Using expressions for \(v_{\text{mp}}\), \(v_{\text{ave}}\), or \(v_{\text{rms}}\), it is fairly simple to derive expressions for kinetic energy from the expression

\[
E_{\text{kin}} = \frac{1}{2} mv^2
\]

It is important to remember that there will be a full distribution of molecular speeds in a thermalized sample of gas. Some molecules will be traveling faster and some more slowly. It is also important to recognize that the most probable, average, and RMS kinetic energy terms that can be derived from the Kinetic Molecular Theory do not depend on the mass of the molecules (Table 2.4.1). As such, it can be concluded that the average kinetic energy of the molecules in a thermalized sample of gas depends only on the temperature. However, the average speed depends on the molecular mass. So, for a given temperature, light molecules will travel faster on average than heavier molecules.

**Table 2.4.1: Kinetic Properties of a Thermalized Ensemble (i.e., follows Maxwell-Boltzmann Distribution)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Speed</th>
<th>Kinetic Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most probable</td>
<td>( \sqrt{\frac{2k_BT}{m}} )</td>
<td>( k_BT )</td>
</tr>
<tr>
<td>Average</td>
<td>( \sqrt{\frac{8k_BT}{\pi m}} )</td>
<td>( \frac{4k_BT}{\pi} )</td>
</tr>
<tr>
<td>Root-mean-square</td>
<td>( \sqrt{\frac{3k_BT}{m}} )</td>
<td>( \frac{3}{2} k_BT )</td>
</tr>
</tbody>
</table>

**The Ideal Gas Law**

The expression for the root-mean-square molecular speed can be used to show that the Kinetic Molecular model of gases is consistent with the ideal gas law. Consider the expression for pressure

\[
p = \frac{N_{\text{tot}}m}{3V} \langle v \rangle^2
\]

Replacing \( \langle v \rangle^2 \) with the square of the RMS speed expression yields

\[
p = \frac{N_{\text{tot}}m}{3V} \left( \frac{3k_BT}{m} \right)
\]

which simplifies to

\[
p = \frac{N_{\text{tot}}k_BT}{V}
\]

Noting that \( N_{\text{tot}} = n \cdot N_A \), where \( n \) is the number of moles and \( N_A \) is Avogadro’s number

\[
p = \frac{nN_Ak_BT}{V}
\]

or

\[
pV = nN_Ak_BT
\]
Finally, noting that \( N_A k_B = R \)

\[ pV = nRT \]

That’s kind of cool, no? The only assumptions (beyond the postulates of the Kinetic Molecular Theory) is that the distribution of velocities for a thermalized sample of gas is described by the Maxwell-Boltzmann distribution law. The next development will be to use the Kinetic Molecular Theory to describe molecular collisions (which are essential events in many chemical reactions.)

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**Collisions with the Wall**

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the “collision volume”.

\[ V_{\text{col}} = v_x \Delta t \cdot A \]

All of the molecules within this volume, and with a velocity such that the x-component exceeds \( v_x \) (and is positive) will collide with the wall. That fraction of molecules is given by

\[ N_{\text{col}} = \frac{N}{V} \frac{\langle v \rangle \Delta t \cdot A}{2} \]

and the frequency of collisions with the wall per unit area per unit time is given by

\[ Z_w = \frac{N}{V} \frac{\langle v \rangle}{2} \]

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

\[ \langle v \rangle = \sqrt{\langle v_x \rangle + \langle v_y \rangle + \langle v_z \rangle} \]

and that

\[ \langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle \]

it can be shown that

\[ \langle \angle v \rangle = \langle \angle v_x \rangle = \langle \angle v_y \rangle = \langle \angle v_z \rangle \]

or

\[ \langle \angle v_x \rangle = \frac{1}{2} \langle \angle v \rangle \]

and so

\[ Z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle \]

The factor of \( N/V \) is often referred to as the “number density” as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately \( 2.5 \times 10^{19} \) molecule/cm\(^3\). (This value is
easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm$^3$.

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**Equipartitioning of Energy**

When the mechanical energy is

$$\mathcal{E}(x) = \mathcal{H}(x) = \sum_{i=1}^{N} \frac{\textbf{p}_i^2}{2m_i} + U \left( \textbf{r}_1, \ldots, \textbf{r}_N \right) \label{1}$$

the canonical distribution function nicely separates into a product of momentum and coordinate distributions:

$$f(x) = \frac{C_N}{Q(N, V, T)} \left[ e^{-\beta \sum_{i=1}^{N} \frac{\textbf{p}_i^2}{2m_i}} \right] \left[ e^{-\beta U \left( \textbf{r}_1, \ldots, \textbf{r}_N \right)} \right] \label{2}$$

where $P \left( \textbf{p}_i \right)$ is the Maxwell-Boltzmann distribution as a function of the momentum $\textbf{p}_i$.

Given this decomposition of the momentum distribution into products of distributions of individual components, we always have, for any system,

$$\left< \sum_{i=1}^{N} \frac{\textbf{p}_i^2}{2m_i} \right> = \frac{3}{2} N k_B T \label{3}$$

However, in addition to this, we also have the following averages:

$$\left< \frac{\textbf{p}_i^2}{2m_i} \right> = \frac{3}{2} k_B T \label{4}$$

and

$$\left< \frac{p_{x, i}^2}{2m_i} \right> = \frac{1}{2} k_B T, \quad \left< \frac{p_{y, i}^2}{2m_i} \right> = \frac{1}{2} k_B T, \quad \left< \frac{p_{z, i}^2}{2m_i} \right> = \frac{1}{2} k_B T \label{5}$$

The fact that these averages can be written for every individual component tells us that each degree of freedom has an average of $\frac{k_B T}{2}$ energy associated with it. This is called **equipartitioning of energy**.

How does equipartitioning happen? It occurs through the interactions in the system, which dynamically, produce collisions, leading to covalent bond breaking and forming events, hydrogen bond breaking and forming events, halogen...
bond breaking and forming events, diffusion, and so forth, all depending on the chemical composition of the system. Each individual collision event leads to a transfer of energy from one particle to another, so that, on average, all particles have the same energy $\frac{k_B T}{2}$. This does not mean that, at any instant, this is the energy of a randomly chosen particle. Obviously, there are considerable fluctuations in the energy of any one particle, however, the average over these fluctuations must produce the value $\frac{k_B T}{2}$.

A system obeys a well defined set of classical equations of motion, so that we can, in principle, determine exactly when the next collision will occur and exactly how much energy will be transferred in the collision. However, since we do not follow the detailed motion of all of the particles, our description of collisions and their consequences must be statistical in nature. We begin by defining a few simple terms that are commonly used for this subject.

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