Statistical Mechanics – Kinetic Theory of Gases

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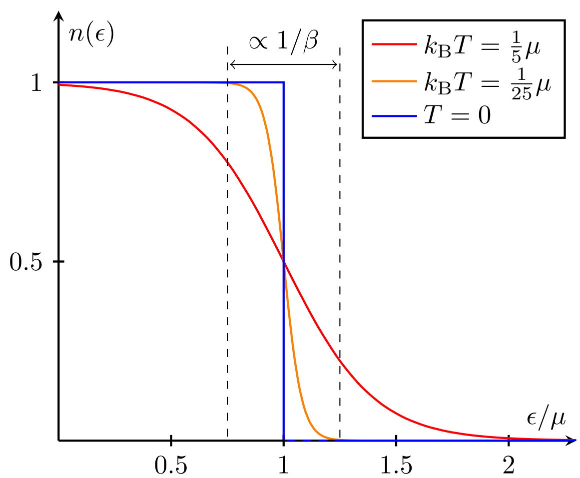


Contents

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

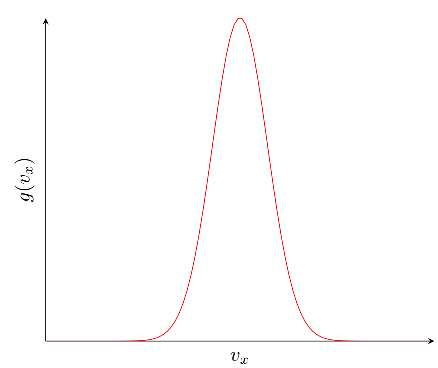
1.1.0.1 The Velocity Distribution

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,

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

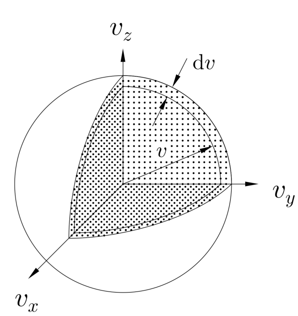
We can then find the following expectation values of this distribution:

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

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

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

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

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

To normalize this function ($\int_0^\infty f(v)dv = 1$), we evaluate the integral. Note* the integration bounds are $0 \to \infty$ 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,

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

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 $\langle v^2 \rangle$

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

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

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

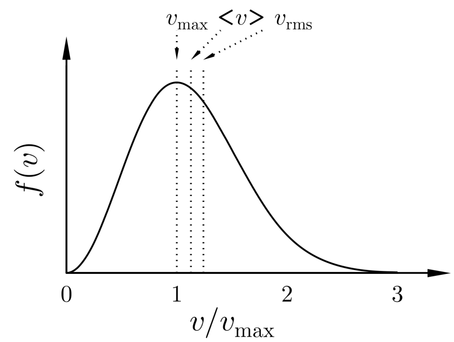
And since,

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

we have that

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

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



1.2 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:

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

The maximum likelihood velocity a gas molecule has:

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

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

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