Chapter 19

The kinetic theory of gases

In this chapter we will introduce the kinetic theory of gases which relates the motion of the constituent atoms to the volume, pressure and temperature of the gas. The following topics will be covered:

((Ludwig Boltzmann))

Ludwig Eduard Boltzmann (February 20, 1844 – September 5, 1906) was an Austrian physicist famous for his founding contributions in the fields of statistical mechanics and statistical thermodynamics. He was one of the most important advocates for atomic theory when that scientific model was still highly controversial.





Boltzmann's equation-curved in stone.

This equation was originally formulated by Ludwig Boltzmann between 1872 to 1875, but later put into its current form by Max Planck in about 1900. To quote Planck, "the logarithmic connection between entropy and probability was first stated by L. Boltzmann in his kinetic theory of gases."

Reference

- Carlo Cercignani, Ludwig Boltzmann The man who trusted atoms (Oxford University Press, 1998)
- E.A. Guggenheim, Boltzmann's distribution law (North-Holland, 1955).
- G. Gallavotti, W.L. Reiter, and J. Yngvason edited, Boltzmann's Legacy (European Mathematical Society, 2008).

1 Molecules colliding with wall

We consider molecules that strike a unit area of the wall of a container. Let v_x denote the velocity component normal to the plane of the wall.



The particles are inside the cube with the volume V. There are N particles. We consider the particle (mass *m*) with the velocity (v_x, v_y, v_z) . After the reflection at the wall, the velocity of the particles is changed into $(-v_x, v_y, v_z)$. The change of the linear momentum gives a force on the plane normal to the *x* axis.

$$\Delta p_x = -2mv_x = F_{1x}\Delta t$$

As a result of the Newton's third law (the action-reaction), the force

$$F_x = -F_{1x} = \frac{2mv_x}{\Delta t}$$

is exerted on the wall (as an impulse), contributing to the pressure. Here we assume that the number of molecules per unit volume (number density), which have velocity componenets of $v_x - (v_x + dv_x)$, $v_y - (v_y + dv_y)$, and $v_z - (v_z + dv_z)$ is given by

$$\frac{1}{V}N(\mathbf{v})d^{3}\mathbf{v} = \frac{1}{V}N(v_{x},v_{y},v_{z})dv_{x}dv_{y}dv_{z}$$

where $N(\mathbf{v})d^3\mathbf{v}$ is the number of molecules whose velocities are $v_x - (v_x+dv_x)$, $v_y - (v_y+dv_y)$, and $v_z - (v_z+dv_z)$.

$$N = \int N(\mathbf{v}) d^3 \mathbf{v}$$

The number of particles (velocity v) colliding with the plane is evaluated as follows.



The volume of the cylinder is given by

$$Av_{x}\Delta t$$

The number of molecules in the cylinder is calculated as

$$(Av_x\Delta t)\frac{1}{V}N(v)d^3v$$

The force applied along the x axis is

$$(Av_{x}\Delta t)\frac{2mv_{x}}{\Delta t}\frac{1}{V}N(\mathbf{v})d^{3}\mathbf{v} = \frac{A}{V}2mv_{x}^{2}N(\mathbf{v})d^{3}\mathbf{v}$$

Then the pressure P is defined by

$$P = \frac{F_x^{total}}{A} = \frac{1}{A} \int \frac{2Amv_x^2}{V} N(\mathbf{v}) d^3 \mathbf{v}$$
$$= \frac{1}{V} \int_{v_x>0} 2mv_x^2 N(\mathbf{v}) d^3 \mathbf{v}$$

where only the particles with $v_x > 0$ contribute to the pressure.

2 Thermal equilibrium

In thermal equilibrium, the gas is assumed to be homogeneous for each direction. So it is natural to consider that N(v) is dependent only on the magnitude of v.

$$PV = \int_{v_x>0} 2mv_x^2 N(\mathbf{v}) d^3 \mathbf{v} = \frac{1}{2} \int 2mv_x^2 N(\mathbf{v}) d^3 \mathbf{v} = \frac{1}{3} \int mv^2 N(\mathbf{v}) d^3 \mathbf{v}$$

where v_x^2 is replaced by $v^2/3$.

Here we note that average of the total energy is

$$\left\langle E\right\rangle = \int \frac{1}{2} m v^2 N(\mathbf{v}) d^3 \mathbf{v}$$

Then we have

$$PV = \frac{2}{3} \left\langle E \right\rangle$$

This equation is called a Bernoulli's equation.

For an ideal gas, we have the Boyle's law

$$PV = Nk_BT$$
,

leading to the expression for $\langle E \rangle$

$$\langle E \rangle = N\varepsilon = \frac{3}{2}Nk_BT$$

Note that ε is the average energy of each particle.

$$\varepsilon = \frac{3}{2}k_BT$$

3 Maxwell velocity distribution *f*(*v*)

3.1 Determination of the form N(v)

It is assumed that N(v) depends only on the magnitude of v. The velocity distribution for v_x is independent of those for v_y and v_z . Then we have the form of N(v) as

$$N(v) = G(v^{2}) = g(v_{x})g(v_{y})g(v_{z})$$
(1)

with $g(0) = \alpha$, where G and g are functions to be determined. In Eq.(1), we put $v_y = v_z = 0$.

$$G(v_x^2) = g(v_x)g(0)g(0) = \alpha^2 g(v_x)$$

Then we have

$$g(v_x) = \frac{1}{\alpha^2} G(v_x^2)$$

Similarly,

$$g(v_y) = \frac{1}{\alpha^2} G(v_y^2)$$
$$g(v_z) = \frac{1}{\alpha^2} G(v_z^2)$$

Then Eq.(1) can be rewritten as

$$G(v^{2}) = G(v_{x}^{2} + v_{y}^{2} + v_{z}^{2}) = g(v_{x})g(v_{y})g(v_{z})$$
$$= \frac{1}{\alpha^{6}}G(v_{x}^{2})G(v_{y}^{2})G(v_{z}^{2})$$

For simplicity we put $v_x^2 = \xi$, $v_y^2 = \eta$, and $v_z^2 = \zeta$. Then we have

$$G(\xi + \eta + \varsigma) = \frac{1}{\alpha^6} G(\xi) G(\eta) G(\zeta) \,.$$

Taking a derivative of the above equation with respect to η and putting $\eta = \zeta = 0$,

$$G'(\xi) = \frac{1}{\alpha^6} G(\xi) G'(0) G(0) = -aG(\xi)$$

or

$$G(\xi) = A e^{-a\xi}$$

where

$$a=-\frac{1}{\alpha^6}G'(0)G(0).$$

The final form of N(v) is obtained as

$$N(\mathbf{v}) = G(v_x^2 + v_y^2 + v_z^2) = A \exp[-a(v_x^2 + v_y^2 + v_z^2)] = A \exp(-a\mathbf{v}^2)$$

(Gaussian form)

Now we determine the values of *A* and *a*.

(a) Determination of A

$$N = \iiint N(\mathbf{v})d^{3}\mathbf{v}$$

=
$$\iiint A \exp[-a(v_{x}^{2} + v_{y}^{2} + v_{z}^{2})]dv_{x}dv_{y}dv_{z}$$

=
$$A[\int \exp(-av_{x}^{2})dv_{x}]^{3}$$

=
$$A(\frac{\pi}{a})^{3/2}$$

or

$$A = \left(\frac{\pi}{a}\right)^{-3/2} N$$

where

$$\int \exp(-av_x^2) dv_x = \int_{-\infty}^{\infty} \exp(-av_x^2) dv_x = \sqrt{\frac{\pi}{a}}$$

((Note)) We can also calculate the above integral as follows.

$$N = A \int_{0}^{\infty} 4\pi v^{2} \exp(-av^{2}) dv$$
$$= \frac{A}{2} 4\pi \int_{-\infty}^{\infty} v^{2} \exp(-av^{2}) dv$$
$$= 2\pi A \frac{1}{2} \sqrt{\pi} a^{-3/2}$$
$$= A \left(\frac{\pi}{a}\right)^{3/2}$$

((Mathematica))

$$J[\underline{n}] := \int_{-\infty}^{\infty} \mathbf{x}^{n} \operatorname{Exp}\left[-\mathbf{a} \mathbf{x}^{2}\right] d\mathbf{x} / / \operatorname{Simplify}[\#, \mathbf{a} > 0] \&$$

list1 = Table[{ n, J[n] }, {n, 0, 10, 2}]; list1 // TableForm

$$0 \quad \frac{\sqrt{\pi}}{\sqrt{a}}$$

$$2 \quad \frac{\sqrt{\pi}}{2 a^{3/2}}$$

$$4 \quad \frac{3\sqrt{\pi}}{4 a^{5/2}}$$

$$6 \quad \frac{15\sqrt{\pi}}{8 a^{7/2}}$$

$$8 \quad \frac{105\sqrt{\pi}}{16 a^{9/2}}$$

$$10 \quad \frac{945\sqrt{\pi}}{32 a^{11/2}}$$

(b) Determination of *a*

The total energy <*E*> is given by

$$\langle E \rangle = \iiint \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) N(\mathbf{v}) dv_x dv_y dv_z$$

$$= \iiint \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) A \exp[-a(v_x^2 + v_y^2 + v_z^2)] dv_x dv_y dv_z$$

$$= \int \frac{1}{2} m v^2 A \exp(-av^2) 4\pi v^2 dv$$

$$= \frac{1}{2} m A 4\pi \int_0^\infty v^4 \exp(-av^2) dv$$

$$= \frac{1}{2} m A 4\pi \frac{1}{2} \int_{-\infty}^\infty v^4 \exp(-av^2) dv$$

$$= \frac{1}{2} m A 4\pi \frac{1}{2} \frac{3\sqrt{\pi}}{4a^{5/2}}$$

$$= m A \frac{3\pi^{3/2}}{4a^{5/2}}$$

where v is the radius of the sphere in the (v_x, v_y, v_z) and $4\pi v^2 dv$ is the volume element enclosed by the spherical shell of inner radius v and outer radius v + dv,

$$v^{2} = v_{x}^{2} + v_{y}^{2} + v_{z}^{2}$$
$$d^{3}v = dv_{x}dv_{y}dv_{z} = 4\pi v^{2}dv$$

Then we have

$$\frac{\langle E \rangle}{N} = \frac{mA\frac{3\pi^{3/2}}{4a^{5/2}}}{A(\frac{\pi}{a})^{3/2}} = \frac{m\frac{3}{4a^{5/2}}}{\frac{1}{a^{3/2}}} = \frac{3m}{4a} = \frac{3}{2}k_BT$$

From this equation, the value of a is determined as

$$a = \frac{m}{2k_BT}$$

In summary we have the Maxwell distribution or Maxwell-Boltzmann distribution,

$$N(\mathbf{v}) = N(\frac{m}{2\pi k_B T})^{3/2} \exp(-\frac{m\mathbf{v}^2}{2k_B T}).$$

We define n(v) as

$$n(\mathbf{v}) = \frac{N(\mathbf{v})}{N} = (\frac{m}{2\pi k_B T})^{3/2} \exp(-\frac{m v^2}{2k_B T})$$

with

$$1 = \int n(\mathbf{v}) d^3 \mathbf{v} = \int n(\mathbf{v}) 4\pi v^2 dv$$

- (1) n(v)dv is the probability of finding particles whose velocities are $v_x (v_x+dv_x)$, $v_y (v_y+dv_y)$, and $v_z (v_z+dv_z)$.
- (2) Note that $n(v)4\pi v^2 dv$ is the probability of finding particles whose magnitude of velocities are between v and (v + dv).

Using the Avogadro number N_A , where

 $N_{\rm A}m = M$ (the molar mass) $N_{\rm A}k_{\rm B} = R$ (gas constant),

n(v) can be rewritten as

$$n(\mathbf{v}) = \left(\frac{M}{2\pi RT}\right)^{3/2} \exp(-\frac{Mv^2}{2RT})$$

The function n(v) has a Gaussian type with a peak at v = 0. Here we introduce the probability f(v) dv of finding the particle having the velocity between v and v + dv, as

$$f(v)dv = 4\pi v^2 n(v)dv$$
$$= \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp(-\frac{mv^2}{2k_B T})dv$$
$$= \left(\frac{M}{2\pi R T}\right)^{3/2} 4\pi v^2 \exp(-\frac{Mv^2}{2R T})dv$$

where

$$\int_{0}^{\infty} f(v) dv = 1$$

f(v) is called the *Maxwell velocity distribution* and is given by

$$f(v) = \left(\frac{M}{2\pi RT}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{Mv^2}{2RT}\right)$$

((Note))

$$\frac{1}{N}N(\mathbf{v})d\mathbf{v} = n(\mathbf{v})d\mathbf{v} = 4\pi v^2 n(v)dv = f(v)dv$$

We note that f(v) has a local maximum at

$$v_{mp} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}} = 1.41421\sqrt{\frac{RT}{M}}$$

(most probable speed)

((Note))

$$\frac{df(v)}{dv} = \left(\frac{M}{2\pi RT}\right)^{3/2} 4\pi \{2v \exp(-\frac{Mv^2}{2RT}) + v^2 \exp(-\frac{Mv^2}{2RT})(-\frac{Mv}{RT}) = -\left(\frac{M}{2\pi RT}\right)^{3/2} 4\pi (-\frac{Mv^2}{2RT})v(\frac{Mv^2}{RT} - 2) = 0$$

The maximum value of f(v) at $v = v_{mp}$ is

$$f_{\rm max} = \frac{2}{e} \sqrt{\frac{2M}{\pi RT}}$$

The distribution function is normalized as

$$\frac{f(v)}{f_{\max}} = (\frac{v}{v_{mp}})^2 \exp[1 - (\frac{v}{v_{mp}})^2]$$



Fig. Plot of the normalized $f(v)/f_{max}$ as a function of a normalized v/v_{mp} .

Green:	most probable speed	$(v_{\rm mp})$
Blue:	averaged speed	$(v_{\rm avg})$
Brown:	root-mean squared speed	$(v_{\rm rms})$

$$1 < \frac{v_{avg}}{v_{mp}} (= 1.128) < \frac{v_{rms}}{v_{mp}} (= \frac{\sqrt{6}}{2} = 1.225)$$

3.2 Calculation of average $\langle v^n \rangle$

Using f(v), we calculate $\langle v^n \rangle$ which is defined by

$$\langle v^n \rangle = \int v^n f(v) dv$$

(a) The average speed v_{avg}

$$v_{avg} = = 2\sqrt{\frac{2RT}{\pi M}} = 1.59577\sqrt{\frac{RT}{M}}$$

(b) The root-mean squared speed $v_{\rm rms}$

$$v_{rms}^{2} = \left\langle v^{2} \right\rangle = \frac{3RT}{M}$$

or

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{M}} = 1.73205 \sqrt{\frac{RT}{M}}$$

((Note)) The definition of v_{rms} v_{rms}^{2} is defined by

$$v_{rms}^{2} = \langle (\mathbf{v} - \langle \mathbf{v} \rangle) \cdot (\mathbf{v} - \langle \mathbf{v} \rangle) \rangle = \langle \mathbf{v} \cdot \mathbf{v} \rangle = \langle v^{2} \rangle$$

where

< v >= 0.

We note that

$$\frac{1}{2}mv_{rms}^{2}=\frac{3k_{B}T}{2}.$$

(c)

$$\langle v^3 \rangle = 8 \sqrt{\frac{2}{\pi}} (\frac{RT}{M})^{3/2} = 6.38308 (\frac{RT}{M})^{3/2}$$

(d)

$$\left\langle v^4 \right\rangle = 15\left(\frac{RT}{M}\right)^2$$

In summary,

$$v_{mp} < v_{avg} < v_{rms}$$

or

$$1 < \frac{v_{avg}}{v_{mp}} (= 1.128) < \frac{v_{rms}}{v_{mp}} (= \frac{\sqrt{6}}{2} = 1.225)$$

3.3 Calculation by Mathematica

Maxwell distribution of velocities

$$\mathbf{f} = \mathbf{4} \pi \left(\frac{\mathbf{M}}{2 \pi \mathbf{R} \mathbf{T}}\right)^{3/2} \mathbf{v}^{2} \mathbf{E} \mathbf{x} \mathbf{p} \left[-\frac{\mathbf{M} \mathbf{v}^{2}}{2 \mathbf{R} \mathbf{T}}\right]$$
$$e^{-\frac{\mathbf{M} \mathbf{v}^{2}}{2 \mathbf{R} \mathbf{T}}} \sqrt{\frac{2}{\pi}} \left(\frac{\mathbf{M}}{\mathbf{R} \mathbf{T}}\right)^{3/2} \mathbf{v}^{2}$$

$$\frac{eq1 = D[f, v] // Simplify}{e^{-\frac{M v^2}{2 R T}} \sqrt{\frac{2}{\pi}} \left(\frac{M}{R T}\right)^{5/2} v \left(2 R T - M v^2\right)}{M}$$

Maximum point of f

eq2 = Solve[eq1 == 0, v];
fmax = f /. eq2[[3]] // Simplify

$$2\sqrt{\frac{2}{\pi}}\sqrt{\frac{M}{RT}}$$

Calculation for the average of \boldsymbol{v}^n

$$f1[n_] := 4 \pi \left(\frac{M}{2 \pi R T}\right)^{3/2} v^{2+n} Exp\left[-\frac{M v^2}{2 R T}\right]$$
$$J1[n_] := Simplify\left[\int_0^\infty f1[n] dv, \\ \{M > 0, R > 0, T > 0\}\right]$$

eq1 =

$$\begin{array}{rcl}
1 & 2 \sqrt{\frac{2}{\pi}} & \sqrt{\frac{R T}{M}} \\
2 & \frac{3 R T}{M} \\
3 & \frac{8 \sqrt{\frac{2}{\pi}} & (M R T)^{3/2}}{M^3} \\
4 & \frac{15 R^2 T^2}{M^2} \\
5 & 48 \sqrt{\frac{2}{\pi}} & \left(\frac{R T}{M}\right)^{5/2} \\
6 & \frac{105 R^3 T^3}{M^3} \\
7 & 384 \sqrt{\frac{2}{\pi}} & \left(\frac{R T}{M}\right)^{7/2} \\
8 & \frac{945 R^4 T^4}{M^4} \\
9 & 3840 \sqrt{\frac{2}{\pi}} & \left(\frac{R T}{M}\right)^{9/2} \\
10 & \frac{10 395 R^5 T^5}{M^5}
\end{array}$$

3.4 Molecular speed

((Molecular velocities))

As is shown above, the most probable speed is given by

$$v_{mp} = 1.41421 \sqrt{\frac{RT}{M}}$$

From this form, we get the relation

$$\sqrt{M}v_{mp} = \sqrt{2}\sqrt{RT}$$

where

$$R = 8.314472 \text{ J/mol K}$$

When $M (kg/mol) = M_0 (g/mol)$, and $v_{mp} (m/s) = v_{mp}^0 (0.1 \text{ km/s})$,

$$M = 10^{-3} M_0, \qquad v_{\rm mp} = 10^2 v_{\rm mp}^0.$$

Then we have

$$\sqrt{10^{-3}M_0} 10^2 v_{mp}^{\ 0} = \sqrt{2}\sqrt{RT}$$
$$\sqrt{M_0} v_{mp}^{\ 0} = \frac{\sqrt{2}}{10^2\sqrt{10^{-3}}}\sqrt{RT} = \frac{1}{\sqrt{5}}\sqrt{RT}$$

Since $v_{rms}^{0} = \frac{\sqrt{6}}{2} v_{mp}^{0}$, we have

$$\sqrt{M_0} v_{rms}^{0} = \frac{\sqrt{6}}{2\sqrt{5}} \sqrt{RT}$$

which is equal to 26.095 at T = 273 K.

Table

The root-mean square speed for various gases (experimental values at T = 273 K)

$$v_{mp}^{0} (0.1 \text{ km/s}) \quad v_{avg}^{0} (0.1 \text{ km/s}) \quad M_{0} (g/\text{mol}) \qquad v_{rms}^{-0} \sqrt{M_{0}}$$
H₂ 18.4 16.9 2.0158 26.0

He	13.1	12.1	4.003	26.2
H_2O	6.2	5.7	18	26.30
Ne	5.8	5.3	20.18	26.05
N_2	4.9	4.5	28	25.93
O_2	4.6	4.2	32	26.02
Ar	4.3	4.0	39.95	27.18
Kr	2.86	2.63	83.9	26.20
Xe	2.27	2.09	131.3	26,0

((Example)) Calculation of v_{mp}, v_{avg}, and v_{rms}

H₂:

 $M = 2.0 \text{ g/mol} = 2.0 \text{ x } 10^{-3} \text{ kg/mol}$ T = 300 K $v_{mp} = 1.579 \text{ x } 10^3 \text{ m/s}$ $v_{avg} = 1.782 \text{ x } 10^3 \text{ m/s}$ $v_{rms} = 1.934 \text{ x } 10^3 \text{ m/s}$



3.5 Zartman-Ko experiment

A beam of molecules that emerged from a slit in the wall of an oven provided that basis of a direct test of the Maxwell-Boltzmann velocity distribution. This experiment, performed in the early 1930s by I.F. Zartman and C.C. Ko, made use of the apparatus shown in Fig. The oven contains Bi (bismuth) vapor at about 800°C, some of which escapes through a slit and is collimated by another slit a short distance away. Above the second slit is a drum that rotates about a horizontal axis at 6,000 rpm. At those instants when the slit in the drum faces the Bi beam, a burst of molecules centers the drum. These molecules reach the opposite face of the drum, where a glass plate is attached, at various times, depending upon their speeds. Because the drum is turning, the faster and slower molecules strike different parts of the plate. From the resulting distribution of deposited Bi on the plate it is possible to infer the distribution of speeds in the beam, and this distribution agrees with the prediction of Maxwell-Boltzmann statistics.



3.6 Neutron diffraction

3.6.1 Moderator

Nuclear reactors provide a copious source of thermal neutrons. To a reasonable approximation, neutrons produced by nuclear fission are moderated within the reactor to form a gas with a Maxell-Boltzmann distribution of speeds corresponding to a temperature equal to that of the moderating material. This moderating material is typically light or heavy water at a temperature somewhat above 300 K, though if more or less energetic neutrons are required it is possible to locally heat or cool a part of the moderator and so produce a hot source or a cold source. Figure plots the Maxwellian flux distribution coming from moderators at 320 K and at 25 K. The peak flux for a temperature of 320 K occurs at a wavenumber of 4.5 Å⁻¹, which corresponds to a neutron wavelength of 1.40 Å. By cooling the moderator to 25 K the peak flux is shifted to a wavenumber of 1.25 Å⁻¹, corresponding to a neutron wavelength of 5.0 Å. These wavelengths are of the order of interatomic distances, so that neutrons are well suited to probe properties on an atomic length scale.



Fig. Flux distribution in the beam of neutrons from a moderator at 25 K and from a moderator at 320 K. The distributions are normalized to have the same total flux (M.F. Collins, Magnetic Critical Scattering, Oxford University Press 1989).

3.6.2 Neutron temperature

In the thermal neutron energy range, the velocity distribution of neutrons follows the Maxwell-Boltzmann distribution according to which the most probable speed of the neutrons is:

 $\begin{array}{ll} 1 \ \mathrm{eV} = 1.602176487 \ \mathrm{x} \ 10^{-19} \ \mathrm{J} \\ m_{\mathrm{n}} = 1.674927211 \ \mathrm{x} \ 10^{-27} \ \mathrm{kg} \\ N_{\mathrm{A}} = 6.02214179 \ \mathrm{x} \ 10^{23} \\ \mathrm{k}_{\mathrm{B}} = 1.380650410 \ \mathrm{x} \ 10^{-23} \ \mathrm{J/mol} \ \mathrm{K} \\ R = 8.314472 \ \mathrm{J/K} \\ M_{n} = m_{n} N_{A} = 1.00728 \ \mathrm{x} \ 10^{-3} \ \mathrm{kg} \end{array} \qquad (\mathrm{molar\ mass\ of\ neutrons})$

At room temperature (20 °C = 293 K)

 $v_{mp} = 2199.34 \text{ m/s}$ $v_{avg} = 2481.69 \text{ m/s}$ $E_{mp} = 25.25 \text{ meV}.$ $E_{avg} = 27.4299 \text{ meV}$

At 25 K (liquid hydrogen temperature)

 $v_{mp} = 642.433 \text{ m/s}$ $v_{avg} = 724.908 \text{ m/s}$ $E_{mp} = 2.15434 \text{ meV}.$ $E_{avg} = 2.74299 \text{ meV}$

At 4.2 K (liquid helium temperature)

 $v_{mp} = 263.319 \text{ m/s}$ $v_{avg} = 297.124 \text{ m/s}$ $E_{mp} = 0.361928 \text{ meV}$ $E_{avg} = 0.460822 \text{ meV}$

The *neutron temperature*, also called the neutron energy, indicates a free neutron's kinetic energy, usually given in eV. The term temperature is used, since hot, thermal and cold neutrons are moderated in a medium with a certain temperature. The neutron energy distribution is then adopted to the Maxwell-Boltzmann distribution known for thermal motion. Qualitatively, the higher the temperature, the higher the kinetic energy is of the free neutron. Kinetic energy, speed and wavelength of the neutron are related through the De Broglie relation.

Fast neutrons have an energy greater than 1 eV, 0.1 MeV or approximately 1 MeV, depending on the definition.
Slow neutrons have an energy less than or equal 0.4 eV.
Epithermal neutrons have an energy from 0.025 to 1 eV.
Hot neutrons have an energy of about .2 eV.
Thermal neutrons have an energy from 5x10⁻⁵ eV to 0.025 eV.
Very cold neutrons have an energy from 3x10⁻⁷ eV to 5x10⁻⁵ eV.
Ultra cold neutrons have an energy less than 3x10⁻⁷ eV.

The wanelength of the neutron is given by

$$\lambda_n = \frac{h}{m_n v_{mp}} = \frac{30.7895}{\sqrt{T(K)}} \text{ Å}$$

6.15789 Å at 25 K 15.0237 Å at 4.2 K

4 Equipartition of energy

The energy $\varepsilon = \frac{3}{2}k_BT$ is ascribed to a contribution $\frac{1}{2}k_BT$ from each "degree of freedom" of each particle, where the number of degrees of freedom is the number of dimensions of the space in which the atoms move: 3 in this example.

$$\frac{1}{2}mv_{rms}^{2} = \left\langle \frac{1}{2}mv^{2} \right\rangle = \frac{1}{2}m\frac{3k_{B}T}{m} = \frac{3}{2}k_{B}T$$
$$< v^{2} > = < v_{x}^{2} > + < v_{y}^{2} > + < v_{z}^{2} > = 3 < v_{x}^{2} >$$

or

$$<\frac{1}{2}mv_{x}^{2} >= \frac{1}{2}k_{B}T$$

$$<\frac{1}{2}mv_{y}^{2} >= \frac{1}{2}k_{B}T$$

$$<\frac{1}{2}mv_{z}^{2} >= \frac{1}{2}k_{B}T$$

$$<\frac{1}{2}m(v_{x}^{2} + v_{y}^{2} + v_{z}^{2}) = \frac{3}{2}k_{B}T$$

Let us now modify one of the basic assumption in the model of the ideal gas. Instead of considering a molecule to be presented as a point particle, let it be considered as two point particles separated by a given distance. This model gives a better description of diatomic gases. Such molecules can acquire kinetic energy by rotating about its center of mass, and it is therefore necessary to consider in the internal energy the contribution of rotational kinetic energy as well as the translational kinetic energy. The rotational kinetic energy of a diatomic molecules can be written as

$$K_{rot} = \frac{1}{2} I_{x'} \omega_{x'}^{2} + \frac{1}{2} I_{y'} \omega_{y'}^{2}$$

where *I* is the rotational inertia of the molecule for rotations about a particular axis. The x'y'z' coordinate system is fixed to the center of mass of the molecule. There is no kinetic energy associated with rotation about the *z*' axis, because $I_z' = 0$.

$$<\frac{1}{2}I_{x'}\omega_{x'}^{2} >= \frac{1}{2}k_{B}T$$
$$<\frac{1}{2}I_{y'}\omega_{y'}^{2} >= \frac{1}{2}k_{B}T$$

5

Heat capacity of the system with the degree of freedom (f)

The specific heat of the gas is best conceptualized in terms of the degrees of freedom of an individual molecule. The different degrees of freedom correspond to the different ways in which the molecule may store energy.

If the molecule could be entirely described using classical mechanics, then we could use the theorem of equipartition of energy to predict that each degree of freedom would have an average energy in the amount of (1/2)kT, where k_B is Boltzmann's constant and Tis the temperature. Our calculation of the heat content would be straightforward. Each molecule would be holding, on average, an energy of $(f/2)k_BT$ where f is the total number of degrees of freedom in the molecule. The total internal energy of the gas would be $(f/2)N_Ak_BT$, where N_A is the total number of molecules. The heat capacity (at constant volume) would then be a constant $(f/2)N_Ak_B$, the specific heat capacity would be $(f/2)k_B$ and the dimensionless heat capacity would be just f/2.

6 The case for diatomic molecules

With complex molecules, other contributions to internal energy must be taken into account. The number of freedom is f = 7. E = fRT. $C_V = fR = 29.1 \text{ J} / \text{mol.K}$ and $\gamma = 1.29$

(a) One possible energy is the translational motion of the center of mass.

The three degrees of freedom described above are associated with the translational motion of the molecules in 3 independent directions. (3)



(b) Rotational motion about the various axes

We can neglect the rotation around the y axis since it is negligible compared to the x and z axes. Rotational motion: 2 degrees of freedom (ω_z and ω_x). Rotational kinetic energy

$$\frac{1}{2}I\omega_{z}^{2} + \frac{1}{2}I\omega_{x}^{2}.$$
 (2)



(c) Vibration of diatomic molecules

The molecule can also vibrate. There is kinetic energy and potential energy associated with the vibrations. This adds two more degrees of freedom. (2)

$$\langle E \rangle = \langle K \rangle + \langle U \rangle = 2 \langle K \rangle = 2 \langle U \rangle = \hbar \omega \approx k_B T = 2(\frac{1}{2}k_B T)$$



7 Agreement with Experiment

At low temperatures, a diatomic gas acts like a monatomic gas $C_V=3/2$ R. At about room temperature, the value increases to $C_V=5/2$ R. This is consistent with adding rotational energy but not vibrational energy. At high temperatures, the value increases to $C_V=7/2$ R. This includes vibrational energy as well as rotational and translational



8. Mean free path *l*

8.1 Definition

The mean free path or average distance between collisions for a gas molecule may be estimated as follows. If the molecules have diameter d, then the effective cross-section for collision can be modeled by



using a circle of diameter 2d to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.



The mean free path (the mean distance per collision) could then be taken as the length of the path divided by the number of collisions.

$$l = \frac{\overline{vt}}{(\pi d^2 vt)n_V} = \frac{1}{\pi d^2 n_V}$$

Where $\pi d^2 v t$ is the volume of interaction, n_V is the number of molecules per unit volume. The problem with this expression is that the average molecular velocity is used, but the target molecules are also moving. The frequency of collisions depends upon the average relative velocity of the randomly moving molecules.



8.2 **Refinement of mean free path**

The intuitive development of the mean free path expression suffers from a significant flaw - it assumes that the "target" molecules are at rest when in fact they have a high average velocity. What is needed is the average relative velocity, and the calculation of that velocity from the molecular speed distribution yields the result.

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

since $v_1 = v_2 = v$ and

$$\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle = v_1 v_2 \langle \cos \theta \rangle = 0$$

Then the average relative velocity is given by

$$\bar{v}_{rel} = \sqrt{\left\langle \left| \mathbf{v}_1 - \mathbf{v}_2 \right|^2 \right\rangle} = \sqrt{2}v$$

which revises the expression for the effective volume swept out in time t. The resulting mean free path is

$$l = \frac{1}{\sqrt{2}\pi d^2 n_V}$$

The number of molecules per unit volume can be determined from Avogadro's number and the ideal gas law, leading to

$$n_V = \frac{N}{V} = \frac{P}{k_B T} = \frac{N_A P}{R T},$$

where

$$PV = Nk_{\rm B}T$$

Then the mean free path is obtained as

$$l = \frac{1}{\sqrt{2}\pi d^2 n_v} = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

The mean free path depends on *T*, *P*, and the diameter of gas atoms.

((Example)) Evaluation of mean free path (He atom)

d = 2.2 Å (atomic diameter) The collision cross section = $\pi d^2 = 15.2 \times 10^{-20} \text{ m}^2$ n_V (the concentration of molecules of an ideal gas at 273 K and 1 atm, which is called a Loschmidt number)

$$n_V = \frac{N_A P}{RT} = 2.6867774 \text{ x } 10^{25} \text{ atoms/m}^3$$

 $l = \frac{1}{\pi d^2 n_V} = 2.44 \text{ x } 10^{-7} \text{ m} = 2440 \text{ Å}$

The rate of collision:

$$\frac{v_{rms}}{l} = \frac{1310}{2.44 \times 10^{-7}} = 5.37 \times 10^9 \,/\,s$$

where $v_{\rm rms} = 1310$ m/s for He gas.

((Note))

Being a measure of number density, the Loschmidt constant is used to define the amagat, a practical unit of number density for gases and other substances:

1 amagat = $n_{\rm V}$ = 2.6867774×10²⁵ m⁻³,

such that the Loschmidt constant is exactly 1 amagat.

8.3 Estimation of the mean free path at high vacuum

Estimate the mean free path of an air molecule at 273 K and 1 atm, assuming it to be a sphere of diameter 4.0 x 10^{-10} m (4Å). Estimate the mean time between collisions for an oxygen molecule under these conditions, using $v = v_{rms} = 517$ m/s

$$l = \frac{RT}{\sqrt{2\pi}d^2 N_A P} = \frac{(8.31J/K)(273K)}{\sqrt{2\pi}(4 \times 10^{-10})^2 (6.02 \times 10^{23})(1.01 \times 10^5 Pa)} = 5.2342 \times 10^{-8} m$$
$$t = \frac{5.2342 \times 10^{-8} m}{517m/s} \approx 1.0 \times 10^{-10} s$$

How about the mean free path at the high vacuum?

 $P = 10^{-n}$ Torr $= 10^{-n}$ mmHg $= (10^{-n})/760$ atm $= (10^{-n})/760$ x (1.01×10^5) Pa

$$l = \frac{RT}{\sqrt{2}\pi d^2 N_A P} = \frac{(8.31J/K)(273K)}{\sqrt{2}\pi (4 \times 10 - 10)(6.02 \times 10^{23})(1.01 \times 10^5 Pa) \times \frac{10^{-n}}{760}}$$
$$= 760 \times 10^n \times 5.2342 \times 10^{-8} m = 3.978 \times 10^{n-5} m$$

For $P = 10^{-5}$ Torr (in the laboratory), we have

l = 3.978 m.

For $P = 10^{-9}$ Torr (ultrahigh vacuum), we have

l = 3978 m.

((Link))

Mean free path calculation

http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/menfre.html

9. Solution of SP-19 and Hint of HW-19.

9.1

Problem 19-17***(SP-19) (10-th edition)

Container A in Fig. holds an ideal gas at a pressure of 5.0×10^5 Pa and a temperature of 300 K. It is connected by a thin tube (and a closed valve) to container B, with four times the volume of A. Container B holds the same ideal gas at a pressure of 1.0×10^5 Pa and a temperature of 400 K. The valve is opened to allow the pressures to equalize, but the temperature of each container is maintained. What then is the pressure in the two containers?



 $\frac{Before opening valve}{P_{A} = 5.0 \text{ x } 10^{5} \text{ Pa}, \quad T_{A} = 300 \text{ K}}$ $\frac{P_{B} = 1.0 \text{ x } 10^{5} \text{ Pa}, \quad T_{B} = 400 \text{ K}, \quad V_{B} = 4 V_{A}}{P_{B} = 1.0 \text{ x } 10^{5} \text{ Pa}, \quad T_{B} = 400 \text{ K}}$

After opening valve,

$$P_{A} \rightarrow P$$
, $T_{A} = 300 \text{ K}$
 $P_{B} \rightarrow P$, $T_{B} = 400 \text{ K}$.

Before opening the valve,

$$P_{A}V_{A} = n_{A}RT_{A} \qquad \qquad n_{A} = \frac{T_{A}V_{A}}{RT_{a}}$$

$$P_{B}V_{B} = n_{B}RT_{B} \qquad \qquad n_{B} = \frac{P_{B}V_{B}}{RT_{B}}$$

After opening the valve

$$PV_{A} = n_{1}RT_{A}$$

$$PV_{B} = n_{2}RT_{B}$$

$$n_{1} = \frac{PV_{A}}{RT_{a}}$$

$$n_{2} = \frac{PV_{B}}{RT_{B}}$$

The total number of moles remains unchanged.

$$n_{A} + n_{B} = \frac{P_{A}V_{A}}{RT_{A}} + \frac{P_{B}V_{B}}{RT_{B}} = \frac{1}{R}\left(\frac{P_{A}V_{A}}{T_{a}} + \frac{P_{B}V_{B}}{T_{B}}\right)$$
$$n_{1} + n_{2} = \frac{PV_{A}}{RT_{a}} + \frac{PV_{B}}{RT_{B}} = \frac{P}{R}\left(\frac{V_{A}}{T_{a}} + \frac{V_{B}}{T_{B}}\right)$$

D V

Since $n_A + n_B = n_1 + n_2$, we have

$$P = \frac{P_A V_A T_B + P_B V_B T_A}{V_A T_B + V_B T_A} = 2.0 \times 10^5 Pa$$

9.2

Problem 19-62***(SP-19) (10-th edition)

An ideal diatomic gas, with rotation but no oscillation, undergoes an adiabatic compression. Its initial pressure and volume are 1.20 atm and 0.200 m^3 . Its final pressure is 2.40 atm. How much work is done by the gas?

((Solution)) $C_{\rm P} = 7R/2$ $C_{\rm V} = 5R/2$ $\gamma = C_P / C_V = 7/5 = 1.40$



 $P_{f} = 2.40 \text{ atm.}$ $P_{i} = 1.20 \text{ atm}$ $V_{i} = 0.2 \text{ m}^{3}$ Adiabatic process

$$PV^{\gamma} = P_i V_i^{\gamma} = P_f V_f^{\gamma}$$
$$\frac{V_f}{V_i} = \left(\frac{P_i}{P_f}\right)^{1/\lambda} = 2^{-1/\gamma}$$
$$V_f = 2^{-1/1.40} V_i = 0.122 m^3$$

The work done on the system is

$$\Delta W = -\int_{V_i}^{V_f} P dV = -\int_{V_i}^{V_f} P_i V_i^{\gamma} V^{-\gamma} dV$$

$$= -\frac{P_i V_i^{\gamma}}{1 - \gamma} [V_f^{1 - \gamma} - V_i^{1 - \gamma}]$$

$$= -\frac{P_f V_f^{\gamma}}{1 - \gamma} V_f^{1 - \gamma} + \frac{P_i V_i^{\gamma}}{1 - \gamma} V_i^{1 - \gamma}$$

$$= -\frac{P_f V_f}{1 - \gamma} + \frac{P_i V_i}{1 - \gamma}$$

$$= \frac{1}{\gamma - 1} (P_f V_f - P_i V_i)$$

$$= -1.3312 \times 10^4 J$$

Then the work done by the system is $+ 1.2156 \times 10^4 \text{ J}.$

Problem 19-63***(SP-19) (10-th edition)

Figure shows a cycle undergone by 1.00 mol of an ideal monatomic gas. The temperatures are $T_1 = 300$ K, $T_2 = 600$ K, and $T_3 = 455$ K. For $1 \rightarrow 2$, what are (a) heat Q, (b) the change in internal energy ΔE_{int} , and (c) the work done W? For $2 \rightarrow 3$, what are (j) Q, (e) ΔE_{int} , and (f) W? For $3 \rightarrow 1$, what are (g) Q, (h) ΔE_{int} , and (i) W? For full cycle, what are (j) Q, (k) ΔE_{int} , and (j) W? The initial pressure at point 1 is 1.00 atm (= 1.013 x 10⁵ Pa). What are the (m) volume and (n) pressure at point 2 and the (o) volume and (p) pressure at point 3?



<u>Path 1-2</u> (a), (b), and (c)

$$\Delta Q = C_V \Delta T = 12.47 \times 300 = 3741.5J$$
$$\Delta W = 0$$
$$\Delta E = \Delta Q + \Delta W = 3741.5J$$

Path 2-3 (adiabatic) (d), (e), and (f)

$$\Delta Q = 0$$

$$\Delta E = C_V \Delta T = 12.47 \times (455 - 600) = -1808.2J$$

$$\Delta W = \Delta E - \Delta Q = -1808.2J$$

Path 3-1

(g), (h), and (i)

$$\Delta Q = C_P \Delta T = 20.78 \times (300 - 455) = -3220.9J$$

$$\Delta E = C_V \Delta T = 12.47 \times (300 - 455) = -1932.9J$$

$$\Delta W = \Delta E - \Delta Q = 1288J$$

(j)

$$\Delta Q_{total} = 3742 + 0 - 3220 = 520J$$

(k)
$$\Delta E_{total} = 3742 - 1808 - 1933 = 0$$

(1)

$$\Delta W_{total} = 0 - 1808 + 1288 = -520J$$

(m)

$$V_1 = \frac{RT_1}{P_1} = \frac{8.31447 \times 300}{1.01325 \times 10^5} = 2.46 \times 10^{-2} \, m^3$$

(n)

$$P_2 = \frac{RT_2}{V_2} = \frac{8.31447 \times 600}{2.46 \times 10^{-2}} = 2.028 \times 10^5 = 2atm$$

9.4

Problem 19-11** (HW-19) (10-th edition)

Air that initially occupies 0.140 m^3 at a gauge pressure of 103.0 kPa is expanded isothermally to a pressure of 101.3 kPa and then cooled at constant pressure until it reaches its initial volume. Compute the work done by the air. (Gauge pressure is the difference between the actual pressure and atmospheric pressure.)



((My solution)) 1 atm = 1.01325 x 10⁵ Pa $V_i = 0.140 \text{ m}^3$, $P_i = 103.0+101.325 = 204.325 \text{ kPa}$ $P_f = 101.3 \text{ kPa}$

Path 1-2 (isothermal process)

$$P_i V_i = P_f V_f$$
$$W_{1-2} = -\int_{V_i}^{V_f} P dV$$

 $\frac{\text{Path 2-3 (isobaric process)}}{W_{2-3} = -P_f(V_i - V_f)}$

9.5

Problem 19-23** (SP-19) (10-th edition)

A beam of hydrogen molecules (H₂) is directed toward a wall, at an angle of 55° with the normal to the wall. Each molecule in the beam has a speed of 1.0 km/s and a mass of 3.3×10^{-24} g. The beam strikes the wall over an area of 2.0 cm², at the rate of 10^{23} molecules per second. What is the beam's pressure on the wall?

 $A = 2.0 \text{ cm}^2 = 2.0 \text{ x } 10^{-4} \text{ m}^2$ m = 3.3 x 10⁻²⁷ kg, $N_0 = 10^{23} \text{ moles/s}, v = 1.0 \text{ x } 10^3 \text{ m/s}$

 $N_0 \Delta t$ is the number of particles striking the wall over an area during the time Δt

The change of the linear momentum along the z axis,

$$\Delta p_z = N_0 \Delta t (2mv \cos \theta) = F_z \Delta t$$

9.6

Problem 19-37** (SP-19) (10-th edition)

Figure shows a hypothetical speed distribution for a sample of N gas particles (note that

$$P(v) = 0$$

for $v > 2v_0$. What are the values of (a) av_0 , (b) v_{avg}/v_0 , and (c) v_{rms}/v_0 ? (d) What fraction of the particles has a speed between 1.5 v_0 and 2.0 v_0 ?



9.7

Problem 19-57** (SP-19) (10-th edition)

The volume of an ideal gas is adiabatically reduced from 200 L to 74.3 L. The initial pressure and temperature are 1.00 atm and 300 K. The final pressure is 4.00 atm. (a) Is

the gas monatomic, diatomic, or polyatomic? (b) What is the final temperature? (c) How many moles are in the gas?

((Solution))

```
T_{i} = 300 \text{ K}, \quad V_{i} = 200 \text{ L}, \quad V_{f} = 74.3 \text{ L}
P_{i} = 1 \text{ atm}, \quad P_{f} = 4.0 \text{ atm}
1 \text{ L} = 1000 \text{ cm}^{3} = 10^{-3} \text{ m}^{3}
P_{f}
P_{f}
P_{i}
V_{f}
V_{i}
V_{i}
```

For the adiabatic process, we have the relation

$$P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

$$\frac{P_f}{P_i} = \left(\frac{V_i}{V_f}\right)^{\gamma}$$

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{f}$$

$$\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i} = nR$$

10.5

Problem 19-70 (SP-19) (10-th edition)

An ideal gas, at initial pressure T_1 and initial volume 2.0 m³, is expanded adiabatically to a volume of 4.0 m³, then expanded isothermally to a volume of 10 m³, and then compressed adiabatically back to T_1 . What is its final volume?



 $V_1 = 2.0 \text{ m}^3$, $V_2 = 4.0 \text{ m}^3$, $V_3 = 10.0 \text{ m}^3$

Adiabatic process (path 1-2)

$$\begin{aligned} P_1 V_1^{\gamma} &= P_2 V_2^{\gamma} \\ \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \end{aligned}, \end{aligned}$$

Isothermal process (path 2-3)

$$T_2 = T_3$$
$$P_2 V_2 = P_3 V_3$$

Adiabatic process (path 3-4)

$$\frac{P_{3}V_{3}^{\gamma} = P_{4}V_{4}^{\gamma}}{\frac{P_{3}V_{3}}{T_{3}} = \frac{P_{3}V_{3}}{T_{4}}}$$

Isothermal process (path 4-1)

$$T_4 = T_1$$

$$P_4 V_4 = P_1 V_1$$

10.6

Problem 19-81 (HW-19) (10-th edition)

An ideal gas is taken through a complete cycle in three steps; adiabatic expansion with work equal to 125 J, isothermal contraction at 325 K, and increases in pressure at

constant volume. (a) Draw a P-V diagram for the three steps. (b) How much energy is transferred as heat in step 3, and (c) is it transferred to or from the gas?



Adiabatic process (path-1) $\Delta Q_1 = 0$ Isothermal process (path-2) $\Delta E_2 = 0$ Isobaric process (path-3) $\Delta W_3 = 0$ $\Delta E = 0 = \Delta E_1 + \Delta E_2 + \Delta E_3$ (Joule's law)

11. Link

Mean free path http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/menfre.html

Lecture note (University of Rochester) http://teacher.pas.rochester.edu/phy121/LectureNotes/Chapter18/Chapter18.html

Kinetic theory

http://en.wikipedia.org/wiki/Kinetic_theory

Maxwell-Boltzmann distribution

http://en.wikipedia.org/wiki/Maxwell-Boltzmann distribution

Molecular speed

http://hyperphysics.phy-astr.gsu.edu/Hbase/kinetic/kintem.html