



Thermodynamics

Maxwell-Boltzmann Distribution

Second Law

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Last time

- adiabatic processes
- the Boltzmann distribution (distribution of energies)
- introduced the Maxwell-Boltzmann distribution (distribution of speeds)

Overview

- the Maxwell-Boltzmann distribution (distribution of speeds)
- the Second Law of thermodynamics
- irreversible processes

Reminder: Maxwell-Boltzmann speed distribution

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**.

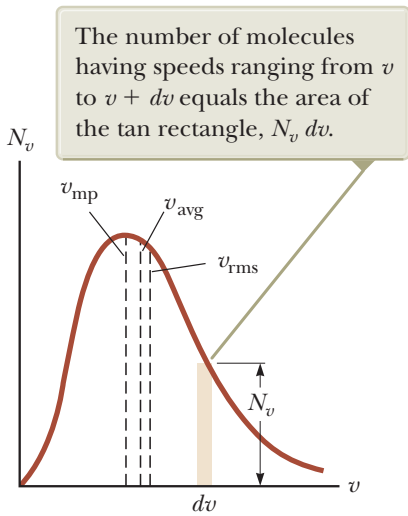
The number of molecules with speeds between v and $v + dv$ is

$$\int_v^{v+dv} N_v dv = \int_v^{v+dv} 4\pi N \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T} dv$$

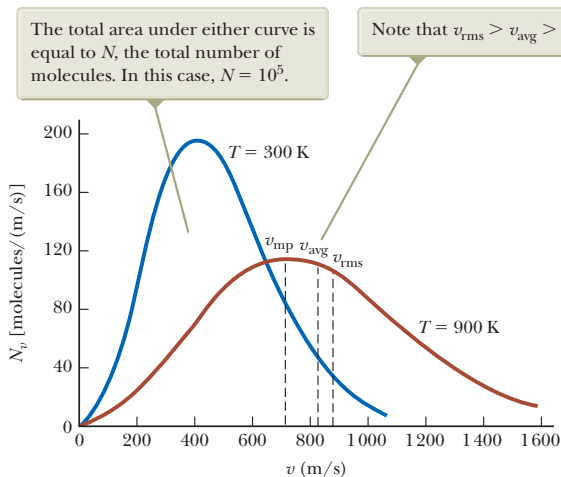
Maxwell-Boltzmann speed distribution

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The Shape of the Maxwell-Boltzmann distribution



From a previous lecture:

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m_0}} = 1.73 \sqrt{\frac{k_B T}{m_0}}$$

The Shape of the Maxwell-Boltzmann distribution

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

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$$v_{\text{avg}} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{k_B T}{m_0}} = 1.60 \sqrt{\frac{k_B T}{m_0}}$$

The Shape of the Maxwell-Boltzmann distribution

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

Then we find:

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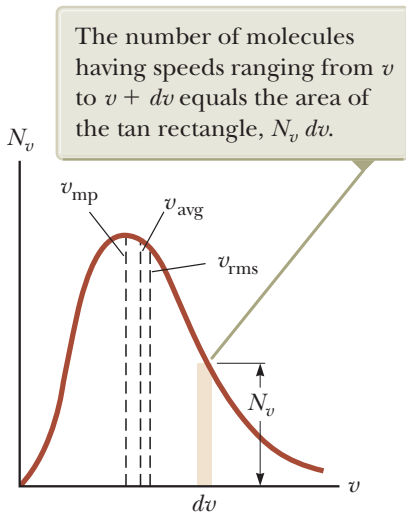
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So,

$$v_{\text{rms}} > v_{\text{avg}} > v_{\text{mp}}$$

The Shape of the Maxwell-Boltzmann distribution



$$v_{rms} > v_{avg} > v_{mp}$$

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

Isolated system

does not exchange energy (work, heat, or radiation) or matter with its environment.

Closed system

does not exchange matter with its environment, but may exchange energy.

Open system

can exchange energy and matter with its environment.

Reversible and Irreversible Processes

Reversible process

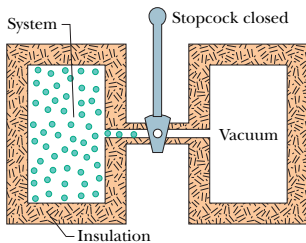
a process that takes a system from an initial state i to a final state f through a series of equilibrium states, such that we can take the same system back again from f to i along the same path in a PV diagram.

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.

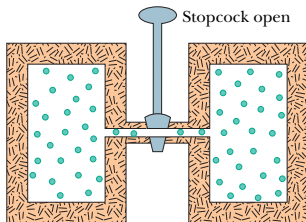
Irreversible Process Example



(a) Initial state i



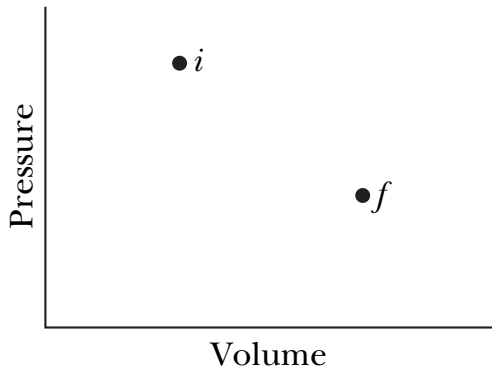
Irreversible
process



(b) Final state f

Irreversible Process Example

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

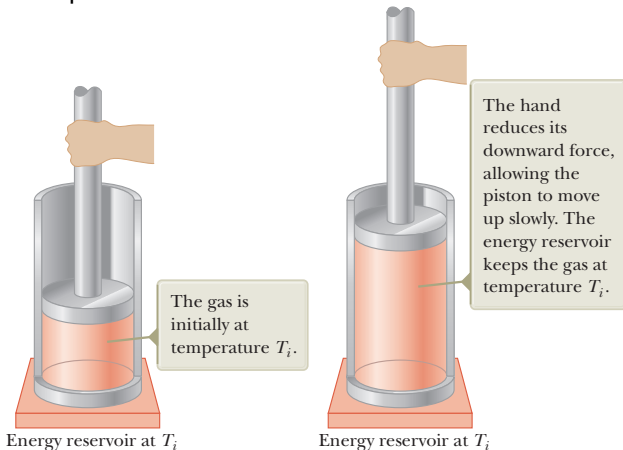


It cannot be plotted on a PV diagram. Also, no work is done on the gas in this process.

A Reversible Counterpart

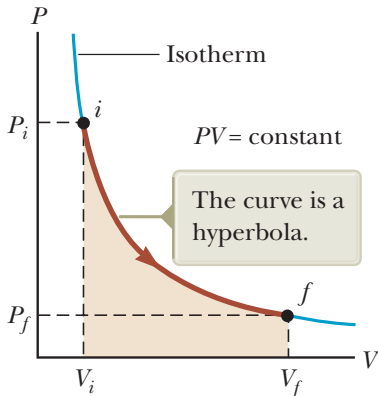
This process has the same starting and ending points.

Allow gas to expand very slowly through equilibrium states at constant temperature.



A Reversible Counterpart

We can plot this isothermal expansion:



Negative work is done on the gas, heat is transferred in, and the internal energy and the temperature remain constant.

Comparing the Processes

In both of these processes the gas expands into a region it was not in previously.

The energy of the system spreads out.

This corresponds to a change of state, but it is not captured by the internal energy of the gas system, which does not change in either process.

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Something does change in these processes and we call it *entropy*.

Summary

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