



Thermodynamics

Boltzmann (Gibbs) Distribution

Maxwell-Boltzmann Distribution

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Last time

- heat capacities for ideal gases
- adiabatic processes

Overview

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

Adiabatic Process in Ideal Gases

For an adiabatic process ($Q = 0$):

$$PV^\gamma = \text{const.}$$

and:

$$TV^{\gamma-1} = \text{const.}$$

(Given the first one is true, the second follows immediately from the ideal gas equation, $P = \frac{nRT}{V}$.)

Example

Based on problem 28, Chapter 21.

How much work is required to compress 5.00 mol of air at 20.0°C and 1.00 atm to one-tenth of the original volume in an adiabatic process? Assume air behaves as an ideal diatomic-type gas.

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One way:

$$PV^\gamma = P_i V_i^\gamma$$

and

$$W = - \int P dV$$

Another way:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

and

$$W = \Delta E_{\text{int}} - \overset{0}{\cancel{Q}} = nC_V \Delta T$$

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$$W = 46.0 \text{ kJ}$$

Weather and Adiabatic Process in a Gas

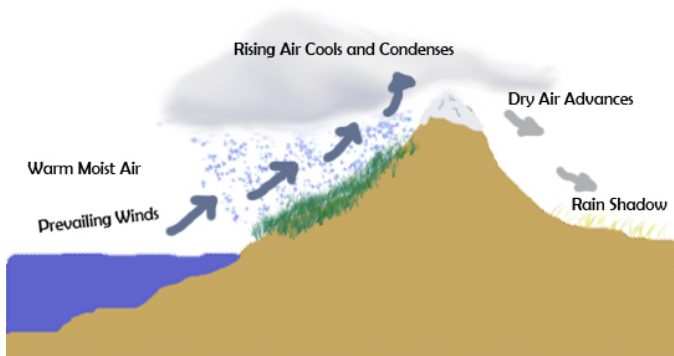
On the eastern side of the Rocky Mountains there is a phenomenon called chinooks.



These eastward moving wind patterns cause distinctive cloud patterns (chinook arches) and sudden increases in temperature.

Weather and Adiabatic Process in a Gas

As the air rises from the ocean it expands in the lower pressure at altitude and cools. The water vapor condenses out of the air and falls as precipitation.



As the air passes over the mountain it absorbs the latent heat from the water condensation, then it stops cooling. As it descends, it is compressed (nearly) adiabatically as the ambient pressure increases. The air temperature rises!

Temperature and the Distribution of Particles' Energies

In a gas at temperature T , we know the average translational KE of the molecules.

However, not all of the molecules have the same energy, that's just the average.

How is the total energy of the gas distributed amongst the molecules?

Temperature and the Distribution of Particles' Energies

Ludwig Boltzmann first found the distribution of the number of particles at a given energy given a thermodynamic system at a fixed temperature.

Assuming that energy takes continuous values we can say that the number of molecules per unit volume with energies in the range E to $E + dE$ is:

$$N_{[E, E+dE]} = \int_E^{E+dE} n_V(E) dE$$

Where

$$n_V(E) = n_0 e^{-E/k_B T}$$

and n_0 is a constant setting the scale: when $E = 0$, $n_V(E) = n_0$.

The Boltzmann Distribution

This particular frequency distribution:

$$n_V(E) \propto e^{-E/k_B T}$$

is called the **Boltzmann distribution** or sometimes the **Gibbs distribution** (after Josiah Willard Gibbs, who studied the behavior of this distribution in-depth).

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The probability for a given particle to be found in a state with energy E_i drawn from a sample at temperature T :

$$p(E_i) = \frac{1}{Z} e^{-E_i/k_B T}$$

where Z is simply a normalization constant to allow the total probability to be 1. (The **partition function**.)

The Boltzmann Distribution

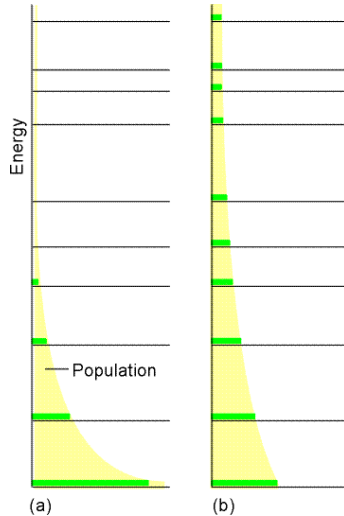
$$p(E_i) = \frac{1}{Z} e^{-E_i/k_B T}$$

If we know the energies of two states E_1 and E_2 , $E_2 > E_1$, we can find the ratio of the number of particles in each:

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

States with lower energies have more particles occupying them.

The Boltzmann Distribution



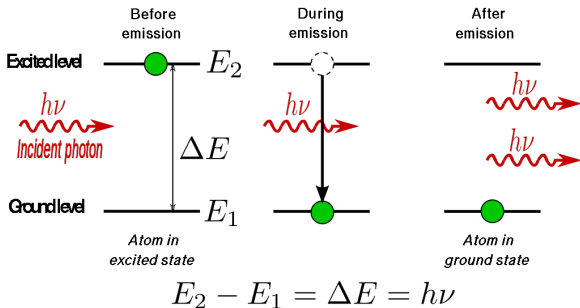
Lower temperature

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**.

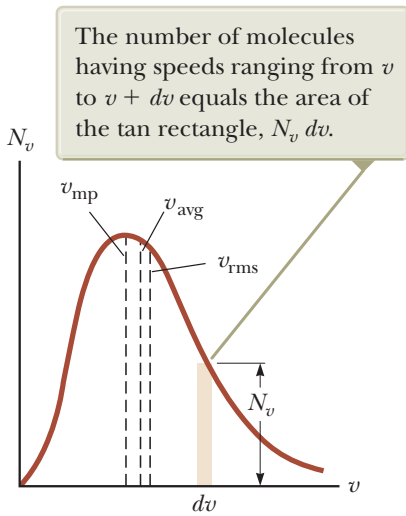
The number of molecules with speeds between v and $v + dv$ is

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

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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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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.

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

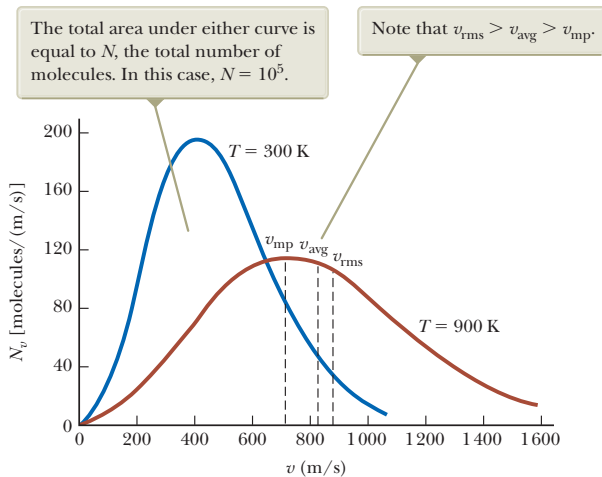
Maxwell-Boltzmann speed distribution

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

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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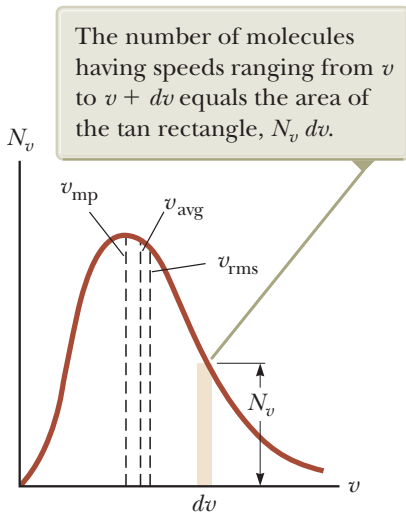
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So,

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

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.

Summary

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

Collected Homework due Monday, May 7.

Test Monday, May 14.

Homework Serway & Jewett:

- new: **Ch 21**, onward from page 644. Probs: 33, 37, 41, 42, 43, 52, 57, 69, 73