Thermodynamics
Boltzmann (Gibbs) Distribution
Maxwell-Boltzmann Distribution
Second Law

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Last time

- adiabatic processes

- the Boltzmann distribution (distribution of energies)
Overview

• the Maxwell-Boltzmann distribution (distribution of speeds)

• the Second Law of thermodynamics

• irreversible processes
The Boltzmann Distribution

Lower temperature  Higher temperature

1 Figure from the website of Dr. Joseph N. Grima, University of Malta.
Aside: Lasers

Lasers emit coherent light. One photon interacts with an atom and causes another to be emitted in the same state.

\[ E_2 - E_1 = \Delta E = h\nu \]

This starts a cascade.

Inside a laser cavity there are atoms that are in a very strange state: a higher energy level is more populated than a lower one. This is called a “population inversion”.

\[ \text{Atom in excited state} \]

\[ \text{Atom in ground state} \]
Aside: Lasers

This is necessary for the photon cascade. Since:

\[
\frac{n_V(E_2)}{n_V(E_1)} = e^{-(E_2 - E_1)/k_B T}, \quad E_2 > E_1
\]

we can associate a “negative temperature”, \( T \), to these two energy states in the atoms.
The Boltzmann distribution for energy can be leveraged to find a distribution of the speeds of the molecules. This is the Maxwell-Boltzmann speed distribution.

The number of molecules with speeds between $v$ and $v + dv$ is

$$\int_{v}^{v+dv} N_v \, dv = \int_{v}^{v+dv} 4\pi N \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T} \, dv$$
Maxwell-Boltzmann speed distribution

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The number of molecules having speeds ranging from $v$ to $v + dv$ equals the area of the tan rectangle, $N_v \, dv$. 

Figure 21.10
The speed distribution of gas molecules at some temperature. The function $N_v$ approaches zero as $v$ approaches infinity.

Figure 21.11
The speed distribution function for 10^5 nitrogen molecules at 300 K and 900 K.

The total area under either curve is equal to $N$, the total number of molecules. In this case, $N = 10^5$.

Note that $v_{rms} \approx 1.73 \, k_B T / m_0$.

$N_v \, dv$

$N_v$ in molecules/(m/s)

$v$ in (m/s)

$N_v$ in molecules

$v_{mp}$

$v_{avg}$

$v_{rms}$

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$N_v \, dv$
The energy of a molecule can be written:

\[ E = K_{\text{trans}} + \epsilon + U \]

where

- **translational kinetic energy**, \( K_{\text{trans}} = \frac{p^2}{2m_0} \)
- \( \epsilon \) includes any rotational or oscillational energy
- \( U \) is potential energy (if relevant) that depends on the location of the molecule

Since we only want to know about the distribution of **speeds**, we will need to get rid of any dependence on \( \epsilon \) and \( U \).
Aside: Reminder about probability distributions

Suppose I have a probability distribution over two variables, $x$ and $y$:  

$$p(x, y)$$

If the two variables are independently distributed then:  

$$p(x, y) = p(x)p(y)$$
Aside: Reminder about probability distributions

Suppose I have a probability distribution over two variables, $x$ and $y$:

$$p(x, y)$$

If the two variables are independently distributed then:

$$p(x, y) = p(x)p(y)$$

We can eliminate the dependence on $x$ by just summing over $x$:

$$\sum_x p(x, y) = \sum_x p(x)p(y) = p(y)\sum_x p(x) = p(y)$$

This is how we eliminate rotational and vibrational motion.
Maxwell-Boltzmann speed distribution

Put this expression in the Boltzmann distribution:

\[ p(\mathbf{r}, \mathbf{p}, \epsilon) \, d^3\mathbf{r} \, d^3\mathbf{p} \, d\epsilon = Ae^{-E/k_BT} \, d^3\mathbf{r} \, d^3\mathbf{p} \, d\epsilon \]

Eliminate dependence on position, rotation, and oscillation:

\[
\int_\epsilon \int_\mathbf{p} p(\mathbf{r}, \mathbf{p}, \epsilon) \, d^3\mathbf{r} \, d^3\mathbf{p} \, d\epsilon
\]

\[
= Ce^{-p^2/2m_0k_BT} \, d\mathbf{p} \left( C' \int_\epsilon e^{-\epsilon/k_BT} \, d\epsilon \right) \left( C'' \int_\mathbf{r} e^{-U/k_BT} \, d^3\mathbf{r} \right)
\]
Maxwell-Boltzmann speed distribution

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p(r, p, \epsilon) \, d^3r \, d^3p \, d\epsilon = A e^{-E/k_B T} \, d^3r \, d^3p \, d\epsilon
\]

Eliminate dependence on position, rotation, and oscillation:

\[
\int_{\epsilon} \int_{p} p(r, p, \epsilon) \, d^3r \, d^3p \, d\epsilon
\]

\[
= C e^{-p^2/2m_0 k_B T} \, dp \left( C' \int_{\epsilon} e^{-\epsilon/k_B T} \, d\epsilon \right) \left( C'' \int_{r} e^{-U/k_B T} \, d^3r \right)
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Eliminate dependence on position, rotation, and oscillation:

\[ \int_\epsilon \int_p p(r, p, \epsilon) \, d^3r \, d^3p \, d\epsilon \]

\[ = Ce^{-p^2/2m_0k_BT} \, dp \left( C' \int_\epsilon e^{-\epsilon/k_BT} \, d\epsilon \right) \left( C'' \int_r e^{-U/k_BT} \, d^3r \right) \]

\[ p(p) \, d^3p = Ce^{-p^2/2m_0k_BT} \, d^3p \]
Maxwell-Boltzmann speed distribution

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Eliminate dependence on position, rotation, and oscillation:

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\int_{\epsilon} \int_{p} p(r, p, \epsilon) \, d^3r \, d^3p \, d\epsilon \\
= Ce^{-p^2/2m_0 k_B T} \, dp \left( C' \int_{\epsilon} e^{-\epsilon/k_B T} \, d\epsilon \right) \left( C'' \int_{r} e^{-U/k_B T} \, d^3r \right)
\]

\[ p(p) \, d^3p = Ce^{-p^2/2m_0 k_B T} \, d^3p \]

replace momentum with velocity components:

\[ p(v) \, d^3v = Ce^{-m_0 (v_x^2 + v_y^2 + v_z^2) / 2k_B T} \, dv_x \, dv_y \, dv_z \]
Maxwell-Boltzmann speed distribution

We can find $C$. The total probability must equal one.

$$\int \int \int C e^{-m_0(v_x^2 + v_y^2 + v_z^2)/2k_B T} \, dv_x \, dv_y \, dv_z = 1$$

Using the identity:

$$\int_{-\infty}^{\infty} e^{-x^2} \, dx = \sqrt{\pi}$$

the three integrals can be evaluated separately:

$$\int_{-\infty}^{\infty} e^{-m_0 v_x^2/2k_B T} \, dv_x = \sqrt{\frac{2\pi k_B T}{m_0}}$$

There are three integrals, so

$$C = \left( \frac{m_0}{2\pi k_B T} \right)^{3/2}$$
Maxwell-Boltzmann speed distribution

Now our distribution is:

\[ p(v) \, d^3v = \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} e^{-m_0(v_x^2 + v_y^2 + v_z^2)/2k_B T} \, dv_x \, dv_y \, dv_z \]

Lastly, we want an expression for how many molecules have speeds between \( v \) and \( v + dv \).

This means we need to get rid of the direction dependence – transform to spherical coordinates.

\[ dv_x \, dv_y \, dv_z = v^2 \sin \theta \, dv \, d\theta \, d\phi \]
Maxwell-Boltzmann speed distribution

\[ \int \int \int \phi \theta p(v) \, d^3v \]

\[ = \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0v^2/2k_B T} \, dv \int_0^{2\pi} \, d\phi \int_0^\pi \sin \theta \, d\theta \]

\[ = 4\pi \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0v^2/2k_B T} \, dv \]

This is the probability density for 1 molecule. For \( N \) molecules:

\[ N_v \, dv = 4\pi N \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0v^2/2k_B T} \, dv \]
The fundamental expression that describes the distribution of speeds of \( N \) gas molecules is

\[
N v^5 = \frac{N a^2}{m_0^2 k_B T} \frac{v^2}{2} e^{2 E/k_B T} \tag{21.41}
\]

where \( m_0 \) is the mass of a gas molecule, \( k_B \) is Boltzmann's constant, and \( T \) is the absolute temperature.

Observe the appearance of the Boltzmann factor \( e^{2 E/k_B T} \) with \( E = \frac{1}{2} m_0 v^2 \).

As indicated in Figure 21.10, the average speed is somewhat lower than the rms speed. The most probable speed \( v_{mp} \) is the speed at which the distribution curve reaches a peak. Using Equation 21.41, we find that

\[
v_{rms} = \sqrt{\frac{3k_B T}{m_0}} = 1.73 \sqrt{\frac{k_B T}{m_0}}
\]

From previous lecture:

\[
v_{rms} = \sqrt{\frac{3k_B T}{m_0}} = 1.73 \sqrt{\frac{k_B T}{m_0}}
\]
The Shape of the Maxwell-Boltzmann distribution

Average speed, can find by integrating over all speeds, then dividing by the number of particles.

\[ \nu_{\text{avg}} = \frac{1}{N} \int_{0}^{\infty} \nu \, N_{\nu} \, d\nu \]

\[ = \int_{0}^{\infty} 4\pi \left( \frac{m_{0}}{2\pi k_{B} T} \right)^{3/2} \nu^{3} \, e^{-m_{0}\nu^{2}/2k_{B}T} \, d\nu \]

\[ = 4\pi \left( \frac{m_{0}}{2\pi k_{B} T} \right)^{3/2} \int_{0}^{\infty} \nu^{3} \, e^{-m_{0}\nu^{2}/2k_{B}T} \, d\nu \]

\[ = 4\pi \left( \frac{m_{0}}{2\pi k_{B} T} \right)^{3/2} \frac{1}{2} \left( \frac{m_{0}}{2k_{B} T} \right)^{-2} \]

\[ \nu_{\text{avg}} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{k_{B} T}{m_{0}}} = 1.60 \sqrt{\frac{k_{B} T}{m_{0}}} \]
The Shape of the Maxwell-Boltzmann distribution

To find the most probable speed (peak of the distribution), can find the value of $v$ for which the derivative of the particle number distribution is zero.

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

Then we find:

$$v_{mp} = \sqrt{\frac{2}{k_B T m_0}} = 1.41 \sqrt{\frac{k_B T}{m_0}}$$

So,

$$v_{rms} > v_{avg} > v_{mp}$$
The Shape of the Maxwell-Boltzmann distribution

To find the most probable speed (peak of the distribution), can find the value of $v$ for which the derivative of the particle number distribution is zero.

Set $\frac{dN_v}{dv} = 0$

Then we find:

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The Shape of the Maxwell-Boltzmann distribution

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So,

$$v_{rms} > v_{avg} > v_{mp}$$
The Shape of the Maxwell-Boltzmann distribution

The number of molecules having speeds ranging from $v$ to $v + dv$ equals the area of the tan rectangle, $N_v dv$.

$N_v$ vs. $v$

$N_v dv$

$v_{mp}$

$v_{avg}$

$v_{rms}$

$vrms > vavg > v_{mp}$

$0$ Graph from Serway & Jewett, page 641.
Speed Distribution and Evaporation

We can understand evaporation as a change of some of our system from the liquid to the gaseous state at the surface of the liquid.

Even well below the boiling point there are some molecules with very high translational KE.

These molecules move fast enough to overcome the strength of the liquid bonds.

Slower moving molecules are left behind, so the remaining liquid is cooler.
The Second Law of Thermodynamics

We will state this law in several different ways. First an intuitive statement:

2nd Law

Unless work is done on a system, heat in the system will flow from a hotter body in the system to a cooler one.

This is obvious from experience, but it’s not obvious why this should happen.

It also indicates there are processes in the physical world that seem not to happen in the same way if time is reversed.
The Second Law of Thermodynamics and Reversibility

Scientists and engineers studying and designing steam engines wanted to make them as efficient as possible.

They noticed there were always losses.

There seemed to be more to it. Energy seems to always spread out. Heat goes from hotter to colder objects. Energy is lost as heating in friction.

These things do not happen in reverse.
# Isolated, Closed, and Open Systems

<table>
<thead>
<tr>
<th>Isolated system</th>
<th>does not exchange energy (work, heat, or radiation) or matter with its environment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed system</td>
<td>does not exchange matter with its environment, but may exchange energy.</td>
</tr>
<tr>
<td>Open system</td>
<td>can exchange energy and matter with its environment.</td>
</tr>
</tbody>
</table>
Reversible and Irreversible Processes

**Reversible process**

A process that takes a system from an initial state \( i \) to a final state \( f \) through a series of equilibrium states, such that we can take the same system back again from \( f \) to \( i \) along the same path in a PV diagram.

**Irreversible process**

Any process that is not reversible.

In real life, all processes are irreversible, but some are close to being reversible. We use reversible processes as an idealization.
Irreversible Process Example

Entropy differs from energy in that entropy does not obey a conservation law. The change in entropy for a process can be calculated using the equation:

\[ \Delta S = \frac{Q}{T} \]

Here, \( \Delta S \) is the change in entropy, \( Q \) is the heat transferred, and \( T \) is the temperature at which the transfer takes place. Because the change in entropy depends not only on the energy transferred as heat but also on the temperature at which the transfer takes place, there are two equivalent ways to define the change in entropy of a system:

1. By counting the number of microstates that correspond to the final state. This approach is useful for understanding the increase in entropy associated with thermodynamic processes.
2. By counting the number of microstates that correspond to the initial state and subtracting the number of microstates that correspond to the final state. This approach is useful for understanding the decrease in entropy associated with thermodynamic processes.

Irreversible processes, the change in entropy is sometimes called “the arrow of time.” For irreversible processes, the entropy of a closed system always increases. Because of this property, the change in entropy cannot be reversed. This is why entropy is always increasing in irreversible processes. The entropy of a closed system always increases. Because of this property, the change in entropy cannot be reversed. This is why entropy is always increasing in irreversible processes.
Irreversible Process Example

This process has well-defined initial and final equilibrium states, but during the expansion of the gas is not in equilibrium.

![Pressure-Volume Diagram](image)

It cannot be plotted on a $PV$ diagram. Also, no work is done on the gas in this process.
Summary

- Boltzmann distribution (energies)
- Maxwell-Boltzmann distribution (speeds)
- the second law

Test Monday, May 14.

Homework Serway & Jewett:

- prev: Ch 21, onward from page 644. Probs: 33, 37, 41, 42, 43, 52, 57, 73