



Thermodynamics

Boltzmann (Gibbs) Distribution

Maxwell-Boltzmann Distribution

Second Law

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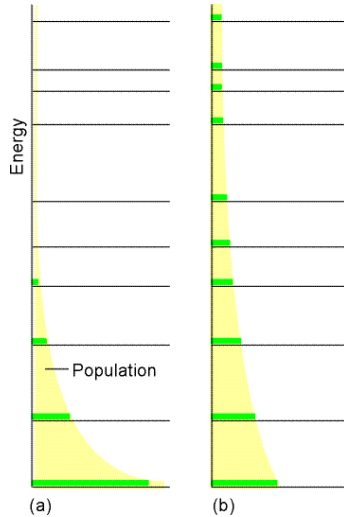
Last time

- adiabatic processess
- the Boltzmann distribution (distribution of energies)

Overview

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

The Boltzmann Distribution



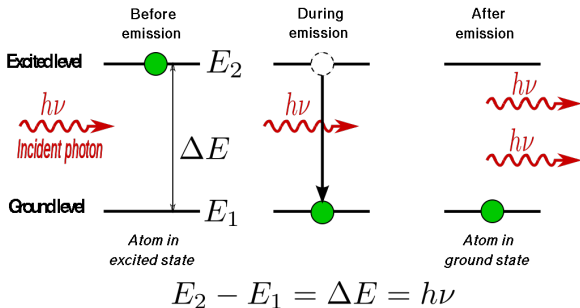
Lower temperature

Higher temperature

¹Figure 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.



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".

Aside: Lasers

This is necessary for the photon cascade. Since:

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

we can associate a “negative temperature”, T , to these two energy states in the atoms.

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**.

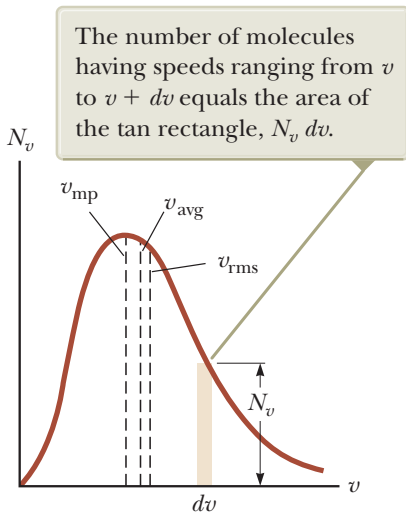
The number of molecules with speeds between v and $v + dv$ is

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

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Maxwell-Boltzmann speed distribution

The energy of a molecule can be written:

$$E = K_{\text{trans}} + \epsilon + U$$

where

- translational kinetic energy, $K_{\text{trans}} = \frac{p^2}{2m_0}$
- ϵ 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 ϵ 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:

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

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If the two variables are independently distributed then:

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

$$\sum_x p(x, y) = \sum_x p(x)p(y) = p(y) \sum_x p(x) \overset{1}{=} p(y)$$

This is how we eliminate rotational and vibrational motion.

Maxwell-Boltzmann speed distribution

Put this expression in the Boltzmann distribution:

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

Eliminate dependence on position, rotation, and oscillation:

$$\begin{aligned} \int_{\epsilon} \int_{\mathbf{p}} p(\mathbf{r}, \mathbf{p}, \epsilon) d^3\mathbf{r} d^3\mathbf{p} d\epsilon \\ = C e^{-\mathbf{p}^2/2m_0 k_B T} d\mathbf{p} \left(C' \int_{\epsilon} e^{-\epsilon/k_B T} d\epsilon \right) \left(C'' \int_{\mathbf{r}} e^{-U/k_B T} d^3\mathbf{r} \right) \end{aligned}$$

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$$p(\mathbf{p}) d^3\mathbf{p} = C e^{-\mathbf{p}^2/2m_0 k_B T} d^3\mathbf{p}$$

replace momentum with velocity components:

$$p(\mathbf{v}) d^3\mathbf{v} = C e^{-m_0(v_x^2 + v_y^2 + v_z^2)/2k_B T} dv_x dv_y dv_z$$

Maxwell-Boltzmann speed distribution

We can find C .

The total probability must equal one.

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

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:

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

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.

$$dv_x dv_y dv_z = v^2 \sin \theta dv d\theta d\phi$$

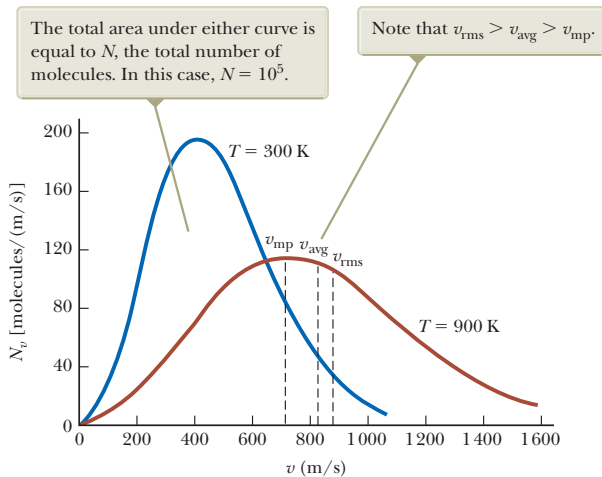
Maxwell-Boltzmann speed distribution

$$\begin{aligned} \int_{\phi} \int_{\theta} p(\mathbf{v}) d^3\mathbf{v} \\ &= \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T} dv \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta \\ &= 4\pi \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T} dv \end{aligned}$$

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

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

The Shape of the Maxwell-Boltzmann distribution



From 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.

$$\begin{aligned}v_{\text{avg}} &= \frac{1}{N} \int_0^{\infty} v N_v dv \\&= \int_0^{\infty} 4\pi \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^3 e^{-m_0 v^2 / 2k_B T} dv \\&= 4\pi \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} v^3 e^{-m_0 v^2 / 2k_B T} dv \\&= 4\pi \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} \frac{1}{2} \left(\frac{m_0}{2k_B T} \right)^{-2}\end{aligned}$$

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

The Shape of the Maxwell-Boltzmann distribution

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.

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

Then we find:

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

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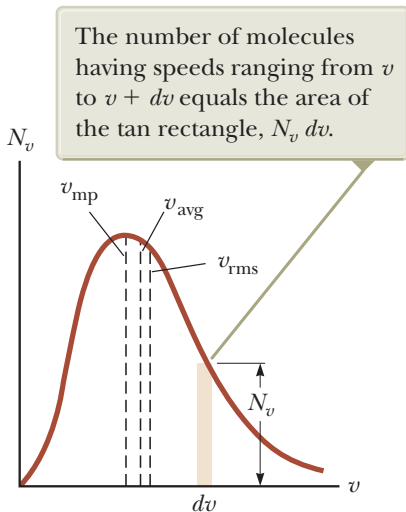
Then we find:

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

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

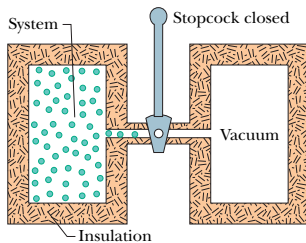
a process that takes a system from an initial state i to a final state f through a series of equilibrium states, such that we can take the same system back again from f to i along the same path in a PV diagram.

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.

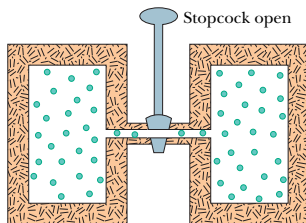
Irreversible Process Example



(a) Initial state i



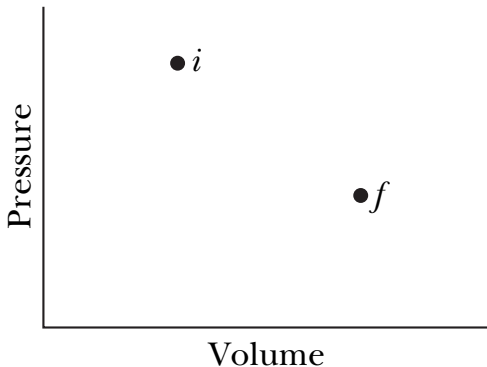
Irreversible
process



(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.

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