Entropy

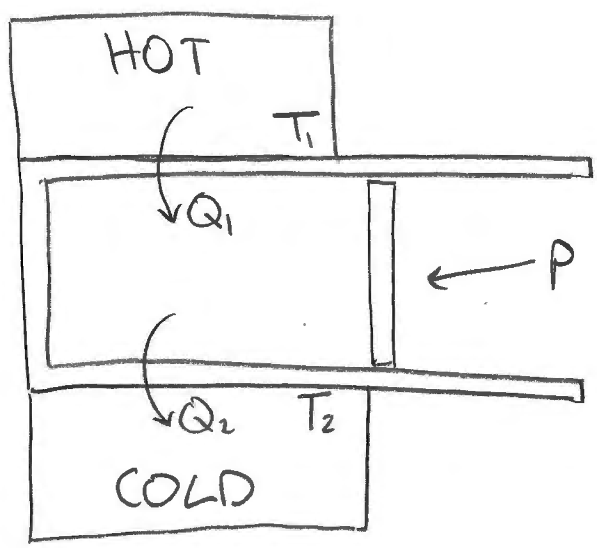
Irreversibility and the Heat Death of the Universe

In thermo, we learned that entropy corresponds to irreversibility, and the key to producing the most efficient possible engine was to avoid irreversibility.

We defined entropy change as

$$\Delta S = \frac{Q}{T}$$

For a reversible engine the entropy flow from a hot bath into a piston Q_1/T_1 was equal to the entropy flow from the piston into the cold bath Q_2/T_2



$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

In any realistic case, the engine will create net entropy during a cycle, and <u>NO</u> engine can reduce the total amount of entropy.

Irreversible increase of entropy is NOT a property of the microscopic laws of nature.

The microscopic laws (our Hamiltonian) are time-reversal invariant, and these laws are the same whether time runs forward or backward.

The direction in which entropy increases is our definition of "FUTURE"

Irreversibility brings about a tough question: what is the entropy of the universe?

Heat Death of the Universe

From the Big Bang to present, and into the future, matter and dark matter are thought to be concentrated in stars, galaxies, and clusters.

Therefore, the universe is NOT in equilibrium. Work can be done.

Our universe is also expanding; Assume the radius grows linearly in time (Hubble's Law)

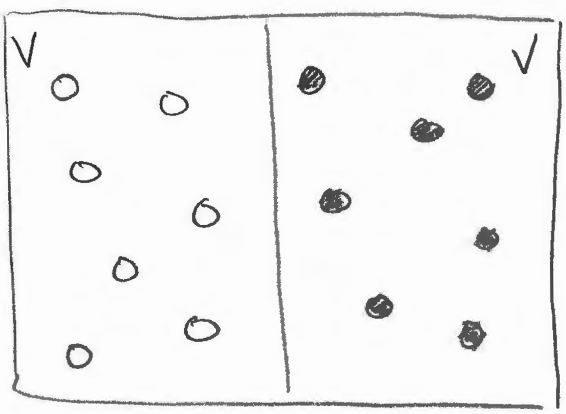
Also, the cosmic microwave background radiation has a characteristic temperature $\Theta(t) \sim \frac{1}{R}$, which gets lower as the universe expands.

As long as work can be done, and the universe is cooling, then we can gain entropy, $\Delta S = \frac{Q}{T}$

Since the idea of a "big bang" was established, the ultimate fate of the universe became a valid cosmological question. The answer is complicated but depends on the physical properties of the mass/energy in the universe, its average density, and the rate of expansion.

Entropy as Disorder: Mixing

Consider N atoms in a box of volume $2V$, except that $N/2$ are white and $N/2$ are black.



$\frac{N}{2}$ undistinguished gas atoms are separated by a partition

All atoms have the same mass and total energy.

What is the change in entropy, if any, between the mixed and unmixed state?

First, we can write the configuration entropy (ignoring momentum space) of the unmixed system

$$S_{unmixed} = k_B \ln\left[\Omega^q(E)\right] = k_B \ln\left[\Omega^q_W(E)\,\Omega^q_B(E)\right]$$

$$= k_B \ln\left[\frac{V^{N/2}}{(N/2)!}\cdot\frac{V^{N/2}}{(N/2)!}\right] = k_B \ln\left[\left(\frac{V^{N/2}}{(N/2)!}\right)^2\right]$$

$$= 2 k_B \ln\left[\frac{V^{N/2}}{(N/2)!}\right]$$

$S_{unmixed}$ is just twice the entropy of each individual gas.

Now, we remove the partition and allow the gasses to mix. What is the entropy change?

Since temp and pressure from both sides are equal, removing the partition results in NO irreversible sound or heat transfer.

Any entropy change is due solely to mixing of white and black atoms

Now that they are mixed, the entropy is

$$S_{mixed} = k_B \ln\left[\left(\frac{(2V)^{N/2}}{(N/2)!}\right)^2\right]$$

$$= 2 k_B \ln\left[\frac{(2V)^{N/2}}{(N/2)!}\right]$$

Let's find ΔS_{mixing}:

$$\Delta S_{mixing} = S_{mixed} - S_{unmixed}$$

$$= 2k_B \ln\left[\frac{(2V)^{N/2}}{(N/2)!}\right] - 2k_B \ln\left[\frac{V^{N/2}}{(N/2)!}\right]$$

$$= 2k_B \ln\left[2^{N/2}\right] + \cancel{2k_B \ln\left[\frac{V^{N/2}}{(N/2)!}\right]} - \cancel{2k_B \ln\left[\frac{V^{N/2}}{(N/2)!}\right]}$$

$$\boxed{\Delta S_{mixing} = N k_B \ln 2}$$

This says that we gain $k_B \ln 2$ worth of entropy for each of the N atoms that we place into one of the two boxes without looking.

In general, we can define a "counting" entropy for systems with a discrete number of choices:

$$S_{counting} = k_B \ln [\# \text{ of configurations}]$$

This shows up all the time in stat mech.

Now, what happens if the partition separates two sides each with $N/2$ black atoms?

The initial entropy is the same:

$$S^B_{unmixed} = 2 k_B \ln \left[\frac{V^{N/2}}{(N/2)!} \right]$$

But the final entropy changes:

$$S^B_{mixed} = k_B \ln \left[\frac{(2V)^N}{N!} \right]$$

compare to

$$S_{mixed} = 2 k_B \ln \left[\frac{(2V)^{N/2}}{(N/2)!} \right]$$

So

$$\Delta S^B = S^B_{mixed} - S^B_{unmixed}$$

$$= k_B \ln\left[\frac{(2V)^N}{N!}\right] - 2k_B \ln\left[\frac{V^{N/2}}{(N/2)!}\right]$$

$$= k_B\left[N \ln 2V - \ln N!\right] - k_B\left[N \ln V - \ln\left(\left(\tfrac{N}{2}\right)!^2\right)\right]$$

use $\ln n! \simeq n \ln n - n$

$$= 0$$

The entropy per atom is UNCHANGED

Without the term $N!$ (Gibbs Factor), this calculation would have lead to an entropy DECREASE of $N \ln 2$ whenever we split a container into 2 parts.

- This was called the "Gibbs Paradox" and is the origin of the Gibbs factor.

Finally, we can connect the entropy of mixing to the thermodynamic entropy of pistons and steam engines.

Suppose that the partition was impermeable to black atoms, but allowed white atoms to go past

In this case, a pressure imbalance would build. If the semipermable membrane was used as a piston, work could be extracted as the black chamber enlarged to fill the volume.

This is the origin of osmosis and osmotic pressure