

$$n = \frac{p}{kT}$$

and using the expression for the average speed of molecules in a gas,

$$\langle v \rangle = \sqrt{\frac{8kT}{m}}$$

we can derive a more precise definition for molecular flux:

$$\boxed{\Phi = \frac{p}{\sqrt{2\pi m kT}}}$$

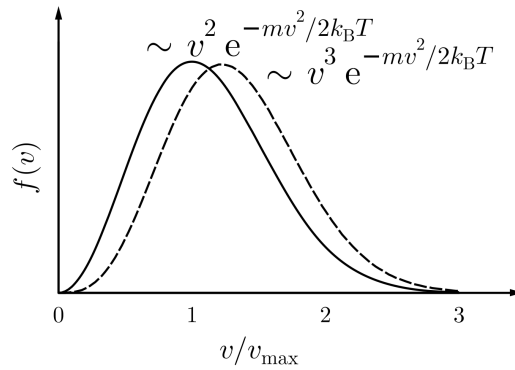
1.2 Effusion

Consider a container of gas with a small hole of area A . Gas will leak out of the hole. The hole is small so that the equilibrium of gas in the container is not disturbed. The # of molecules escaping per unit time is just the # of molecules hitting the hole area in the closed box per second, so is given by ΦA . This is the **effusion rate**.

$$\Phi A = \frac{pA}{\sqrt{2\pi mkT}}$$

Effusion preferentially selects faster molecules. Therefore the speed distribution of molecules effusing out the hole is not Maxwellian. Faster molecules inside the box travel more quickly and have a greater probability of reaching the hole than their slower counterparts. Mathematically, we get an extra factor of v for the distribution of molecules effusing in some interval of time:

$$g(v) \propto v^3 e^{-mv^2/2k_B T}$$



Maxwellian gas has an average energy of $E_{KE} = \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T$. Let's calculate the mean kinetic energy of molecules effusing out of a small hole.

$$\begin{aligned} \langle E_{KE} \rangle &= \frac{1}{2}m\langle v^2 \rangle \\ &= \frac{\frac{1}{2}m \int_0^\infty v^2 v^3 e^{-\frac{1}{2}mv^2/k_B T} dv}{\int_0^\infty v^3 e^{-\frac{1}{2}mv^2/k_B T} dv} \\ &= \frac{1}{2}m \left(\frac{2k_B T}{m} \right) \frac{\int_0^\infty u^2 e^{-u} du}{\int_0^\infty u e^{-u} du} \end{aligned}$$

where the substitution $u = mv^2/2k_B T$ was made. Using the standard integral,

$$\int_0^\infty x^n e^{-x} dx = n!,$$

we have that

$$\langle E_{KE} \rangle = 2k_B T$$

which is larger by a factor of $\frac{4}{3}$ than the mean kinetic energy of molecules in the gas.

1.3 Chapter Summary

The molecular flux, Φ is the # of molecules striking unit area per second and is given by

$$\Phi = \frac{1}{4} n \langle v \rangle$$

This expression, together with the ideal gas law helps us derive an alternative expression for molecular flux:

$$\Phi = \frac{p}{\sqrt{2\pi m k_B T}}$$

The average kinetic energy of molecules *effusing* out of the container:

$$\langle E_{KE} \rangle = 2k_B T$$

which is $\frac{4}{3}$ larger than the mean kinetic energy of molecules *in* the gas $-\frac{3}{2}k_B T$

2 The Mean Free Path & Collisions

Processes such as the diffusion of one gas into another would be instantaneous were it not for the occurrence of *collisions* between molecules. Collisions are fundamentally quantum mechanical, but in a dilute gas, molecules spend most of their time between collisions so we can consider them as classical billiard balls and ignore the details of what *actually happens* during a collision. All we care about is that after collisions molecules velocities become essentially randomized. In this section we model the effect of collisions in a gas and develop concepts of mean collision time, the collision cross section, and mean free path.

2.1 The Mean Collision Time

We aim to calculate the average time molecules spend between collisions. Let's consider a molecule moving in a gas of other similar molecules. To make things simple to start with, we suppose that the molecule under consideration is traveling at speed v and that the other molecules in the gas are stationary. We also attribute a collision cross-section σ to our molecule

In a time dt , our molecule sweeps out a volume $\sigma v dt$. If another molecule happens to lie inside this volume, a collision will occur. With n molecules per unit volume, the probability of a collision in time dt is therefore $n\sigma v dt$. Let us define $P(t)$ as follows:

$$P(t) = \text{the probability of a molecule NOT colliding up to time } t$$

Elementary calculus then implies

$$P(t + dt) = P(t) + \frac{dP}{dt}dt,$$

but $P(t + dt)$ is also the probability of a molecule not colliding up to time t *multiplied* by the probability of not colliding in subsequent time dt , i.e.,

$$P(t + dt) = P(t)(1 - n\sigma v dt)$$

Rearranging gives us

$$\frac{1}{P} \frac{dP}{dt} = -n\sigma v$$

Solving yields

$$P(t) = P_0 e^{-n\sigma v t} = e^{-n\sigma v t}$$

Now the probability of surviving without collision up to time t but then colliding in the next dt is

$$e^{-n\sigma v t} n\sigma v dt$$

We can check this is a solid probability by integrating it:

$$\int_0^{\infty} e^{-n\sigma vt} n\sigma v dt = 1$$

we can now calculate the **mean scattering time** τ , which is the average time elapsed between collisions for a given molecule:

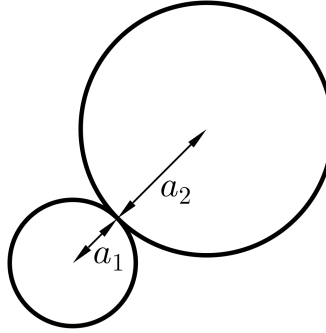
$$\begin{aligned}\tau &= \int_0^{\infty} t e^{-n\sigma vt} n\sigma v dt \\ &= \frac{1}{n\sigma v} \int_0^{\infty} (n\sigma vt) e^{-n\sigma vt} d(n\sigma vt) \\ &= \frac{1}{n\sigma v} \int_0^{\infty} x e^{-x} dx\end{aligned}$$

We find that

$$\tau = \frac{1}{n\sigma v}$$

2.2 The Collision Cross-Section

Consider two spherical molecules of radii a_1 and a_2 .

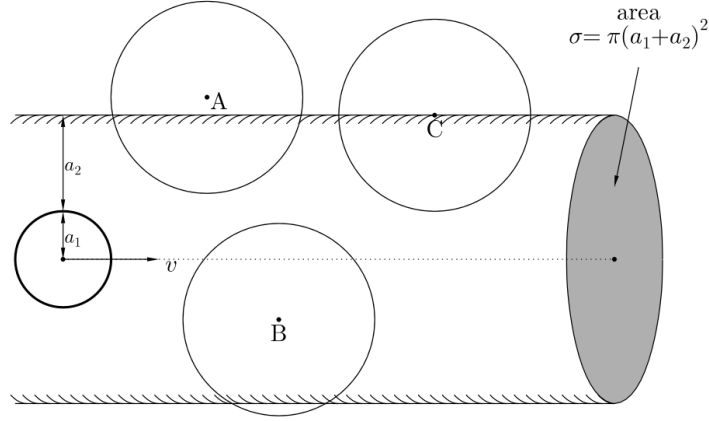


A collision will only take place if the center of these other molecules comes inside a tube of radius $a_1 + a_2$. Thus our first molecule can be considered to sweep out an imaginary tube space of cross-sectional area $\pi(a_1 + a_2)^2$ that defines its “personal space.” The area of this tube is called the **collision cross-section** σ and is then given by

$$\sigma = \pi(a_1 + a_2)^2.$$

If all the molecules are the same (have the same diameter d),

$$\sigma = \pi d^2$$



2.3 The Mean Free Path

Having derived the mean collision time, it is tempting to derive the **mean free path** as

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{n \sigma v}.$$

But what should we use for v ? Our approach to determining the mean collision time assumed all other molecules are stationary. The reality is that all molecules whizz around extremely fast. We should therefore take v as the average *relative* velocity $\langle v_r \rangle$, where

$$\vec{v}_r = \vec{v}_1 - \vec{v}_2$$

Therefore,

$$\langle v_r^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2\vec{v}_1 \cdot \vec{v}_2$$

which yields

$$\langle v^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle = 2\langle v^2 \rangle$$

And since $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 0$ (all molecules are moving in random directions so $\langle \cos \theta \rangle = 0$). However, the quantity we want is $\langle v_r \rangle$, not $\langle v_r^2 \rangle$. If the probability distribution describing molecular speed

is the Maxwellian Distribution, then the error in writing $\langle v_r \rangle \approx \sqrt{\langle v_r^2 \rangle}$ is only around 8%. So to a reasonable degree of approximation we can write

$$\langle v_r \rangle \approx \sqrt{\langle v_r^2 \rangle} \approx \sqrt{2} \langle v \rangle$$

Hence, we obtain an expression for λ :

$$\boxed{\lambda = \frac{1}{\sqrt{2}n\sigma}}$$

While this equation was derived using an approximation, it turns out to be exact. Substitution of $p = nk_B T$ yields the expression:

$$\lambda = \frac{k_B T}{\sqrt{2}p\sigma}$$

2.4 Chapter Summary

The mean scattering time is given by

$$\tau = \frac{1}{n\sigma \langle v_r \rangle},$$

where the collision cross-section is $\sigma = \pi d^2$, and $\langle v_r \rangle \approx \sqrt{2} \langle v \rangle$.

The mean free path is exactly equal to

$$\lambda = \frac{1}{\sqrt{2}n\sigma} = \frac{k_B T}{\sqrt{2}p\sigma}.$$