

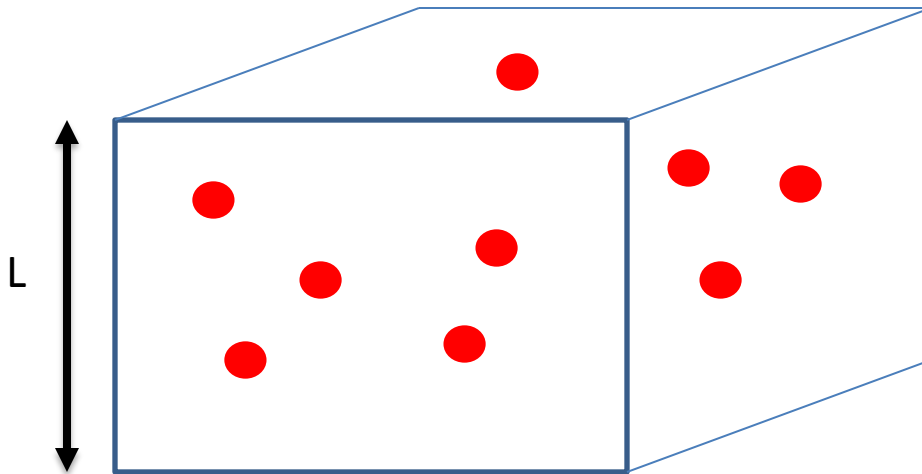
Topic 3b: Kinetic Theory

What is temperature?

We have developed some statistical language to simplify describing measurements on physical systems.

When we measure the temperature of a system, what underlying microscopic quantity are we actually detecting?

We will see that temperature is a property of the disordered motion of a system

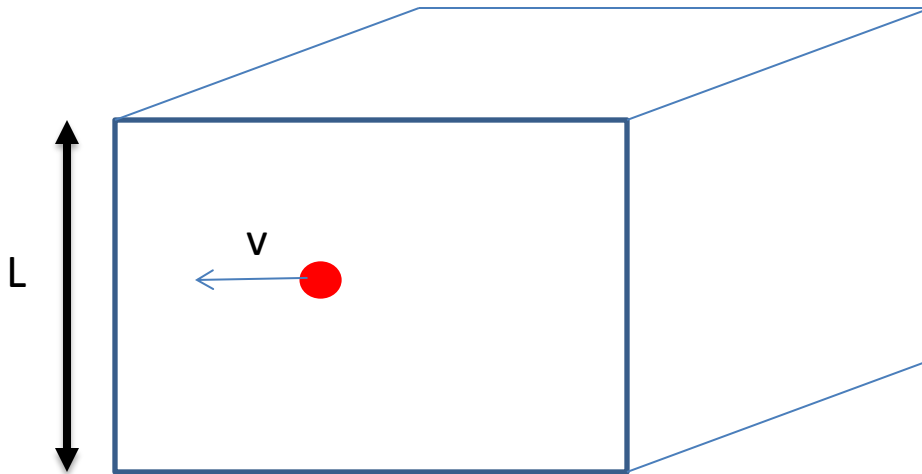


Let's consider an ideal gas in a box:

$$PV = N k_B T$$

here N is the total number of gas molecules in box.

Pressure of ideal gas



The pressure arises from the gas molecules colliding with the walls of the container.

What is the force due to these collisions?

1st year definition

\xrightarrow{x}
 $-v_x m$
 $\xrightarrow{+v_x}$
 wall Now

$F_i = \frac{\Delta p_i}{\Delta t}$ \approx rate of change of momentum

$\Delta p = p_f - p_i = m v_x - (-m v_x) = 2m v_x$

What is Δt ? Δt is time between collisions with wall
 \equiv time for round trip

so $\Delta t = 2L/v_x$

so $F_i = \frac{\Delta p}{\Delta t} = \frac{2m v_x}{(2L/v_x)} = \frac{m v_x^2}{L}$

Pressure as a microscopic average:

The total force is a sum over all the particles in the box:

$$F_x = \sum_{i=1}^N m \frac{(v_i)_x^2}{L} = \frac{Nm}{L} \langle v_x^2 \rangle$$

← average

recall: $\langle x \rangle = \frac{1}{N} \sum_i x_i$

• If atoms are moving randomly in each direction then $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$

so
$$F_x = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{L}$$

Pressure:
$$P = \frac{F}{A} = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{AL} = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{\underbrace{AL}_{\text{Volume}}}$$

or

$$PV = \frac{1}{3} Nm \langle v^2 \rangle = \frac{2}{3} N \left(\frac{1}{2} m \langle v^2 \rangle \right)$$

Microscopics of temperature

But we know that for an ideal gas, the relationship between macroscopic quantities is, $PV = N k_B T$. So equating the last result with this, we get

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

Thus temperature is equal to the average kinetic energy associated with the motion of the particles. Each degree of freedom, (i.e. motion in x, y or z) has $\frac{1}{2} k_B T$ worth of energy associated with its random motion.

From this we can define a root mean squared speed for particles at a given temperature

$$\sqrt{\langle v^2 \rangle} = v_{rms} = \sqrt{\frac{3 k_B T}{m}}$$

For the O₂ molecules in this room, with $T = 293 \text{ K}$, $v = 480 \text{ m/s}$

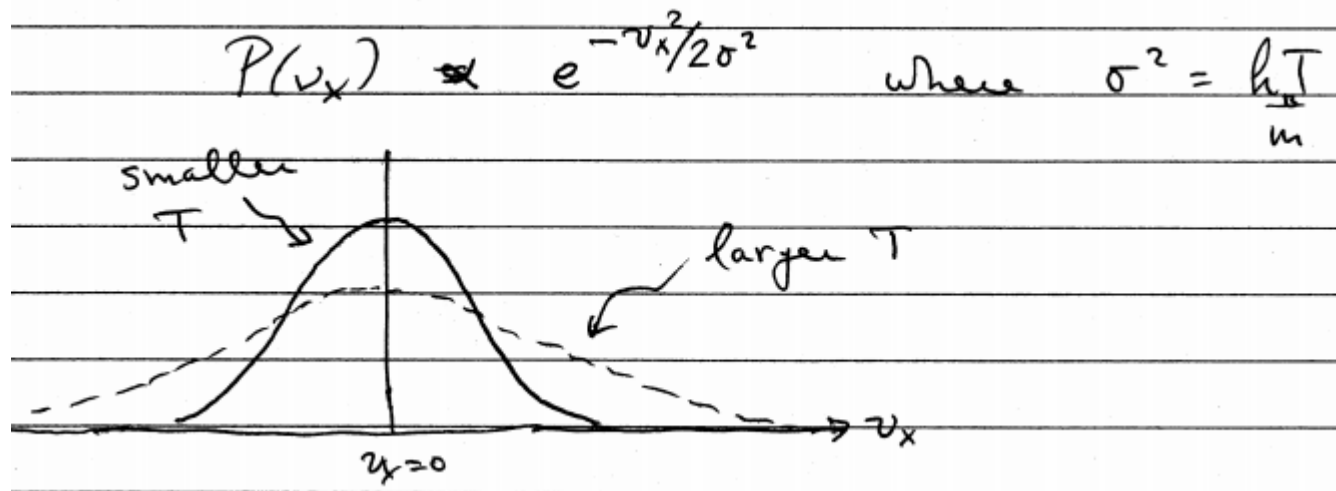
Distribution of velocities

Temperature is related to the variance of the velocities of the gas molecules, $\langle v^2 \rangle$, since $\langle v \rangle = 0$. (recall $\sigma_x^2 = \langle x^2 - \langle x \rangle^2 \rangle$)

Can we determine the probability distribution of the velocities? The distribution must satisfy:

1. equal number of particles move to left and to the right so, $\langle v \rangle = 0$
2. the probability of observing $-v$ is the same as $+v$, so the distribution must be symmetric
3. the variance is given by $\sigma^2 = k_B T / m$

a distribution that satisfies this is the Gaussian distribution with $\langle v \rangle = 0$ and above variance.



Probability of a state:

So we now know the probability of observing a single gas molecule with velocity v .

What is the probability of observing a state of N gas molecules with velocities = $\{v_1, v_2, v_3, \dots, v_N\}$? (it's the probability of v_1 AND v_2 AND v_3 AND etc)

$$P(v_1, v_2, v_3, v_4, \dots, v_N) = P(v_1) \cdot P(v_2) \cdot P(v_3) \cdot \dots \cdot P(v_N)$$

$$\propto e^{-mv_1^2/2kT} e^{-mv_2^2/2kT} \dots e^{-mv_N^2/2kT}$$

$$= \exp\left[-\frac{1}{kT} \left(\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \dots + \frac{1}{2}mv_N^2\right)\right]$$

$$= \exp\left[-E/kT\right]$$

In general, for any system:

$$P(\text{state}) \propto \exp\left(-\frac{E(\text{state})}{k_B T}\right)$$

The Boltzmann distribution:

This is the most important equation in the course, the Boltzmann distribution

$$P(\text{state}) \propto \exp\left(-\frac{E(\text{state})}{k_B T}\right)$$

It gives the probability of a system being in a given state with energy, E , at a temperature, T .

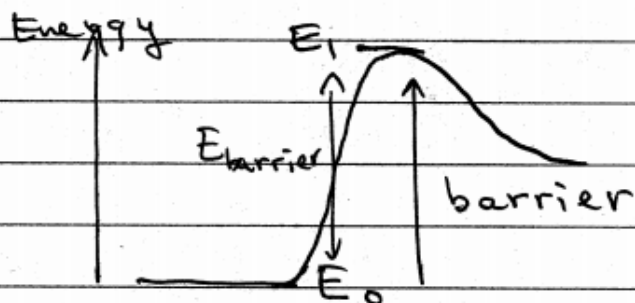
We can use it as it is to compute the relative probability of two states in a system:

$$\frac{P(\text{state } 1)}{P(\text{state } 0)} = e^{-(E_1 - E_0)/k_B T} \leftarrow \text{only depends on energy difference}$$

Thus the relative probability between two states only depends on the energy difference between them.

Arrhenius Law:

Think about chemical reactions



• In order for reaction to take place the molecule needs to get over the energy barrier

• The probability that a molecule will have enough energy to get over the barrier, $E_{\text{barrier}} = E_1 - E_0$ is

$$P \propto e^{-\frac{E_{\text{barrier}}}{k_B T}} \equiv \text{Arrhenius Law}$$

• So ① if $E_{\text{barrier}} \gg k_B T$ the reaction will rarely occur

② as T increases, the reaction will become more probable

Entropy of an ideal gas

We've looked at the probability of a particular state of an ideal gas, but how many states are there with a given energy E ? i.e. what is the entropy?

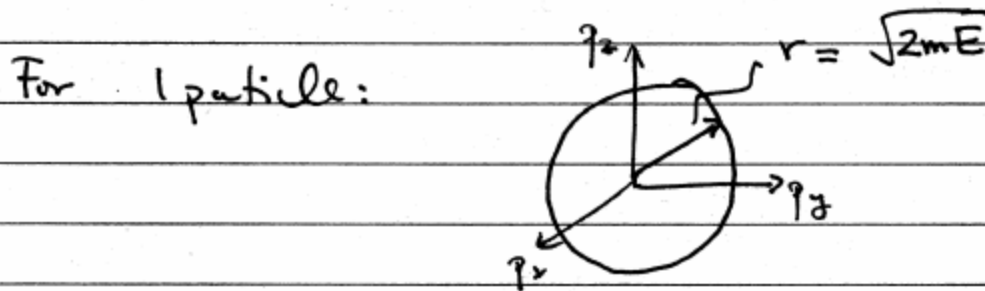
$$S = k_B \log \Omega(E)$$

where

$$E = \sum_{i=1}^N \frac{m \vec{v}_i^2}{2} = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i^2 = \frac{1}{2m} \sum_{i=1}^N (p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2)$$

Now how many $p_{i,x}$, $p_{i,y}$, $p_{i,z}$ are there that all give the same value E ? that's the number of states that we have to count. How are we going to count that?

eqn: $x^2 + y^2 + z^2 = R^2$, equation of a sphere.



Counting momentum states:

• (p_x, p_y, p_z) reside on sphere with radius $\sqrt{2mE}$

• # of states is \propto area of sphere
 $= r^2 = r^{(3N-1)}$

• N -dimensional hyper-sphere: $A_N \propto r^{3N-1} \approx r^{3N}$

• However for each set of p_x, p_y, p_z we can also put the particles at any position in the volume V

• # of relabeling of N particles $\sim V^N$

So the # of states for an N particle ideal gas.

$$\Omega \propto r^{3N} \cdot V^N = (\sqrt{2mE})^{3N} V^N$$

so

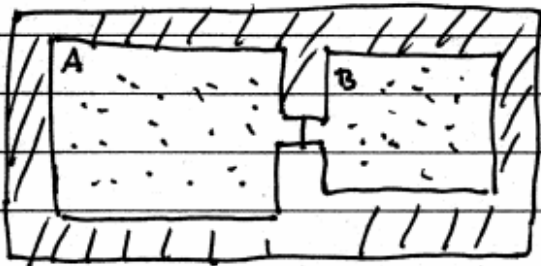
$$S = k_B \ln \Omega = N k_B \ln(E^{3/2} V) + \text{const}$$

Can we get some well known results from this?

Zeroth law of thermodynamics:

The zeroth law says that two bodies in contact will come to the same temperature.

Can we use the entropy of an ideal gas to prove this?



- Two boxes, N_A & V_A & N_B & V_B
- $E_{tot} = E_A + E_B$, fixed.

• ~~at equilibrium~~ If E_A goes up then E_B must go down to maintain E_{tot} .

• @ equilibrium all states @ E_{tot} are equally probable

recall: $P(\text{state}) \propto \exp\left(-\frac{E_{tot}}{k_B T}\right)$

• If we take a snapshot, what will the most likely value of E_A be? (Answer follows)

• Consider Total Entropy: $S_{tot} = S_A(E_A) + S_B(E_B)$

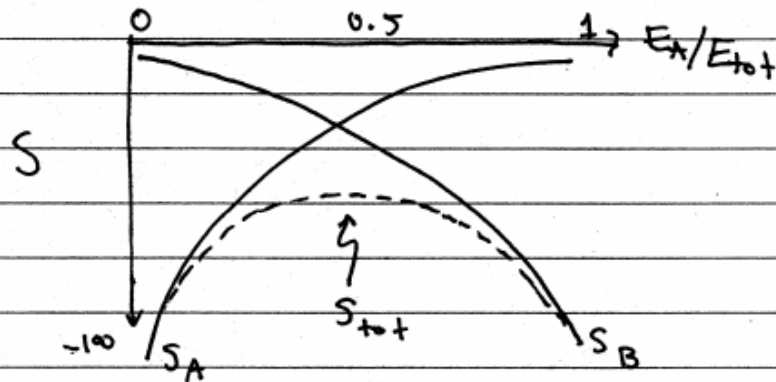
$$= S_A(E_A) + S_B(E_{tot} - E_A)$$

Thermodynamic laws continued

Using ideal gas S :

$$S_{tot}(E_A) = k_B \left[N_A \left(\frac{3}{2} \ln E_A + \ln V_A \right) + N_B \left(\frac{3}{2} \ln (E_{tot} - E_A) + \ln V_B \right) \right] + \text{const.}$$

Graphs:



- The most likely E_A occurs when S_{tot} is maximum which is where $dS_{tot}/dE_A = 0$

$$\Rightarrow \frac{3}{2} k_B \left(\frac{N_A}{E_A} - \frac{N_B}{E_B} \right) = 0$$

OR

$$E_A = \langle E_A \rangle = E_B = \langle E_B \rangle$$

recall: $\langle E \rangle = \frac{3}{2} k_B T$, so

$$T_A = T_B$$

Thermodynamic definition of temperature:

New definition of temperature:

equilibrium: $T_A - T_B = 0$

Define: $T = \left(\frac{dS}{dE} \right)^{-1}$

Check units: $[k_B] = \frac{[E]}{[T]}$, $\left(\frac{[S]}{[E]} \right)^{-1} = \left(\frac{1}{[T]} \right)^{-1} = [T]$

• Thus the two systems will exchange energy & entropy so that $T_A = \left(\frac{\Delta S_A}{\Delta E_A} \right)^{-1} = T_B = \left(\frac{\Delta S_B}{\Delta E_B} \right)^{-1}$

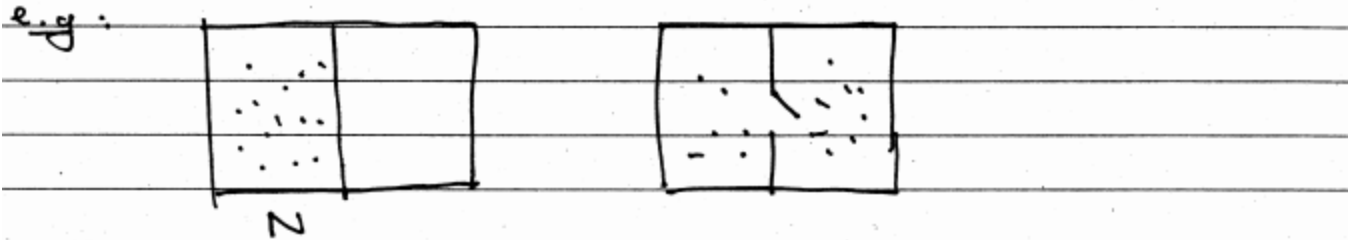
• So temperature only has a statistical definition, it is related to how much a system's disorder changes when we change the system's energy.

• if $\frac{\Delta S}{\Delta E} \gg 1$ then T is low

• if $\frac{\Delta S}{\Delta E} \ll 1$ then T is high

2nd Law and ideal gas

When an ideal gas expands, does the entropy go up?



$$\Delta S? \quad S_1 = Nk_B \ln V + \text{const} ; S_2 = Nk_B \ln 2V$$

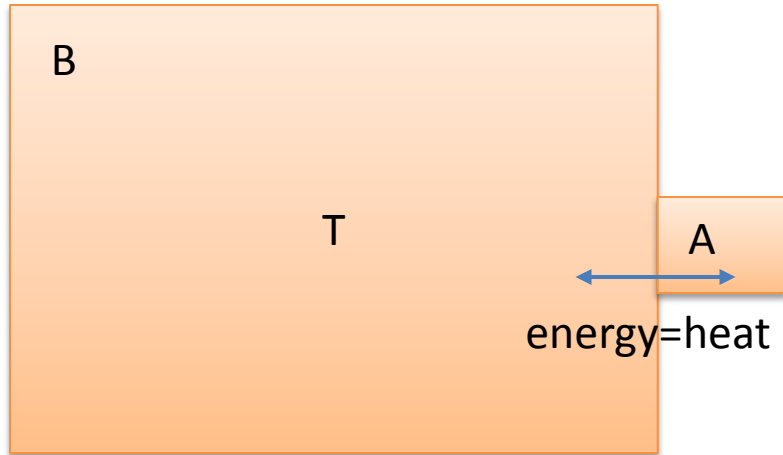
$$\text{so } \Delta S = S_2 - S_1 = Nk_B (\ln 2V - \ln V) = Nk_B \ln 2$$

> 0

Could we ever put the molecules back on the LHS? Yes, but we'd have to do work by compressing it \rightarrow heating it up.

Thus to create order we must use up mechanical work & turn it into heat.

Open systems and free energy:



consider a small system, A in contact with a huge system B, both at temperature T.

any energy change from system A corresponds to a gain or loss of heat to system B, but its temperature does not change because it's so big

So, $\Delta E_A = -\Delta E_B$ and we have that the temperature defined as $T \Delta S_B = \Delta E_B = -\Delta E_A$

If we consider the total change in entropy, we must have $\Delta S_{tot} = \Delta S_A + \Delta S_B \geq 0$, or

$$T\Delta S_A + T\Delta S_B = T\Delta S_A - \Delta E_A \geq 0$$

which is just changes for the small system, A:

$$-(E_f - E_i) + T(S_f - S_i) \geq 0 \quad \text{or} \quad E_f - TS_f \leq E_i - TS_i \quad (\text{this looks familiar})$$

Open systems and free energy:

So in an open system, where a small system is in contact with a thermal bath, energy will be exchanged so that the quantity $E - TS$ is lowered. We define this quantity to be the free energy.

$$G = E - TS$$

for open systems, this is the quantity that gets lowered. Both energy and entropy can change for the small system in order to lower the free energy.

We will often write the free energy, G , in terms of some changeable parameter, x , of the open system, for example a protein's size, or the number of bound factors to DNA etc.

Equilibrium occurs when the free energy is at a minimum with respect to this parameter,

$$\frac{dG}{dx} = 0$$

Summary

- we found that temperature is related to the average kinetic energy
- the distribution of velocities for an ideal gas follows a Gaussian
- the probability of a state is proportional to $\exp(-E/kT)$
- the entropy of an ideal gas led us to some familiar results from thermodynamics
- we showed that for open systems the quantity $G = E - TS$ is minimized