Boltzmann Distribution Law

- The motion of molecules is extremely chaotic
- Any individual molecule is colliding with others at an enormous rate
  - Typically at a rate of a billion times per second
- We introduce the **number density** $n_V(E)$
  - This is called a distribution function
  - It is defined so that $n_V(E) \, dE$ is the number of molecules per unit volume with energy between $E$ and $E + dE$
- From statistical mechanics, the number density is
  
  $$n_V(E) = n_0 e^{-E/k_B T} \quad \textbf{Boltzmann distribution law}$$
The Boltzmann distribution law states that the probability of finding the molecule in a particular energy state varies exponentially as the energy divided by $k_B T$.

The observed speed distribution of gas molecules in thermal equilibrium is shown at right.

$P(v)$ is called the Maxwell-Boltzmann speed distribution function.
The fundamental expression that describes the distribution of speeds in $N$ gas molecules is

$$P(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}$$

$m$ is the mass of a gas molecule, $k_B$ is Boltzmann’s constant and $T$ is the absolute temperature.

The average speed is somewhat lower than the \textit{rms} speed.

The most probable speed, $v_{mp}$ is the speed at which the distribution curve reaches a peak

$$v_{mp} = \sqrt{\frac{2k_BT}{m}} = 1.41 \sqrt{\frac{k_BT}{m}}$$
The peak shifts to the right as $T$ increases

- This shows that the average speed increases with increasing temperature

The asymmetric shape occurs because the lowest possible speed is 0 and the highest is infinity

$$N_v = NP(v)$$
- $P(v)$ is a probability distribution function, it gives the fraction of molecules whose speeds lie in the interval $dv$ centered on the speed $v$.
  \[ \int_{0}^{\infty} P(v)dv = 1 \]

- The distribution of molecular speeds depends both on the mass and on temperature.

- The speed distribution for liquids is similar to that of gases even though the speeds are smaller in liquids than in gases.

- In solids, atoms do not have translational energy anymore, they vibrate. The only exception is solid helium, which is known to be a “quantum solid” where atoms can still move around.
Some molecules in the liquid are more energetic than others.

Some of the faster moving molecules penetrate the surface and leave the liquid.

This occurs even before the boiling point is reached.

The molecules that escape are those that have enough energy to overcome the attractive forces of the molecules in the liquid phase.

The molecules left behind have lower kinetic energies.

Therefore, evaporation is a cooling process.
Example: What is the \textit{rms} speed of hydrogen at \( T=300 \) K? How much slower are \( \text{O}_2 \) molecules compared to \( \text{H}_2 \)?

\[ v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \]

\( M(\text{H}_2) = 2.016 \) g/mole \( \Rightarrow v_{\text{rms}}^{\text{H}_2} = 1930 \) m/s at \( T = 300 \) K

\[
\frac{v_{\text{rms}}(\text{O}_2)}{v_{\text{rms}}(\text{H}_2)} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{O}_2}}} \]

\[
\frac{v_{\text{rms}}(\text{O}_2)}{v_{\text{rms}}(\text{H}_2)} = \sqrt{\frac{2}{32}} = \frac{1}{4} \]

\( \text{O}_2 \) is 4 times slower than \( \text{H}_2 \)
A molecule moving through a gas collides with other molecules in a random fashion.

This behavior is sometimes referred to as a random-walk process.

The mean free path increases as the number of molecules per unit volume decreases.
The molecules move with constant speed along straight lines between collisions.

The average distance between collisions is called the **mean free path**.

The path of an individual molecule is random in 3-dimensional space.

The mean free path is related to the diameter of the molecules and the density of the gas.

We assume that the molecules are spheres of diameter $d$.

No two molecules will collide unless their paths are less than a distance $d$ apart as the molecules approach each other.
The mean free path, \( l \), equals the average distance \( \nu \Delta t \) traveled in a time interval \( \Delta t \) divided by the number of collisions that occur in that time interval:

\[
l = \frac{\bar{v} \Delta t}{\left( \pi d^2 \bar{v} \Delta t \right) n_v} = \frac{1}{\pi d^2 N / V}
\]

The number of collisions per unit time is the collision frequency:

\[
f = \pi d^2 \bar{v} N / V \quad \text{(units: particles s}^{-1})\]

The inverse of the collision frequency is the collision mean free time.
Several processes can change the temperature of an ideal gas

Since $\Delta T$ is the same for each process, $\Delta E_{int}$ is also the same

The heat is different for the different paths, as is the work (1st law)

The heat and work associated with a particular change in temperature is **not** unique
We define specific heats for two processes that frequently occur:

- Changes with constant pressure
- Changes with constant volume

Using the number of moles, \( n \), we can define molar specific heats for these processes

Molar specific heats:

- \( Q_m = nC_V \Delta T \) for constant-volume processes
- \( Q_m = nC_P \Delta T \) for constant-pressure processes

\( Q_{P\ const.} > Q_{V\ const.} \) for given values of \( n \) and \( \Delta T \), because additional work has to be done for \( P\ const. \) to change the volume, larger \( \Delta T \) required \( C_P > C_V \)
An ideal monatomic gas contains non-interacting atoms

When energy is added to a monatomic gas in a container with a fixed volume, all of the energy goes into increasing the translational kinetic energy of the gas

- There is no other way to store energy in such a gas

Therefore, $E_{\text{int}}$ is a function of $T$ only:

$$E_{\text{int}} = \frac{3}{2} nRT$$

- The exact relationship depends on the type of gas

At constant volume, $Q = \Delta E_{\text{int}} = nC_V \Delta T$

- This applies to all ideal gases, not just monatomic ones
- Solving for $C_V$ gives $C_V = \frac{3}{2} \, R = 12.5 \, \text{J/mol} \cdot \text{K}$
  - For all monatomic gases
  - This is in good agreement with experimental results for monatomic gases
- In a constant-pressure process, $\Delta E_{\text{int}} = Q + W$ and $C_P - C_V = R$
  - This also applies to any ideal gas
    $$C_P = \frac{5}{2} \, R = 20.8 \, \text{J/mol} \cdot \text{K}$$
- We can also define
  $$\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = \frac{5}{3} = 1.67$$
Theoretical values of $C_V$, $C_P$, and $\gamma$ are in excellent agreement for monatomic gases.

But they are in serious disagreement with the values for more complex molecules.

Not surprising since the analysis was done for monatomic gases.
Molar Specific Heats of Other Materials

- The internal energy of more complex gases must include contributions from the rotational and vibrational motions of the molecules.

- In the cases of solids and liquids heated at constant pressure, very little work is done since the thermal expansion is small and $C_P$ and $C_V$ are approximately equal.
Equipartition of Energy

- With complex molecules, other contributions to internal energy must be taken into account.
- One possible energy is the translational motion of the center of mass.
- Rotational motion about the various axes also contributes.
  - We can neglect the rotation around the $y$ axis in a diatomic since it is negligible compared to the $x$ and $z$ axes.
The molecule can also vibrate

There is kinetic energy and potential energy associated with the vibrations

Rotational and vibrational motions at the microscopic level are described by quantum theory through the famous **Schrödinger equation**
The translational motion adds three degrees of freedom (each degree = 1/2 $R$)

The rotational motion in a linear molecule adds two degrees of freedom (each degree = 1/2 $R$)

The vibrational motion for a diatomic adds one more degree of freedom (each degree = 1 $R$)

Therefore, $E_{int} = \frac{7}{2} nRT$ and $C_V = \frac{7}{2} R$

This is inconsistent with experimental results as the molar specific heat is a function of temperature

At low temperatures, a diatomic gas acts like a monatomic gas

$C_V = \frac{3}{2} R$
At about room temp. the value increases to $C_V = \frac{5}{2} R$
- This is consistent with adding rotational energy but not vibrational energy

At high temperatures, the value increases to $C_V = \frac{7}{2} R$
- This includes vibrational energy as well as rotational and translational

For molecules with more than two atoms, the vibrations are more complex ($3N_{\text{atoms}} - 6(5)$ degrees of freedom)

The number of degrees of freedom becomes larger

The more degrees of freedom available to a molecule, the more “ways” there are to store energy
- This results in a higher molar specific heat
diatomic molecule

$C_v (J/mol \cdot K)$

Temperature (K)

- **Translation**
- **Rotation**
- **Vibration**

$\frac{7}{2}R$
$\frac{5}{2}R$
$\frac{3}{2}R$
Quantization of Energy

- To explain the results of the various molar specific heats, we must use some **quantum mechanics**
  - Classical mechanics is not sufficient
- In quantum mechanics, the energy is proportional to the frequency of an atomic or molecular wave-function
- The energies of atoms and molecules are quantized, as mentioned before for the black-body radiation
- Energies are not continuous, they are separated by certain amounts. One obtains an energy level diagram showing the rotational and vibrational states of a molecule
- The lowest allowed state is the **ground state**
Quantization of Energy

Vibrational states

Rotational states

Rotational states

zero-point energy

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The vibrational states are separated by larger energy gaps than are rotational states.

At low temperatures, the energy gained during collisions is generally not enough to raise it to the first excited state of either rotation or vibration.

Even though rotation and vibration are classically allowed, such movements are quantized and classical physics fails to describe such motions.

As the temperature increases, the total energy of the molecules increases.
- In some collisions, the molecules have enough energy to excite to the first excited rotational or (at higher temperatures) vibrational state
- As the temperature continues to increase, more molecules are in excited rotational states
- At about room temperature, rotational energy is the dominant contribution
- At about 1000 K, excited vibrational energy levels are reached
- At about 10 000 K, vibration is contributing mostly to the internal energy
Molar specific heats in solids also demonstrate a marked temperature dependence.

Solids have molar specific heats that generally decrease in a nonlinear manner with decreasing temperature. At low $T$ we have $C_v = a T^3$

It approaches zero as the temperature approaches absolute zero.

At high temperatures, the molar specific heats of solids approach the value of $3R$

- This usually occurs above 300 K for most solids.

Very high temperatures will cause bond breaking (melting).
The molar specific heat of a solid at high temperature can be explained by the *equipartition* theorem.

- Each atom of the solid has three degrees of vibrational freedom (each equal to $1 \, R$).
- The internal energy is $3nRT$ and $C_v = 3R$.

At high temperatures, $C_V$ becomes a constant at $\sim 3R$ (The *Dulong-Petit Rule*).
Example: Heat 0.25 mole of air from 0°C to 100 °C at constant $P$ (isobaric process).

Heat: $Q = nC_p \Delta T$

Air mainly consists of diatomic molecules ($N_2$ and $O_2$) in the vibrational ground state

$C_p = C_v + R = \frac{5}{2}R + R = \frac{7}{2}R,$

$Q = 728 \text{ J} \quad (R = 8.3145 \text{ J mol}^{-1}\text{K}^{-1})$

Internal Energy: $\Delta E_{int} = nC_v \Delta T = 520 \text{ J}$

Work done by the gas: $W = \Delta E_{int} - Q = -208 \text{ J}$

Proportion of heat converted to work:

$$\frac{W}{Q} = \frac{-208 \text{ J}}{728 \text{ J}} = -0.29$$