Thermodynamics
Boltzmann (Gibbs) Distribution
Maxwell-Boltzmann Distribution

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Last time

- heat capacities for ideal gases
- adiabatic processes

Overview

- adiabatic process in weather
- the Boltzmann distribution (distribution of energies)
- the Maxwell-Boltzmann distribution (distribution of speeds)

Reminder: 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, $P = \frac{nRT}{V}$.)

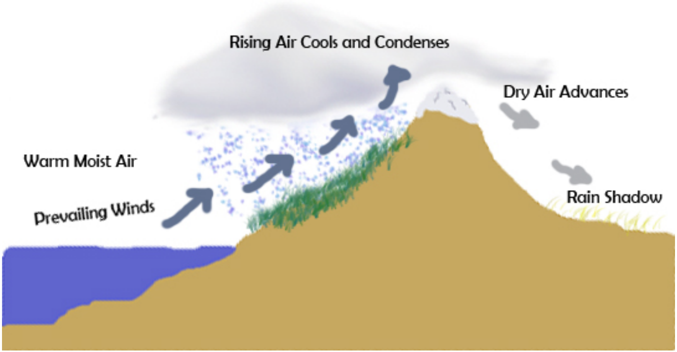
Weather and Adiabatic Process in a Gas

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:

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

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).

This distribution is even easier to understand for discrete energy levels.

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This distribution is even easier to understand for discrete energy levels.

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

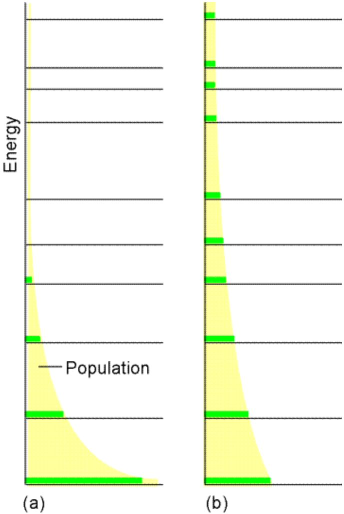
$$p(E_i) = \frac{1}{Z} e^{-E_i/k_B T}$$

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

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[1] Figure from the website of Dr. Joseph N. Grima, University of Malta.

(Somewhat Contrived) Example

Suppose a type of atom has only 2 energy states, separated in energy by 12.0 eV.[1] For a very large sample of these atoms, at what temperature would 1% of the atoms in the sample be in the excited (higher energy) state?

$$\Delta E = E_2 - E_1 = 12 \text{ eV}$$

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$$
\begin{aligned}
\frac{n_V(E_2)}{n_V(E_1)} &= \frac{1}{99} \\
e^{-(E_2-E_1)/k_B T} &= \frac{1}{99} \\
\frac{-(E_2-E_1)}{k_B T} &= -\ln(99) \\
T &= \frac{(E_2-E_1)}{k_B \ln 99} \\
&= \frac{12 \text{ eV} \times 1.602 \times 10^{-19} \text{ J/eV}}{(1.38 \times 10^{-23}) \ln 99} \\
&= 30,300 \text{ K} \quad \text{(3 sig figs)}
\end{aligned}
$$

---

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(Somewhat Contrived) Example

Suppose a type of atom has only 2 energy states, separated in energy by 12.0 eV.[2] For a very large sample of these atoms,

$$\Delta E = E_2 - E_1 = 12 \text{ eV}$$

At what temperature would the number of atoms in each state be equal?

---

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$$\frac{n_V(E_2)}{n_V(E_1)} \quad = \quad 1$$

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(Somewhat Contrived) Example

Suppose a type of atom has only 2 energy states, separated in energy by 12.0 eV.[2] For a very large sample of these atoms,

$$\Delta E = E_2 - E_1 = 12 \text{ eV}$$

At what temperature would the number of atoms in each state be equal?

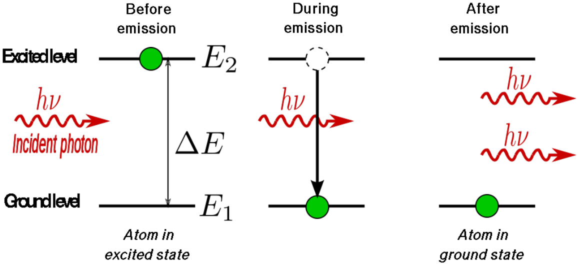
$$\begin{aligned} \frac{n_V(E_2)}{n_V(E_1)} &= 1 \\ e^{-(E_2-E_1)/k_B T} &= 1 \\ \frac{-(E_2-E_1)}{k_B T} &= 0 \\ T &\to \infty \end{aligned}$$

---

[2] This does not describe any real atom.

Aside: Lasers

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



$$E_2 - E_1 = \Delta E = h\nu$$

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".

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 $v + \mathrm{dv}$ is

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

Maxwell-Boltzmann speed distribution

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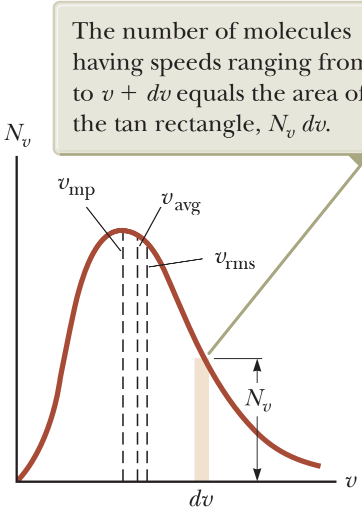

The number of molecules having speeds ranging from v to $v + dv$ equals the area of the tan rectangle, $N_v \, dv$.

Maxwell-Boltzmann speed distribution (Skipping)

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 (Skipping)

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 (Skipping)

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:

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

This is how we eliminate rotational and vibrational motion.

Maxwell-Boltzmann speed distribution (Skipping)

Put this expression in the Boltzmann distribution:

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

Eliminate dependence on position, rotation, and oscillation:

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

Maxwell-Boltzmann speed distribution (Skipping)

Put this expression in the Boltzmann distribution:

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

Eliminate dependence on position, rotation, and oscillation:

$$\int_\epsilon \int_{\mathbf{p}} p(\mathbf{r}, \mathbf{p}, \epsilon)\, \mathrm{d}^3\mathbf{r}\, \mathrm{d}^3\mathbf{p}\, \mathrm{d}\epsilon$$

$$= Ce^{-\mathbf{p}^2/2m_0 k_B T}\, \mathrm{d}\mathbf{p} \cancelto{1}{\left(C' \int_\epsilon e^{-\epsilon/k_B T} \mathrm{d}\epsilon \right)} \cancelto{1}{\left(C'' \int_{\mathbf{r}} e^{-U/k_B T}\, \mathrm{d}^3\mathbf{r} \right)}$$

Maxwell-Boltzmann speed distribution (Skipping)

Put this expression in the Boltzmann distribution:

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

Eliminate dependence on position, rotation, and oscillation:

$$\begin{aligned}&\int_\epsilon\int_{\mathbf{p}} p(\mathbf{r},\mathbf{p},\epsilon)\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p}\,\mathrm{d}\epsilon\\ &= Ce^{-\mathbf{p}^2/2m_0k_BT}\,\mathrm{d}\mathbf{p}\,\cancelto{1}{\left(C'\int_\epsilon e^{-\epsilon/k_BT}\,\mathrm{d}\epsilon\right)}\cancelto{1}{\left(C''\int_{\mathbf{r}} e^{-U/k_BT}\,\mathrm{d}^3\mathbf{r}\right)}\end{aligned}$$

$$p(\mathbf{p})\,\mathrm{d}^3\mathbf{p} = Ce^{-\mathbf{p}^2/2m_0k_BT}\,\mathrm{d}^3\mathbf{p}$$

Maxwell-Boltzmann speed distribution (Skipping)

Put this expression in the Boltzmann distribution:

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

Eliminate dependence on position, rotation, and oscillation:

$$\int_\epsilon\int_{\mathbf{p}} p(\mathbf{r},\mathbf{p},\epsilon)\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p}\,\mathrm{d}\epsilon$$

$$= Ce^{-\mathbf{p}^2/2m_0k_BT}\,\mathrm{d}\mathbf{p}\,\cancelto{1}{\left(C'\int_\epsilon e^{-\epsilon/k_BT}\,\mathrm{d}\epsilon\right)}\cancelto{1}{\left(C''\int_{\mathbf{r}} e^{-U/k_BT}\,\mathrm{d}^3\mathbf{r}\right)}$$

$$p(\mathbf{p})\,\mathrm{d}^3\mathbf{p} = Ce^{-\mathbf{p}^2/2m_0k_BT}\,\mathrm{d}^3\mathbf{p}$$

replace momentum with velocity components:

$$p(\mathbf{v})\,\mathrm{d}^3\mathbf{v} = Ce^{-m_0(v_x^2+v_y^2+v_z^2)/2k_BT}\,\mathrm{dv_x}\,\mathrm{dv_y}\,\mathrm{dv_z}$$

Maxwell-Boltzmann speed distribution (Skipping)

We can find C.

The total probability must equal one.

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

Using the identity:

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

the three integrals can be evaluated separately:

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

There are three integrals, so

$$C = \left(\frac{m_0}{2\pi k_B T}\right)^{3/2}$$

Maxwell-Boltzmann speed distribution (Skipping)

Now our distribution is:

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

Lastly, we want an expression for how many molecules have speeds between v and $v + \mathrm{dv}$.

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

$$\mathrm{dv_x}\,\mathrm{dv_y}\,\mathrm{dv_z} = v^2 \sin\theta\ \mathrm{dv}\ \mathrm{d}\theta\,\mathrm{d}\phi$$

Maxwell-Boltzmann speed distribution (Skipping)

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

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

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

Summary

- Boltzmann distribution (energies)
- Maxwell-Boltzmann distribution (speeds)

Homework

- Full-solution HW2, due today
- WebAssign, due today

Serway & Jewett (additional problems you might like to look at):

- Ch 21, onward from page 644. Probs: 52, 58, 65
- new: Ch 21, onward from page 644. Probs: 41, 42, 43