Gas Pressure and Simple Kinetic Theory (SKT)

SKT = atoms/molecules in random motion colliding with each other and with walls of container
- we directly analyze the motions of the atoms/molecules to deduce macroscopic properties of the system.
- treat perfect gas of point atoms, no forces, elastic collisions (somehow!) between atoms.
  The gas is in equilibrium = properties are uniform in the container and time-independent.

Start with a very crude model to calculate the pressure of the gas (1-dimensional).

Imagine an atom with speed $v$ bouncing back and forth between two walls a distance $L$ apart.

After each collision with the right wall, the particle recoils with velocity $(-v)$ directed to the left. The mean impulsive force delivered to the wall in a time interval $\Delta t$ between successive impacts is (from Newton's 2nd & 3rd laws)

$$ F_{\text{wall}} = -F_{\text{particle}} = -\int_{0}^{\Delta t} m \frac{dv}{dt} \, dt = \frac{2mv}{\Delta t} $$

Since $\Delta t = \frac{2L}{v}$ and the pressure $\overline{p}$ is force/area, we find the contribution to $\overline{p}$ for a single atom

$$ \overline{p} = \frac{m v^2}{AL} \quad (\text{where } A = \text{area of the wall}) $$

Now imagine that the box of volume $AL$ contains $N$ molecules, of which $\frac{1}{3}$ move in the $x$-direction.
\[ \frac{1}{3} \text{ in the } y \text{-direction, and } \frac{1}{3} \text{ in the } z \text{-direction.} \]

(assume atoms collide only with walls.

Then the mean pressure on any wall of the box is

\[ \bar{p} = \frac{N mv^2}{3V} = \frac{2N}{3V} \left( \frac{2}{2} mv^2 \right) = \frac{2Nk}{3V} \]

\[ \bar{p} \text{ equals } \frac{2}{3} \text{ times the total kinetic energy of the atoms in the box. Despite the crudeness of this model, this is essentially a correct result!} \]

**Improved Model**

Now let's improve the calculation by allowing the atoms to move in random directions with different velocities. Also because of collisions with other atoms, only atoms close to a wall and moving towards it will actually hit it. So let's count up the # of atoms with correct velocity \( \vec{v} \) that will hit the wall in a time interval \( \Delta t \). Let \( \overline{SA} \) be the area of wall to be hit. Imagine a parallel piped of length \( \overline{st} \) affixed to the rectangular area \( \overline{SA} \) and oriented along the direction of \( \vec{v} \) (let \( z \) be \( 90^\circ \) to \( \overline{SA} \))

\[ \text{volume of II-piped} = dV = v_z \overline{St} \overline{SA} \]

\[ \# \text{ of atoms in II-piped} = \frac{N}{V} \cdot dV = \frac{N}{V} v_z \overline{St} \overline{SA} \]
The fraction of these atoms with the correct "value" of \( \vec{u} \) will be denoted as \( f(\vec{u})d^3\vec{u} \).

- \( f(\vec{u}) \) is the probability density for molecular velocities.

\[ f(\vec{u})d^3\vec{u} = f(\vec{v})dv_x dv_y dv_z = \text{probability that the components of } \vec{v} \text{ lie in the ranges} \]

- \( v_x \) to \( v_x + dv_x \),
- \( v_y \) to \( v_y + dv_y \),
- \( v_z \) to \( v_z + dv_z \)

Let \( dN \) = \# of atoms that hit the wall in \( ST \)

\[
= \left( \text{# in } 1 \text{-piped} \right) \times \left( \text{fraction with correct } \vec{u} \right) \\
= \left( \frac{N}{V} v_z ST SA \right) \left( f(\vec{u}) \right) d^3\vec{u}
\]

The momentum transferred to the wall by these atoms is \( (2m v_z^2) dN \). The mean pressure is the total momentum transferred in \( ST \), divided by \( ST \) (i.e., the mean impulsive force), divided by \( SA \).

\[
\bar{P} = \frac{2m N v_z ST SA}{ST SA} \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z v_z^2 f(\vec{u})
\]

- only count those \( \vec{u} \) moving to the right
- count all \( x, y \) directions

Note that \( f(\vec{u}) \) is normalized \( \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\vec{u})d^3\vec{u} = 1 \)

and that, by symmetry, \( f(\vec{u}) \) must be an even function of \( v_x, v_y, \) and \( v_z \) (separately).

Thus, we may extend the integration range over \( v_z \) (formally) to reinterpret the result as a mean value

\[
\frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{v_z}^{\infty} v_z^2 f(\vec{u})d\vec{u}}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\vec{u})d^3\vec{u}} = \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{v_z}^{\infty} v_z^2 f(\vec{u})d\vec{u} = \frac{1}{2} v_z^2
\]
\[ \overline{p} = \frac{N}{V} \overline{m v^2} \]

Now consider \( \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \)

Take mean \( \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \)

Motion in each direction should be equivalent

so \( \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \)

and \( \overline{v^2} = 3 \overline{v_z^2} \)

Thus we obtain \( \overline{p} = \frac{1}{3} \frac{N}{V} m \overline{v^2} = \frac{2}{3} \frac{N}{V} \left( \frac{1}{2} m \overline{v^2} \right) \)

Let \( \overline{K} = \frac{1}{2} m \overline{v^2} \) - mean kinetic energy per particle

We get

\( \overline{p} \overline{v} = \frac{2}{3} N \overline{K} \) \( \text{very general result} \)

or \( \overline{p} = \frac{2}{3} n \overline{K} \) \( \text{valid for all ideal gases} \)

with \( n = \frac{N}{V} \) \( \text{the number density} \)

(\( \overline{p} = \frac{1}{3} n \overline{K} \) \( \text{but for a photon "gas"} \))

Now restrict attention to classical gases: empirical ideal gas law

\( \overline{p} \overline{v} = N k T \) \( k = \text{Boltzmann's const} \)

\( = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \)

Compare \( \Rightarrow \overline{K} = \frac{3}{2} k T \)

- the mean kinetic energy per particle is \( \frac{3}{2} k T \)

Why \( 3 ? \) because 3 space dimensions

\( \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3 \overline{v_x^2} = 3 \overline{v_y^2} = 3 \overline{v_z^2} \)

\( \Rightarrow \) Each degree of freedom gets \( \frac{1}{2} k T \) - Classical equi-partition of Energy

\( \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{k T}{m} \)

in 2-d \( \overline{K} = k T \); in 1-d \( \overline{K} = \frac{1}{2} k T \)

We found statistical mechanical expressions for \( \overline{p}, T \) (with help from expt.) \( T \) is an average property of a system with many particles. Single atoms or molecules do not have temperatures, only energy !
Maxwellian Velocity Distribution -

Think of the gas molecules as undergoing N independent random walks in velocity space - each direction is independent - the outcome is the velocity, not the position.

Recall \( P(x)dx = \frac{1}{\sqrt{2\pi} \sigma_x} e^{-\frac{(x-x_0)^2}{2\sigma_x^2}} dx \)

Then \( f(v_x)dv_x = \text{fraction of molecules with } v_x \text{ to } v_x + dv_x \)

\[ f(v_x) = \frac{1}{\sqrt{2\pi} v_x} e^{-\frac{v_x^2}{2v_x^2}} \]

What is \( v_x^2 = \frac{kT}{m} \)

so \( f(v_x) = \frac{1}{\sqrt{\frac{m}{2\pi kT}}} e^{-\frac{m v_x^2}{2 kT}} \) - 1-d Maxwellian velocity dist.

Note: \( v_x \) and \(-v_x\) are equally probable.

To get 3-d version, just assume \( x-y-z \) motion is independent.

\[ f(\vec{v}) = f(v_x) f(v_y) f(v_z) \]

\[ = \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{\frac{-m v^2}{2 kT}} \]

\[ v^2 = v_x^2 + v_y^2 + v_z^2 \]

Note each dimension separately normalized.

\[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\vec{v}) d^3v = 1 \]

\[ \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z f(\vec{v}) = f(v_x) \]

\[ v_x^\text{rms} = \sigma_v = \sqrt{\frac{v_x^2}{\int v_x^2 f(v_x) dv_x}} = \sqrt{\frac{kT}{m}} \]

\[ v_x \rightarrow \sqrt{\frac{3 kT}{m}} \]

\[ \overline{v_x} = \int_{-\infty}^{\infty} v_x f(v_x) dv_x = 0 \text{ (just as many moving right as left)} \]
T dependence of the Maxwellian distribution

At high T, fraction of molecules with high velocities is larger; fraction with low velocities is smaller.
Maxwellian Velocity versus Speed Distributions

Velocity - a vector implies magnitude (speed) and direction.

Speed - a scalar - no information about direction.

Let \( R(v) \, dv = \text{fraction of molecules with speeds in the range } v \text{ to } v + dv \), then \( R(v) \, dv = \int_{v}^{v+dv} f(v) \, d^3v \, dv \)

where \( f(v) \) is the 3-d Maxwellian velocity distribution.

\( f(v) \, d^3v \) corresponds to \( R(v) \, dv \) corresponds to the full shell.

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Fig. 4-8. (a) Three-dimensional velocity space. (b) Spherical shell.

Using spherical coordinates and noting \( f(\theta) = f(1 \theta) \)

\[
R(v) \, dv = \int_{0}^{\pi} d\phi \int_{0}^{2\pi} d\theta \sin \theta f(v) \, v^2 \, dv
\]

\[
\theta = \left( \frac{m}{2 \pi kT} \right)^{\frac{3}{2}} \cdot \frac{mv^2}{2kT} \cdot \sin \theta \cdot \cos \theta \left( \frac{m}{2 \pi kT} \right)^{\frac{3}{2}}
\]

\[
R(v) \, dv = 4\pi \left( \frac{m}{2 \pi kT} \right)^{\frac{3}{2}} \, v^2 \, e^{-\frac{mv^2}{2kT}} \, dv
\]
Molecular Speed Distributions at three different temperatures.

**FIG. 4.11** Relative probabilities of molecular speeds in nitrogen at three different temperatures. The density function is

\[
R(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-mv^2/2kT}
\]

(7.10.10)
Maxwell’s approach to the velocity distribution function - Ph311

Maxwell’s derivation is based on two assumptions. These can be justified, but not in the present development. The two assumptions are: (1) space is isotropic and all directions are equivalent, (2) motion in each direction \((x, y, z)\) is independent.

Let \(f(v)\) denote the velocity probability density. Then \(f(v)dv\) is the probability that a molecule has velocity \(v\) with components in the ranges \(v_x + dv_x\), \(v_y + dv_y\), and \(v_z + dv_z\). Note that the function \(f(v)\) used here and the function \(i(v)\) used by Reif differ by a factor of \(n\), the number density.

The first assumption implies that \(f(v)\) is only a function of \(v^2\), where \(v^2 = v_x^2 + v_y^2 + v_z^2\).

\[ f(v) = h(v^2) . \]

The second assumption implies that \(f(v)\) and \(h(v^2)\) each factors into a product of the form

\[ h(v^2) = g(v_x^2)g(v_y^2)g(v_z^2) . \]

To simplify the notation, we make the following change of variables:

\[ s = v_x^2, \ t = v_y^2, \ u = v_z^2, \]

and

\[ w = v^2 = s + t + u . \]

This allows us to rewrite Eq.(2) as

\[ h(w) = g(s)g(t)g(u) . \]

To solve this equation, we first differentiate both sides of Eq.(5) with respect to \(s\). We use the chain rule on the left-hand side (with \(\partial w/\partial s = 1\)) to find

\[ \frac{\partial h}{\partial s} = \frac{dh}{dw} \frac{\partial w}{\partial s} = \frac{dh}{dw} . \]

On the right-hand side, we have the result \(g(t)g(u)dg(s)/ds\). Thus, we see that

\[ \frac{dh}{dw} = g(t)g(u)\frac{dg(s)}{ds} , \]

which reduces to

\[ \frac{1}{h} \frac{dh}{dw} = \frac{1}{g(s)} \frac{dg(s)}{ds} , \]

after dividing each side by \(h\). Note that the right-hand side of Eq.(8) is, at most, only a function of \(s\), while the left-hand-side is, in principle, still a function of \(s, t,\) and \(u\). Now repeat the above procedure, but this time differentiate with respect to the variable \(t\). Then, instead of Eq.(8), we obtain

\[ \frac{1}{h} \frac{dh}{dw} = \frac{1}{g(t)} \frac{dg(t)}{dt} . \]
Supplement 3-2

Notice that the left-hand sides of Eqs.(8) and (9) are identical. Hence, it must follow that
\[ \frac{1}{g(s)} \frac{dg}{ds} = \frac{1}{g(t)} \frac{dg}{dt}, \]
which can be true only if each of these ratios equals some constant \(-\alpha\), where \(\alpha > 0\). (The reason for the minus sign will soon be apparent.) Thus, we may conclude that
\[ \frac{1}{h} \frac{dh}{dw} = -\alpha. \]
The solution to this simple differential equation is the familiar exponential function
\[ h(w) = C \exp(-\alpha w), \]
where \(C\) is another constant. It follows from Eqs.(1), (4), and (12) that
\[ f(v) = C \exp(-\alpha v^2). \]
To complete the solution we need to evaluate the constants \(\alpha\) and \(C\). Let’s do this by taking advantage of the relationships implied by Eqs.(1) and (2) to write
\[ f(v) = f_x(v_x)f_y(v_y)f_z(v_z), \]
where, for example,
\[ f_x(v_x) = A \exp(-\alpha v_x^2), \]
and \(A\) is another constant such that \(C = A^3\). The constant \(A\) is found by normalizing Eq.(15). The minus sign ensures that the integral will converge. We have
\[ 1 = \int_{-\infty}^{\infty} f_x(v_x) dv_x = A \int_{-\infty}^{\infty} \exp(-\alpha v_x^2) dv_x = A \sqrt{\frac{\pi}{\alpha}}. \]
To fully determine \(A\) we must evaluate \(\alpha\). Since Eq.(15) is a one-dimensional Gaussian function, we know immediately that the value of \(\alpha\) must satisfy the relation
\[ \alpha = \frac{1}{2v_x^2} = \frac{m}{2kT}. \]
Upon substituting Eq.(17) for \(\alpha\), Eq.(16) gives
\[ A = \sqrt{\frac{m}{2\pi kT}}. \]
Finally, Eqs. (14)-(18) yield the explicit form for the Maxwellian velocity distribution function:
\[ f(v) = \left( \frac{m}{2\pi kT} \right)^{3/2} \exp\left( -\frac{mv^2}{2kT} \right). \]