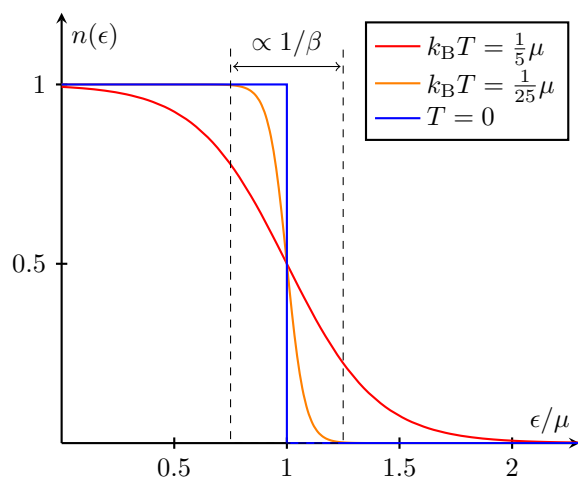


Statistical Mechanics – Kinetic Theory of Gases

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1 Kinetic Theory of Gases

This section deals with the **kinetic theory of gases**, in which we study the behavior of individual gas atoms and determine quantities such as the pressure of a gas, the speed probability distribution of atoms, and the rate of effusion.

1.1 The Maxwell-Boltzmann Distribution

Neglecting any rotational or vibrational motion of molecules – strictly monotomic gases), the energy of a molecule is given by

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{1}{2}mv^2$$

where $\vec{v} = \langle v_x, v_y, v_z \rangle$ is the molecular velocity and $v = |\vec{v}|$ is the molecular speed. Our goal is to determine the distribution of molecular speeds. We will make a couple of assumptions:

1. molecular size \ll intermolecular separation
2. ignore any intermolecular forces

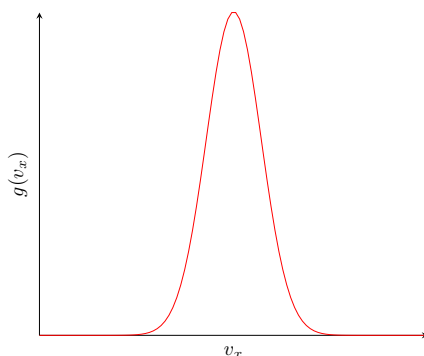
1.1.0.1 The Velocity Distribution

We define the **velocity distribution function** as the fraction of molecules with velocities say, in the x direction, between v_x and $v_x + dv_x$ as $g(v_x)dv_x$. The velocity distribution function is proportional to the Boltzmann Factor:

$$p_i \propto e^{\left(-\frac{\varepsilon_i}{kT}\right)}$$

where p_i is the probability of the system being in state i and ε_i is the energy of that state. Therefore, for molecules having velocities in the x direction,

$$g(v_x) \propto e^{\left(\frac{-mv_x^2}{2kT}\right)}$$



The velocity distribution function is sketched above. To normalize this function ($\int_{-\infty}^{\infty} g(v_x) dv_x = 1$), we need to evaluate this integral:

$$\int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x = \sqrt{\frac{\pi}{m/2kT}} = \frac{2\pi kT}{m}$$

Therefore,

$$g(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv_x^2}{2kT}}$$

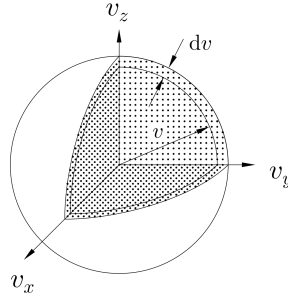
We can then find the following expectation values of this distribution:

$$\begin{aligned}\langle v_x \rangle &= \int_{-\infty}^{\infty} v_x g(v_x) dv_x = 0, \\ \langle |v_x| \rangle &= 2 \int_0^{\infty} v_x g(v_x) dv_x = \sqrt{\frac{2kT}{\pi m}} \\ \langle v_x^2 \rangle &= \int_{-\infty}^{\infty} v_x^2 g(v_x) dv_x = \frac{kT}{m}\end{aligned}$$

It does not matter which component of velocity was initially chosen. Hence the fraction of molecules with velocities between (v_x, v_y, v_z) and $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ is given by

$$\begin{aligned}g(v_x)dv_x g(v_y)dv_y g(v_z)dv_z \\ \propto e^{-mv_x^2/2kT} dv_x e^{-mv_y^2/2kT} dv_y e^{-mv_z^2/2kT} dv_z \\ = e^{-mv^2/2kT} dv_x dv_y dv_z.\end{aligned}$$

1.1.0.2 The Speed Distribution To work out the distribution of molecular speeds in a gas, we want the fraction of molecules which are traveling with speeds between $v = |\vec{v}|$ and $v + dv$. This corresponds to a spherical shell in velocity space of radius v and thickness dv .



The volume of velocity space corresponding to speeds between v and $v + dv$ is therefore equal to

$$4\pi v^2 dv$$

The fraction of molecules with speeds between v and $v + dv$ is defined as $f(v) dv$, where $f(v)$ is given by

$$f(v) dv \propto v^2 dv e^{-mv^2/2kT}$$

To normalize this function ($\int_0^\infty f(v) dv = 1$), we evaluate the integral. Note* the integration bounds are $0 \rightarrow \infty$ because the speed $v = |\vec{v}|$ is a positive quantity.

$$\int_0^\infty v^2 e^{-mv^2/2kT} dv = \frac{1}{4} \sqrt{\frac{\pi}{(m/2kT)^3}}$$

Therefore,

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

This speed distribution function is known as the **Maxwell-Boltzmann Distribution**. We can now derive some of its properties.

1.1.0.3 $\langle v \rangle$ and $\langle v^2 \rangle$

$$\begin{aligned} \langle v \rangle &= \int_0^\infty v f(v) dv = \sqrt{\frac{8kT}{m}} \\ \langle v^2 \rangle &= \int_0^\infty v^2 f(v) dv = \frac{3kT}{m} \end{aligned}$$

This makes sense since,

$$\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \frac{kT}{m} + \frac{kT}{m} + \frac{kT}{m} = \frac{3kT}{m} = \langle v^2 \rangle$$

The root mean squared speed of a molecule, v_{rms}

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

1.1.0.4 The Mean Kinetic Energy of a Gas Molecule

The mean kinetic energy of a gas molecule is given by

$$\langle E_{KE} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

This shows that the speed of molecules is proportional to the temperature. The average energy of a molecule in gas depends *only* on temperature.

1.1.0.5 The Maximum of $f(v)$

The maximum value of $f(v)$ is found by setting

$$\frac{df}{dv} = 0$$

As $f(v)$

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} v^2 e^{-mv^2/2kT},$$

Differentiating,

$$\begin{aligned} \frac{df}{dv} &= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} \frac{d}{dv} v^2 e^{-mv^2/2kT} \\ &= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} e^{-mv^2/2kT} \left(-\frac{mv^3}{kT} + 2v \right) \end{aligned}$$

For $\frac{df}{dv} = 0$,

$$-\frac{mv^3}{kT} + 2v = 0 \quad \Rightarrow \quad v_{\max} = \sqrt{\frac{2kT}{m}}$$

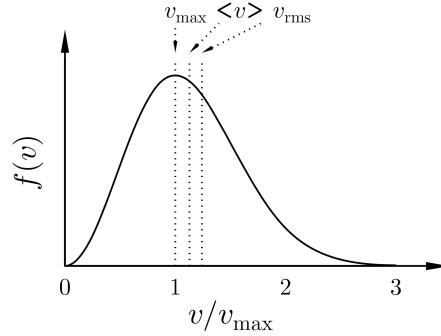
And since,

$$\sqrt{2} < \sqrt{\frac{8}{\pi}} < \sqrt{3},$$

we have that

$$v_{\max} < \langle v \rangle < v_{\text{rms}}$$

Note* v_{\max} is not the maximum velocity a particle can have – it is the *most probable* velocity a particle would have.



1.1.0.6 Chapter Summary

A physical situation that is very important in kinetic theory is the *translational* motion of atoms or molecules in a gas. The probability distribution for a given component of velocity is given by

$$g(v_x) \propto e^{-mv_x^2/2kT}$$

The corresponding expression for the probability distribution for molecular speeds is given by

$$f(v) \propto v^2 e^{-mv^2/2kT}$$

This is known as the **Maxwell-Boltzmann Distribution**. Two important average values of the Maxwellian Distribution are:

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}, \quad \langle v^2 \rangle = \frac{3kT}{m}$$

The maximum likelihood velocity a gas molecule has:

$$v_{\max} = \sqrt{\frac{2kT}{m}}$$

The rms velocity of a gas molecule, $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

1.2 Pressure

The pressure p due to a gas is defined as the ratio of the perpendicular contact force to the area of contact. The pressure p of a volume V of gas with a # molecule density n depends on the temperature T via an **equation of state**:

$$p = f(T, V, n) = nk_B T$$

1.3 Molecular Distributions

Previously, we derived the Maxwell-Boltzmann speed distribution function $f(v)$. We denote the total # of molecules per unit volume by the symbol n . The # of molecules per unit volume traveling with speeds between v and $v + dv$ is then given by $n f(v)$. We now seek to determine the distribution function of molecules traveling in different directions.

1.3.0.1 Solid Angles

An angle θ in a circle is defined by dividing the arc length s which the angle subtends by the radius r :

$$\theta = \frac{s}{r}$$

The angle is measured in radians. The angle subtended by the whole circle at its center is then,

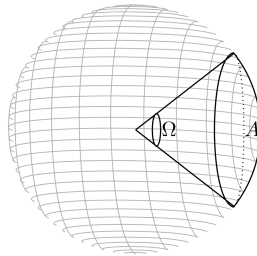
$$\frac{2\pi r}{r} = 2\pi$$

Analogously, the solid angle Ω in a sphere is defined by dividing the surface area A which the solid angle subtends by the radius squared, so that

$$\Omega = \frac{A}{r^2}$$

The solid angle is measured in steradians. The solid angle subtended by the whole sphere at its center is then,

$$\frac{4\pi r^2}{r^2} = 4\pi$$



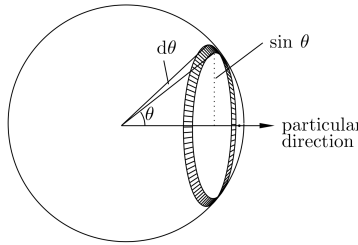
1.3.0.2 The # of Molecules Traveling in a Direction at a Certain Speed

Since all molecules are equally likely to be traveling in any direction, the fraction whose trajectories lie in an elemental solid angle $d\Omega$ is

$$\frac{d\Omega}{4\pi}$$

If we choose any direction, then the solid angle $d\Omega$ corresponding to molecules traveling at angles between θ and $\theta + d\theta$ to that direction is equal to the area of the annular region given by

$$d\Omega = 2\pi \sin \theta d\theta,$$



so that

$$\frac{d\Omega}{4\pi} = \frac{1}{2} \sin \theta d\theta$$

Therefore, the # of molecules per unit volume that have speeds between v and $v + dv$ and are traveling at angles between θ and $\theta + d\theta$ to the chosen direction is given by

$$nf(v) dv \frac{1}{2} \sin \theta d\theta$$

1.3.0.3 The # of Molecules Hitting a Wall

We now let our direction lie perpendicular to a wall of area A . In a small time dt , the molecules traveling at angle θ to the normal to the wall sweep out a volume

$$A(v dt) \cos \theta$$

Multiplying this volume by the above boxed expression (the # of molecules per unit volume with speeds $\in (v, v + dv)$ and traveling at angles $\in (\theta, \theta + d\theta)$) implies that in time dt , the # of molecules hitting a wall of area A is

$$Av dt \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta$$

Hence, the # of molecules hitting a unit area of wall in unit time, with speeds between v and $v + dv$ and traveling at angles between θ and $\theta + d\theta$ is given by

$$v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta$$

1.3.0.4 The Ideal Gas Law We can now calculate the pressure of a gas on its container. Each molecule hitting the wall of its container has a momentum change of $2mv \cos \theta$ perpendicular to the wall. If we multiply $2mv \cos \theta$ (the normal momentum change for one molecule) by the # of molecules hitting the wall per unit area per unit time, with the speed and θ in the right direction, integrating over θ and v should yield the pressure p .

This should make sense as,

$$\text{d pressure} = \frac{F}{A} = \frac{\frac{dp}{dt}}{A} = \frac{dp}{At}$$

Integrating,

$$\begin{aligned} p &= \int_0^\infty \int_0^{\pi/2} (2mv \cos \theta) \left(v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta \right) \\ &= mn \int_0^\infty v^2 f(v) dv \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta, \end{aligned}$$

Using the integral $\int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta = \frac{1}{3}$, we get

$$p = \frac{1}{3} nm \langle v^2 \rangle.$$

Using $\langle v^2 \rangle = \frac{3kT}{m}$,

$$p = nk_B T$$

which is the **ideal gas equation**. This completes the kinetic theory derivation of the ideal gas law