Molecular effusion

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton

(Date: January, 17, 2019)

1. Introduction

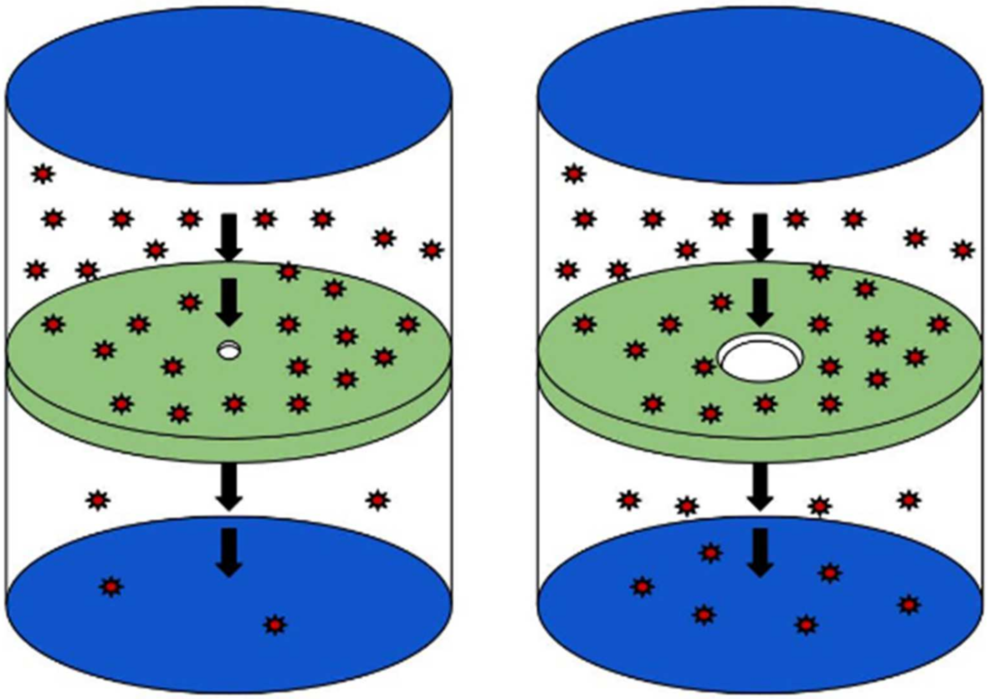


Fig. Effusion (left) where a small hole size is smaller than a mean free path of molecules. and diffusion (right) where a hole is larger than the mean free path.

Effusion is the process in which a gas escapes through a hole of diameter considerably smaller than the mean free path of the molecules. Under these conditions, essentially all molecules which arrive at the hole continue and pass through the hole, since collisions between molecules in the region of the hole are negligible. Conversely, when the diameter is larger than the mean free path of the gas, flow obeys the Sampson flow law.
https://en.wikipedia.org/wiki/Effusion

1. Derivation of the expression of pressure (conventional method)

We just show the conventional method for the derivation of pressure (we will discuss in more detail somewhere).

The force along the *x* direction:

$$
\begin{aligned}
F_x &= \int_{v_x>0} \frac{2mv_x}{\Delta t}(Av_x\Delta t)\frac{N(\boldsymbol{v})}{V}d\boldsymbol{v} \\
&= \frac{N}{V}\int_{v_x>0} \frac{2mv_x}{\Delta t}(Av_x\Delta t)\frac{N(\boldsymbol{v})}{N}d\boldsymbol{v} \\
&= \frac{AN}{V}\int_{v_x>0} 2m{v_x}^2\overline{n}(\boldsymbol{v})d\boldsymbol{v} \\
&= \frac{AN}{2V}\int 2m{v_x}^2\overline{n}(\boldsymbol{v})d\boldsymbol{v} \\
&= \frac{AN}{2V}\int 2m{v_x}^2 4\pi v^2\overline{n}(v)dv \\
&= \frac{AN}{2V}\int 2m{v_x}^2 f(v)dv
\end{aligned}
$$

where

$$
\frac{N(\boldsymbol{v})}{N} = \overline{n}(\boldsymbol{v})\,, \qquad\qquad f(v)dv = 4\pi v^2\overline{n}(\boldsymbol{v})dv
$$

The pressure:

$$
\begin{aligned}
P &= \frac{F_x}{A} \\
&= \frac{N}{2V}\int \frac{2m}{3}v^2 f(v)dv \\
&= \frac{N}{2V}\frac{2}{3}2\int \frac{m}{2}v^2 f(v)dv \\
&= \frac{2N}{3V}\int \frac{m}{2}v^2 f(v)dv \\
&= \frac{2N}{3V}\varepsilon \\
&= \frac{2N}{3V}\frac{3}{2}k_BT \\
&= \frac{N}{V}k_BT
\end{aligned}
$$

leading to an equation of state,

$$
PV = Nk_BT \qquad\qquad \text{(for ideal gas)}
$$

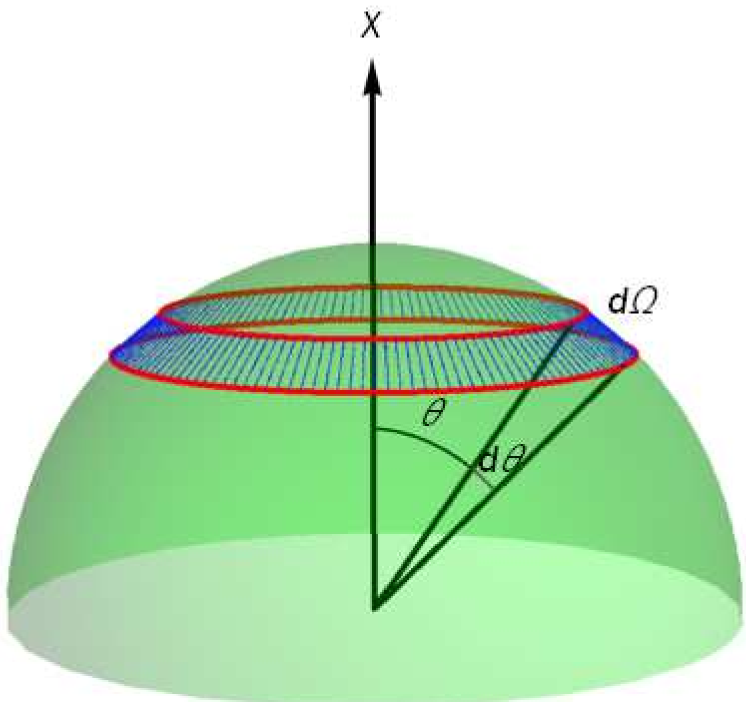
Note that

$$\varepsilon = \frac{3}{2} k_B T$$

2. The method using the textbook (Blundell and Blundell)

The fraction whose trajectories lie in an elemental solid angle $d\Omega$ is

$$\frac{d\Omega}{4\pi} = \frac{2\pi \sin\theta d\theta}{4\pi} = \frac{1}{2}\sin\theta d\theta$$



The number density between v and $v + dv$ is

$$nf(v)dv$$

where $f(v)$ is the Maxwell-Boltzmann distribution function with

$$\int_0^{\infty} f(v)dv = 1$$

The corresponding number density is

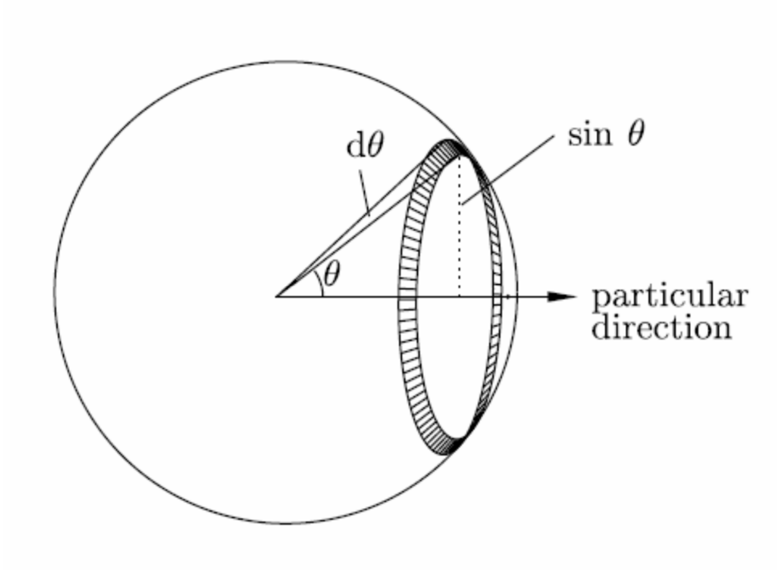
$$nf(v)dv\,\frac{d\Omega}{4\pi} = \frac{1}{2}\sin\theta d\theta\; nf(v)dv$$

where $n = \frac{N}{V}$ (number density). The force along the positive x-direction is

$$\Delta F_x = (\frac{2mv\cos\theta}{\Delta t})(Av\cos\theta\Delta t)[\frac{1}{2}\sin\theta d\theta\; nf(v)dv]$$

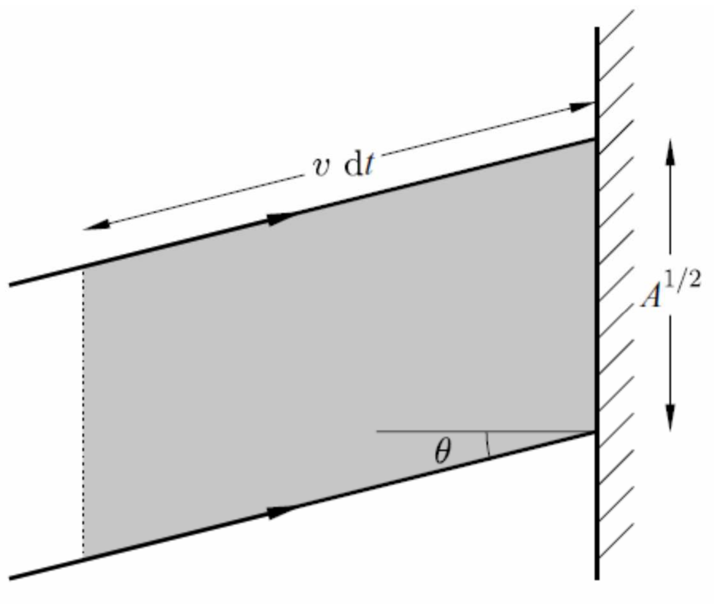
where $(\frac{2mv\cos\theta}{\Delta t})$ is the change of momentum along the x axis during a time Δt, $(Av\cos\theta\Delta t)$ is the volume, and $\frac{1}{2}\sin\theta d\theta\; nf(v)dv$; the number density of molecules having velocity between v and v+dv and travelling at angles between θ and $\theta + d\theta$ to the chosen direction. The resulting pressure P is given by

$$\begin{aligned}
P &= \frac{F}{A} \\
&= n\int_0^\infty mv^2 f(v)dv \int_0^\pi \sin\theta\cos^2\theta d\theta \\
&= \frac{n}{3}\int_0^\infty mv^2 f(v)dv \\
&= \frac{2n}{3}\int_0^\infty \frac{mv^2}{2} f(v)dv \\
&= \frac{2n}{3}\varepsilon \\
&= \frac{2N}{3V}\frac{3}{2}k_B T \\
&= \frac{Nk_B T}{V}
\end{aligned}$$



3. Flux

The flux is defined to be the number of molecules which strike unit area per second.



Since the number is given by

$$nf(v)dv\frac{d\Omega}{4\pi} = \frac{1}{2}\sin\theta d\theta \, nf(v)dv$$

where $n = \dfrac{N}{V}$ (number density), the number of the particles passing through a surface area A during a time the positive x-direction is given by

$$\Delta N = (Av\cos\theta\,\Delta t)[\frac{1}{2}\sin\theta d\theta\, nf(v)dv]$$
$$= \frac{1}{2}A\Delta tv\cos\theta\,[\sin\theta d\theta\, nf(v)dv]$$
$$= \frac{1}{2}n(A\Delta t)vf(v)dv\cos\theta\sin\theta d\theta$$

The number flux (per unit area and per unit time) is

$$\Phi_N = \frac{1}{2}n\int_0^{\infty} vf(v)dv\int_0^{\pi/2}\cos\theta\sin\theta d\theta = \frac{1}{4}n\langle v\rangle \tag{1}$$

since

$$\int_0^{\pi/2}\cos\theta\sin\theta d\theta = \frac{1}{2}, \qquad \langle v\rangle = \int_0^{\infty} vf(v)dv = 2\sqrt{\frac{2k_BT}{\pi m}}$$

An alternative expression for Φ_N can be found as follows: rearranging the ideal gas law

$$P = nk_BT \qquad \text{or} \qquad \frac{P}{k_BT} = n$$

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

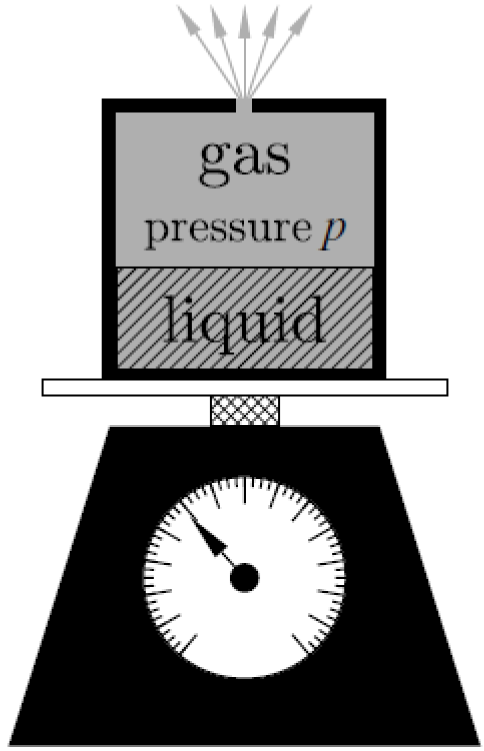
$$\langle v\rangle = \int_0^{\infty} vf(v)dv = 2\sqrt{\frac{2k_BT}{\pi m}}$$

we can substitute these expressions into Eq.(1) and obtain

$$\Phi_N = \frac{1}{4}\frac{P}{k_BT}2\sqrt{\frac{2k_BT}{\pi m}} = \frac{P}{\sqrt{2\pi mk_BT}} \tag{2}$$

Note that consideration of Eq.(2) shows us that the effusion rate depends inversely on the square root of the mass in agreement with Graham's law.

5. Knudsen method



In the Knudsen method of measuring vapor pressure P from a liquid containing molecules of mass m at temperature T, the liquid is placed in the bottom of a container which has a small hole of area A at the top. The container is placed on a weighing balance and its weight Mg is measured as a function of time. In equilibrium, the effusion rate is

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

So that the rate of change in mass, $\left|\frac{dM}{dt}\right|$ is given by $A\Phi_N$. Thus we have

$$mA\Phi_N = \frac{mAP}{\sqrt{2\pi m k_B T}} = \left|\frac{dM}{dt}\right|$$

leading to the pressure as

$$P = \sqrt{\frac{2\pi k_B T}{m}}\frac{1}{A}\left|\frac{dM}{dt}\right|.$$

5. Average energy of particles hitting the surface

We also calculate the average energy using the number of particle defined by

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

The average energy is given by

$$\begin{aligned}
\left\langle \frac{1}{2} m v^2 \right\rangle_{II} &= \frac{\int \frac{1}{2} m v^2 \frac{1}{2} n v f(v) dv \sin\theta \cos\theta d\theta \Delta t A}{\int \frac{1}{2} n v f(v) dv \sin\theta \cos\theta d\theta \Delta t A} \\
&= \frac{\int_0^\infty \frac{1}{2} m v^3 f(v) dv}{\int_0^\infty v f(v) dv} \\
&= \frac{1}{2} m \frac{\langle v^3 \rangle}{\langle v \rangle} \\
&= \frac{1}{2} m \frac{4 k_B T}{m} \\
&= 2 k_B T
\end{aligned}$$

where

$$\langle v^3 \rangle = \int_0^\infty v^3 f(v) dv = 8 \sqrt{\frac{2}{\pi}} \left(\frac{k_B T}{m} \right)^{3/2}$$

APPENDIX-I

The total energy passing through a surface area A during a time the positive x-direction is

$$\begin{aligned}
\Delta E &= \frac{1}{2} m v^2 \Delta N \\
&= \frac{1}{2} m v^2 \frac{1}{2} A \Delta t v \cos\cos\theta)[\sin\theta d\theta \, n f(v) dv] \\
&= \frac{1}{4} n A \Delta t (m v^2) f(v) dv [\cos\theta \sin\theta d\theta]
\end{aligned}$$

The energy flux (energy per unit area and per unit time)

$$\Phi_E = \frac{1}{4} nm \int_0^{\infty} v^2 f(v) dv \int_0^{\pi/2} \cos\theta \sin\theta d\theta = \frac{1}{8} nm \langle v^2 \rangle = \frac{1}{4} n(\frac{1}{2} m v_{rms}{}^2)$$

since

$$\int_0^{\pi/2} \cos\theta \sin\theta d\theta = \frac{1}{2}, \qquad \langle v^2 \rangle = \int_0^{\infty} v^2 f(v) dv = \frac{3}{m} k_B T$$

APPENDIX II **The number hitting a plane for the calculation of flux**

Derivation of The number hitting a plane with unit surface area $(A = 1)$, per unit time $(\Delta t = 1)$

$$A v \cos\theta \Delta t \frac{N(v)}{V} v^2 dv (2\pi) \sin\theta d\theta = \frac{N}{V} A v \cos\theta \Delta t \frac{N(v)}{N} v^2 dv (2\pi) \sin\theta d\theta$$

$$= \frac{N}{V} A v \cos\theta \Delta t [\overline{n}(v)] v^2 dv (2\pi) \sin\theta d\theta$$

where

$$\overline{n}(v) = \frac{N(v)}{N}, \qquad f(v) = 4\pi v^2 \overline{n}(v) \qquad \text{with} \qquad \int_0^{\infty} f(v) dv = 1.$$

The number hitting a plane with unit surface area $(A = 1)$, per unit time $(\Delta t = 1)$

$$n v \cos\theta \frac{2\pi}{4\pi} f(v) dv \sin\theta d\theta = \frac{1}{2} n v f(v) dv \cos\theta \sin\theta d\theta$$

where

$$n = \frac{N}{V}$$