

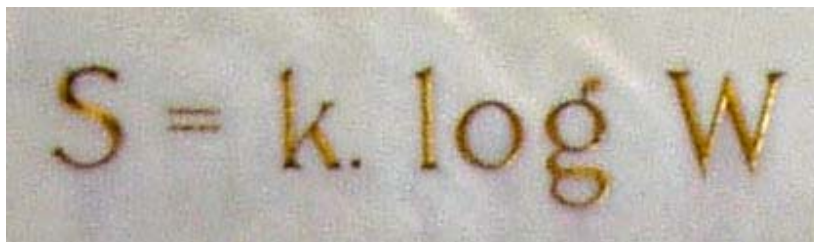
Maxwell-Boltzmann distribution function
Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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The kinetic theory of gases

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.



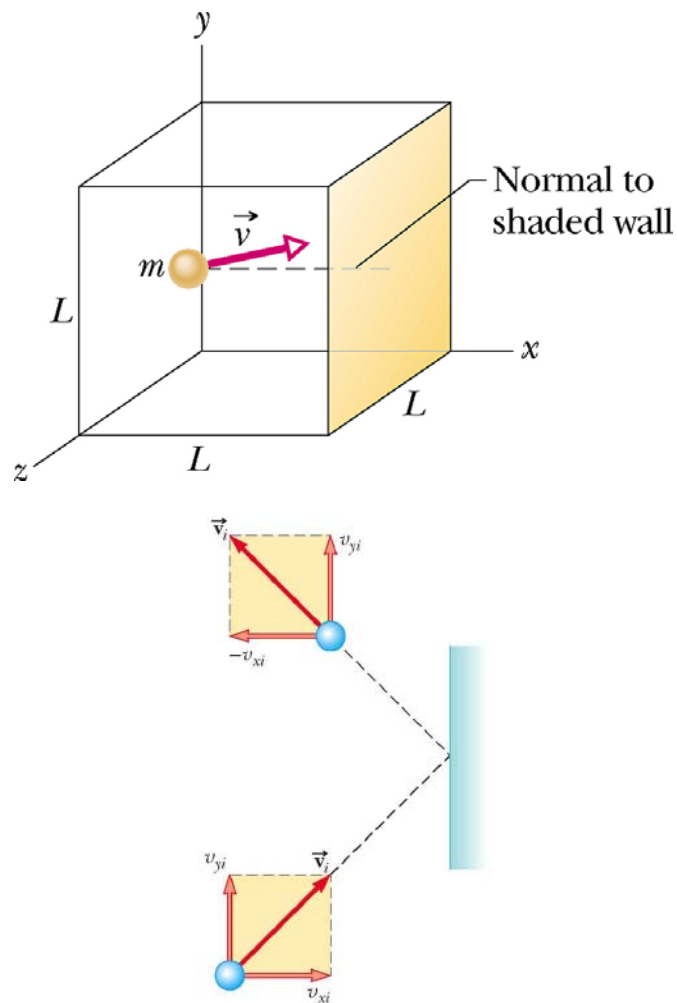
Boltzmann's equation-carved in stone.

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."

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

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

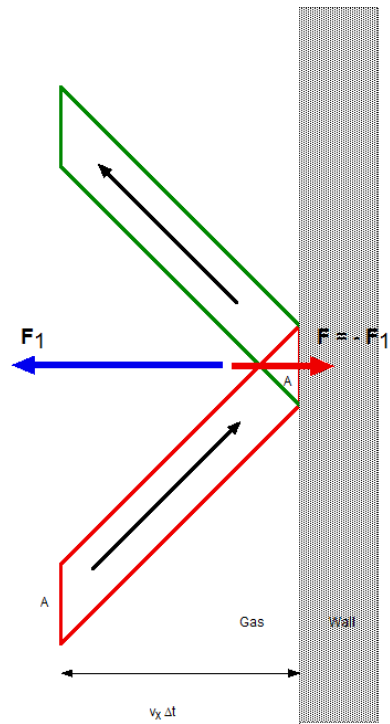
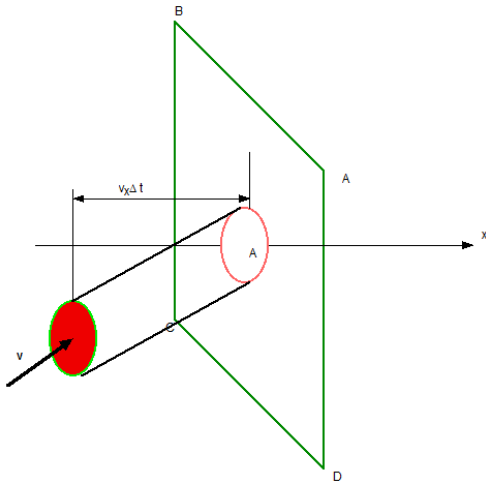
is exerted on the wall (as an impulse), contributing to the pressure. Here we assume that the number of molecules (per unit volume), which have velocity components of $v_x - (v_x+dv_x)$, $v_y - (v_y+dv_y)$, and $v_z - (v_z+dv_z)$ is given by

$$\frac{1}{V} N(\mathbf{v})d^3\mathbf{v} = \frac{1}{V} N(v_x, v_y, v_z)dv_x dv_y dv_z$$

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

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

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

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

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

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

Then we have

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

This equation is called a Bernoulli's equation.

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

$$PV = Nk_B T,$$

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

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

Note that ε is the average energy of each particle.

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

3 Maxwell velocity distribution $f(\mathbf{v})$

3.1 Determination of the form $N(\mathbf{v})$

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

$$N(\mathbf{v}) = G(v^2) = g(v_x)g(v_y)g(v_z) \quad (1)$$

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

$$\begin{aligned} G(v^2) &= G(v_x^2 + v_y^2 + v_z^2) = g(v_x)g(v_y)g(v_z) \\ &= \frac{1}{\alpha^6} G(v_x^2)G(v_y^2)G(v_z^2) \end{aligned}$$

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

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

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

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

where

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

The final form of $N(\mathbf{v})$ is obtained as

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

Now we determine the values of A and a .

(a) Determination of A

$$\begin{aligned} N &= \iiint N(\mathbf{v}) d^3\mathbf{v} \\ &= \iiint A \exp[-a(v_x^2 + v_y^2 + v_z^2)] dv_x dv_y dv_z \\ &= A \left[\int \exp(-av_x^2) dv_x \right]^3 \\ &= A \left(\frac{\pi}{a} \right)^{3/2} \end{aligned}$$

or

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

where

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

((Mathematica))

$$J[n_] := \int_{-\infty}^{\infty} x^n \text{Exp}[-a x^2] dx // \text{Simplify}[\#, a > 0] \&$$

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

0	$\frac{\sqrt{\pi}}{\sqrt{a}}$
2	$\frac{\sqrt{\pi}}{2 a^{3/2}}$
4	$\frac{3 \sqrt{\pi}}{4 a^{5/2}}$
6	$\frac{15 \sqrt{\pi}}{8 a^{7/2}}$
8	$\frac{105 \sqrt{\pi}}{16 a^{9/2}}$
10	$\frac{945 \sqrt{\pi}}{32 a^{11/2}}$

(b) Determination of a

The total energy $\langle E \rangle$ is given by

$$\begin{aligned} \langle E \rangle &= \iiint \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) N(\mathbf{v}) dv_x dv_y dv_z \\ &= \iiint \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) A \exp[-a(v_x^2 + v_y^2 + v_z^2)] dv_x dv_y dv_z \\ &= \int \frac{1}{2} m v^2 A \exp(-a v^2) 4\pi v^2 dv \\ &= \frac{1}{2} m A 4\pi \int_0^{\infty} v^4 \exp(-a v^2) dv \\ &= \frac{1}{2} m A 4\pi \frac{1}{2} \int_{-\infty}^{\infty} v^4 \exp(-a v^2) dv \\ &= \frac{1}{2} m A 4\pi \frac{1}{2} \frac{3\sqrt{\pi}}{4a^{5/2}} \\ &= m A \frac{3\pi^{3/2}}{4a^{5/2}} \end{aligned}$$

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 $v + dv$,

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$d^3\mathbf{v} = dv_x dv_y dv_z = 4\pi v^2 dv$$

Then we have

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

From this equation, the value of a is determined as

$$a = \frac{m}{2k_B T}$$

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

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

We define $n(\mathbf{v})$ as

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

with

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

- (1) $n(\mathbf{v})d\mathbf{v}$ 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

$$N_A m = M \text{ (the molar mass)}$$

$$N_A k_B = R \text{ (gas constant),}$$

$n(\mathbf{v})$ can be rewritten as

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

The function $n(\mathbf{v})$ 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

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

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))

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

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

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}} = 1.41421 \sqrt{\frac{RT}{M}} \quad (\text{most probable speed})$$

((Note))

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

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

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

The distribution function is normalized as

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

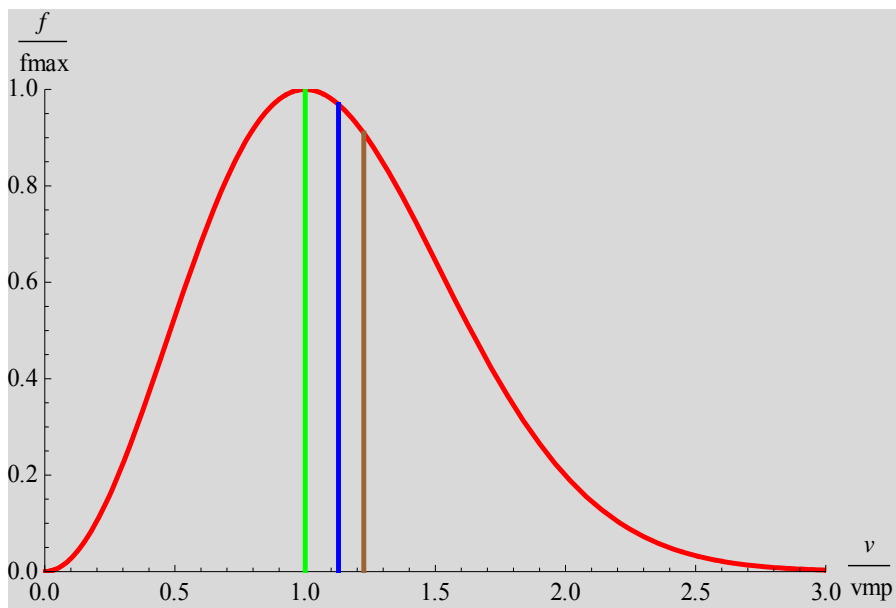


Fig. Plot of the normalized $f(v)/f_{\max}$ as a function of a normalized v/v_{mp} .

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

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

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

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

or

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

(c)

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

(d)

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

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

$$f = 4 \pi \left(\frac{M}{2 \pi R T} \right)^{3/2} v^2 \text{Exp} \left[-\frac{M v^2}{2 R T} \right]$$

$$e^{-\frac{M v^2}{2 R T}} \sqrt{\frac{2}{\pi}} \left(\frac{M}{R T} \right)^{3/2} v^2$$

eq1 = D[f, v] // Simplify

$$\frac{e^{-\frac{M v^2}{2 R T}} \sqrt{\frac{2}{\pi}} \left(\frac{M}{R T} \right)^{5/2} v (2 R T - M v^2)}{M}$$

Maximum point of f

eq2 = Solve[eq1 == 0, v];

fmax = f /. eq2[[3]] // Simplify

$$\frac{2 \sqrt{\frac{2}{\pi}} \sqrt{\frac{M}{R T}}}{e}$$

Calculation for the average of v^n

$$f1[n_] := 4 \pi \left(\frac{M}{2 \pi R T} \right)^{3/2} v^{2+n} \text{Exp} \left[-\frac{M v^2}{2 R T} \right]$$

$$J1[n_] := \text{Simplify} \left[\int_0^\infty f1[n] dv, \{M > 0, R > 0, T > 0\} \right]$$

eq1 =

Table[{n, J1[n]}, {n, 1, 10}] //
Simplify // TableForm

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	$\frac{10395 R^5 T^5}{M^5}$

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 km/s),

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

Then we have

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

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 $T = 273 \text{ K}$.

Table

The root-mean square speed for various gases (experimental values at $T = 273 \text{ K}$)

	v_{mp}^0 (0.1 km/s)	v_{avg}^0 (0.1 km/s)	M_0 (g/mol)	$v_{rms}^0 \sqrt{M_0}$
H ₂	18.4	16.9	2.0158	26.0

He	13.1	12.1	4.003	26.2
H ₂ O	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:

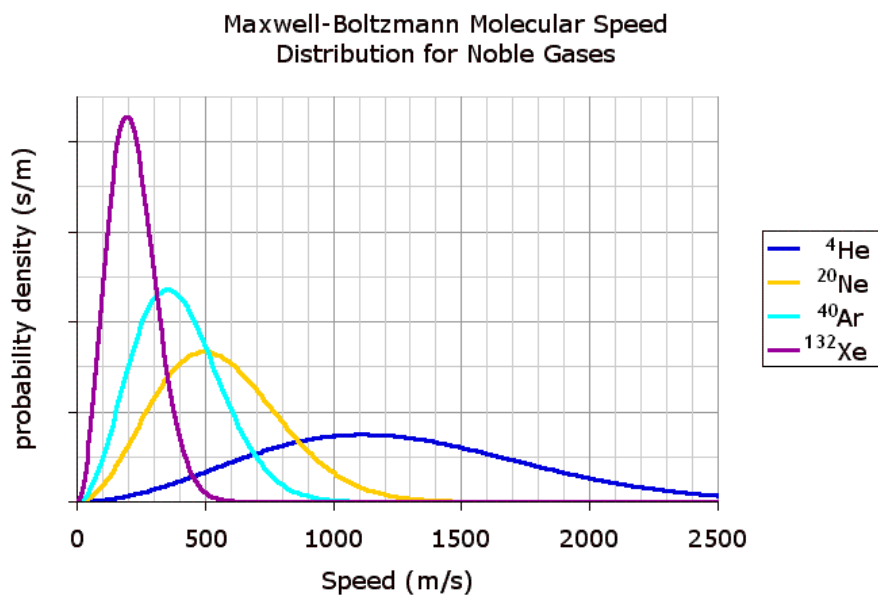
$$M = 2.0 \text{ g/mol} = 2.0 \times 10^{-3} \text{ kg/mol}$$

$$T = 300 \text{ K}$$

$$v_{mp} = 1.579 \times 10^3 \text{ m/s}$$

$$v_{avg} = 1.782 \times 10^3 \text{ m/s}$$

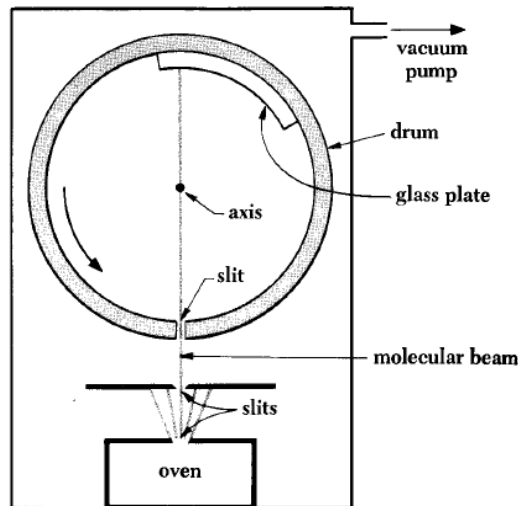
$$v_{rms} = 1.934 \times 10^3 \text{ m/s}$$



3.5 Zartman-Ko experiment

A beam of molecules that emerged from a slit in the wall of an oven provided the 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 Maxwell-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 \AA^{-1} , which corresponds to a neutron wavelength of 1.40 \AA . By cooling the moderator to 25 K the peak flux is shifted to a wavenumber of 1.25 \AA^{-1} , corresponding to a neutron wavelength of 5.0 \AA . These wavelengths are of the order of interatomic distances, so that neutrons are well suited to probe properties on an atomic length scale.

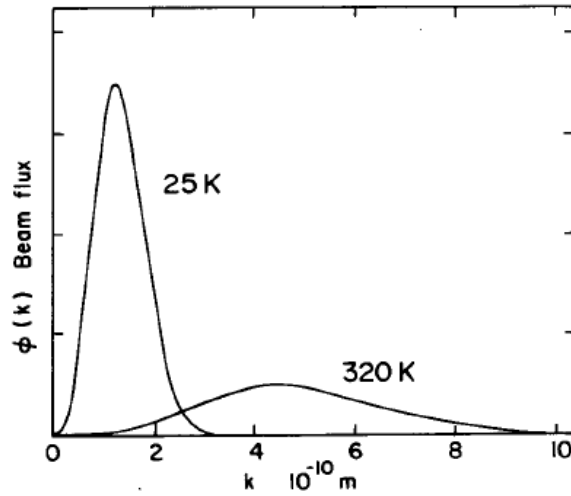


Fig. Flux distribution in the beam of neutrons from a moderator at 25 K and from a moderator at 320 K. The distributions are normalized to have the same total flux (M.F. Collins, Magnetic Critical Scattering, Oxford University Press 1989).

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:

$$\begin{aligned}
 1 \text{ eV} &= 1.602176487 \times 10^{-19} \text{ J} \\
 m_n &= 1.674927211 \times 10^{-27} \text{ kg} && \text{(mass of neutron)} \\
 N_A &= 6.02214179 \times 10^{23} \\
 k_B &= 1.380650410 \times 10^{-23} \text{ J/mol K} && \text{(Boltzmann constant)} \\
 R &= 8.314472 \text{ J/K} && \text{(gas constant)} \\
 M_n &= m_n N_A = 1.00728 \times 10^{-3} \text{ kg} && \text{(molar mass of neutrons)}
 \end{aligned}$$

At room temperature (20 °C = 293 K)

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

At 25 K (liquid hydrogen temperature)

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

At 4.2 K (liquid helium temperature)

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

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 of about 0.025 eV.

Cold neutrons have an energy from 5×10^{-5} eV to 0.025 eV.

Very cold neutrons have an energy from 3×10^{-7} eV to 5×10^{-5} eV.

Ultra cold neutrons have an energy less than 3×10^{-7} eV.

The wavelength of the neutron is given by

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

$$1.79874 \text{ \AA at } 293 \text{ K}$$

$$6.15789 \text{ \AA at } 25 \text{ K}$$

$$15.0237 \text{ \AA at } 4.2 \text{ K}$$

4 Equipartition of energy

The energy $\varepsilon = \frac{3}{2} k_B T$ is ascribed to a contribution $\frac{1}{2} k_B T$ 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.

$$\begin{aligned}
\frac{1}{2} m v_{rms}^2 &= \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{1}{2} m \frac{3 k_B T}{m} = \frac{3}{2} k_B T \\
\langle v^2 \rangle &= \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle
\end{aligned}$$

or

$$\begin{aligned} \langle \frac{1}{2}mv_x^2 \rangle &= \frac{1}{2}k_B T \\ \langle \frac{1}{2}mv_y^2 \rangle &= \frac{1}{2}k_B T \\ \langle \frac{1}{2}mv_z^2 \rangle &= \frac{1}{2}k_B T \\ \langle \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \rangle &= \frac{3}{2}k_B T \end{aligned}$$

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 $I_z' = 0$.

$$\begin{aligned} \langle \frac{1}{2}I_x\omega_x'^2 \rangle &= \frac{1}{2}k_B T \\ \langle \frac{1}{2}I_y'\omega_y'^2 \rangle &= \frac{1}{2}k_B T \end{aligned}$$

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.

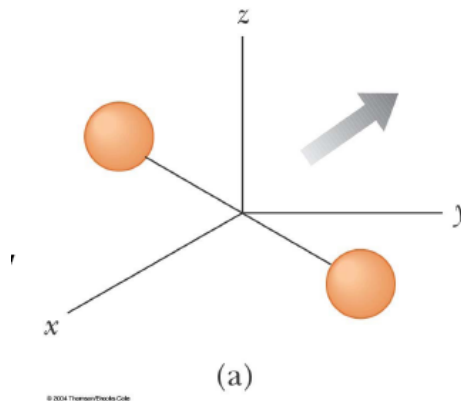
If the molecule could be entirely described using classical mechanics, then we could use the theorem of equipartition of energy to predict that each degree of freedom would have an average energy in the amount of $(1/2)k_B T$, where k_B is Boltzmann's constant and T is the temperature. Our calculation of the heat content would be straightforward. Each molecule would be holding, on average, an energy of $(f/2)k_B T$ where f is the total number of degrees of freedom in the molecule. The total internal energy of the gas would be $(f/2)N_A k_B T$, where N_A is the total number of molecules. The heat capacity (at constant volume) would then be a constant $(f/2)N_A k_B$, 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 $f = 7$. $E = fRT$. $C_V = fR = 29.1 \text{ J / mol.K}$ and $\gamma = 1.29$

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

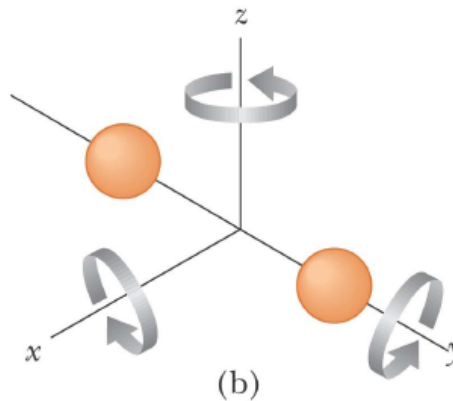
The three degrees of freedom described above are associated with the translational motion of the molecules in 3 independent directions. (3)



(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

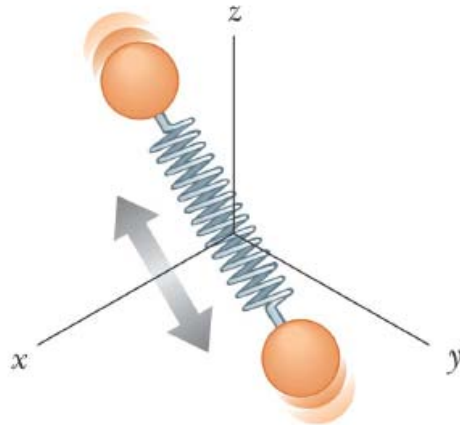
$$\frac{1}{2}I\omega_z^2 + \frac{1}{2}I\omega_x^2. \quad (2)$$



(c) Vibration of diatomic molecules

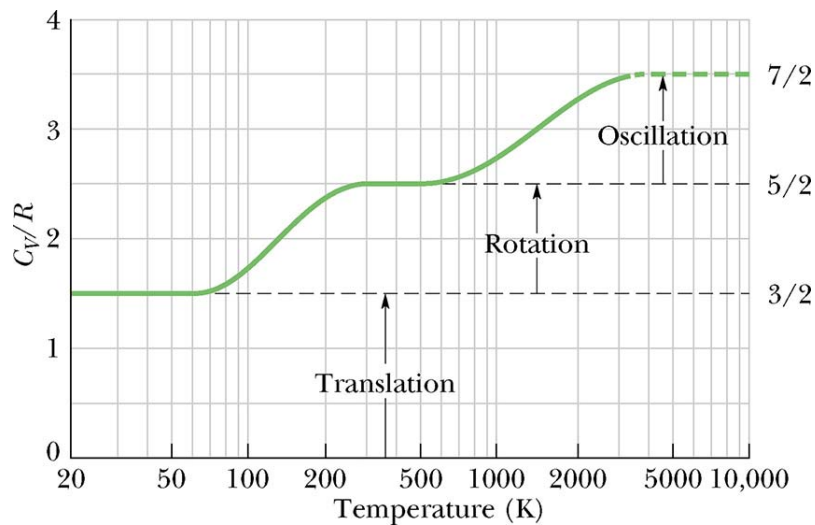
The molecule can also vibrate. There is kinetic energy and potential energy associated with the vibrations. This adds two more degrees of freedom. (2)

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



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



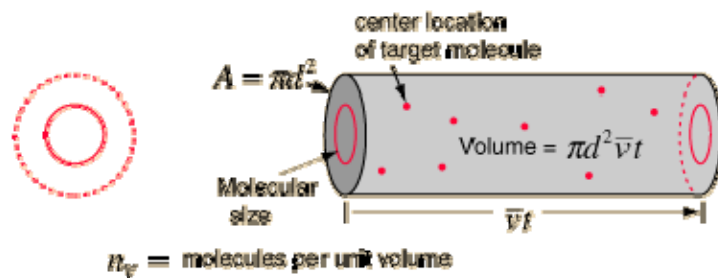
8. Mean free path l

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



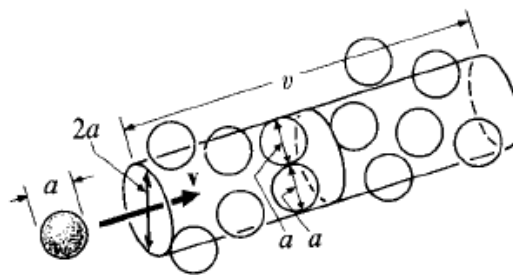
using a circle of diameter $2d$ to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t , the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.



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.

$$l = \frac{\bar{v}t}{(\pi d^2 \bar{v}t)n_v} = \frac{1}{\pi d^2 n_v}$$

Where $\pi d^2 \bar{v}t$ 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

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

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

$$n_v = \frac{N}{V} = \frac{P}{k_B T} = \frac{N_A P}{RT},$$

where

$$PV = Nk_B T$$

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)

$d = 2.2 \text{ \AA}$ (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)

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

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

The rate of collision:

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

where $v_{rms} = 1310 \text{ m/s}$ 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:

$$1 \text{ amagat} = n_V = 2.6867774 \times 10^{25} \text{ m}^{-3},$$

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 $4.0 \times 10^{-10} \text{ m}$ (4 \AA). Estimate the mean time between collisions for an oxygen molecule under these conditions, using $v = v_{rms} = 517 \text{ m/s}$

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

$$t = \frac{5.2342 \times 10^{-8} \text{ m}}{517 \text{ m/s}} \approx 1.0 \times 10^{-10} \text{ s}$$

How about the mean free path at the high vacuum?

$$P = 10^{-n} \text{ Torr} = 10^{-n} \text{ mmHg} = (10^{-n})/760 \text{ atm} = (10^{-n})/760 \times (1.01 \times 10^5) \text{ Pa}$$

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

$$= 760 \times 10^n \times 5.2342 \times 10^{-8} \text{ m} = 3.978 \times 10^{n-5} \text{ m}$$

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

$$l = 3.978 \text{ m.}$$

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

$$l = 3978 \text{ m.}$$

((Link))

Mean free path calculation

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

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>