Irreversible Processes and Entropy

- Irreversible processes are associated with an increase in entropy. We will illustrate this with examples

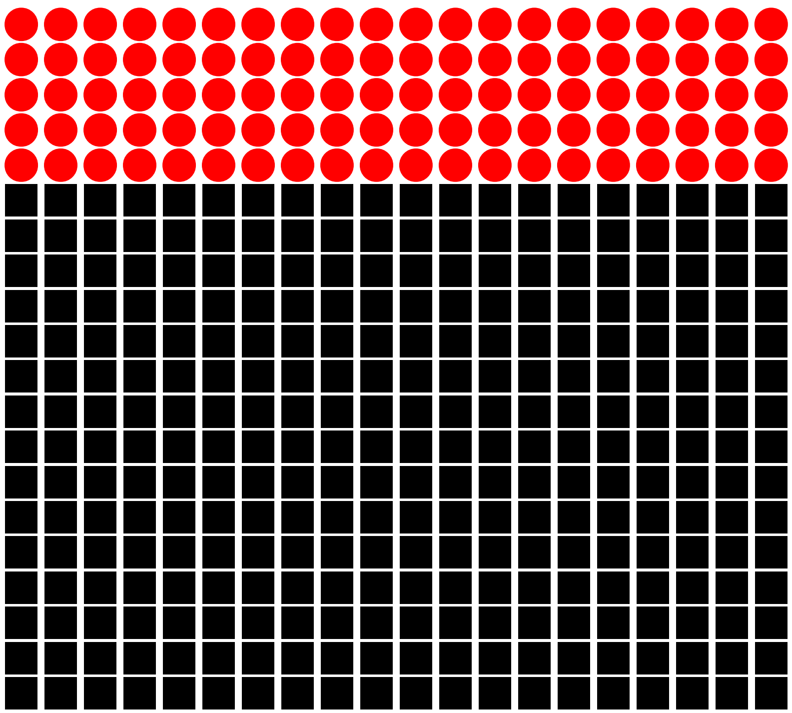
- First consider a completely ordered state of N harmonic oscillators, shown in (a). By a sequence of random hops transferring energy from site to site (see previous lectures) the system ends up in slide (b). It is equally to be in any of its states. It will never hop back to the completely ordered state although this is allowed energetically. The transition is irreversible and associated with an increase in the total # of possible states, $\Delta S_{univ} > 0$
(see also previous lectures)

- Next consider a gas initially on the left side (see slide) a container. The microstates are labelled by the positions and momenta of all particles $x_1, p_1 \ldots x_N, p_N$. When the plug is removed the available volume to each particle is increased. The gas will rush and fill the container, increasing the entropy of the system. For instance initially each particle was in the Left state. Afterwards it is either in Left or Right state. The number of states per particle has doubled and $\Omega_{final} / \Omega_{init} = 2^N$.

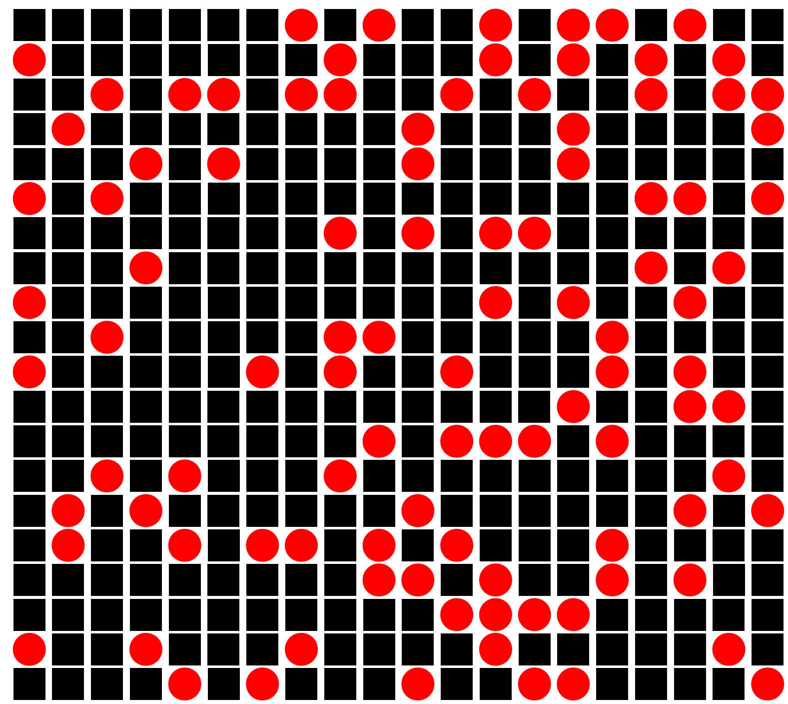
Left ≡ L

(E.g. take two particles $N=2$. The initial state is LL. The possible final states are LL, LR, RL, RR: this is 4 times the number of initial states)

Ordered versus typical state: e^{225} states in total



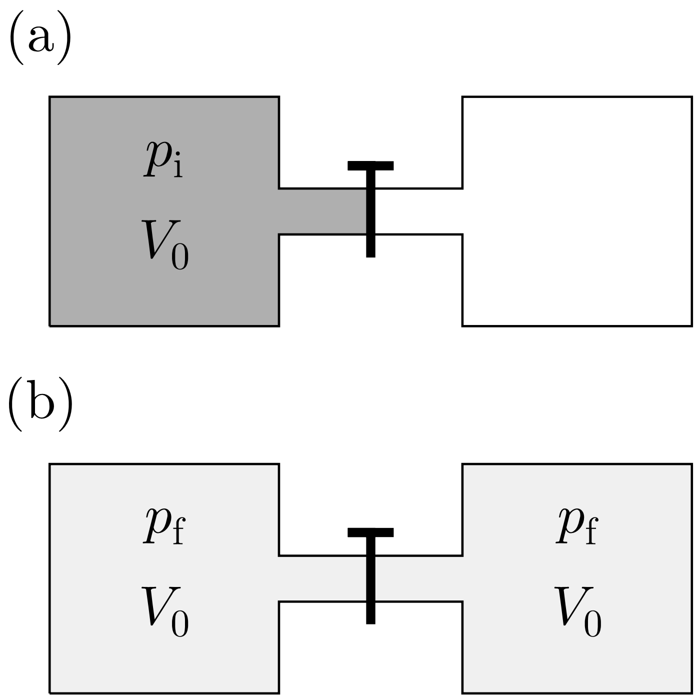
Ordered state: 400 atoms, 1/4 are excited, $E = 100\,\Delta$



a typical state: the energy is still, $E = 100\,\Delta$

Joule Expansion

The gas is initially all on the left. When the valve is openned the gas rushes to fill the right hand side of the container.



The expansion
is a highly non-equilibrium process.

During the expansion no heat
enters the system. Thus the
energy initial equals the final energy

So

$$\Delta S = k_B \ln \Omega_{final} - k_B \ln \Omega_{init} = N k_B \ln 2$$

We will derive this more formally later.
The particles will never go back to being on the left side (although it is not forbidden) since there a just way more configurations with the particles more equitably distributed.

- Summarizing all irreversible processes have

$$\boxed{\Delta S_{univ} > 0}$$

It is the weight of possibilities. There are of order 2^N more configurations with the gas completely filling the room, then with the gas on completely on the left. The gas explores these configurations for eternity, never returning to being only on the left.

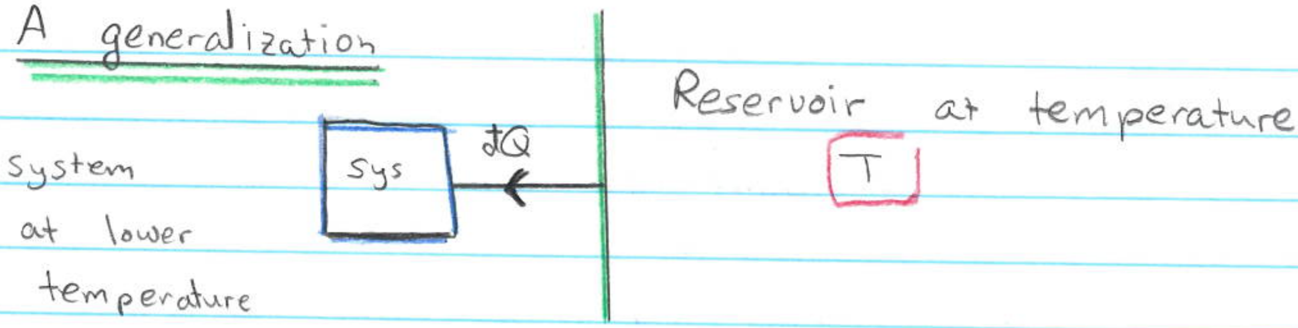
When the system is fully equilibrated, S has increased as much as it can, and

$$\Delta S_{univ} = 0$$

So in general:

$$\boxed{\Delta S_{univ} \geq 0}$$

A generalization



Consider a system interacting with a reservoir. A Reservoir is a large body (e.g. a lake or an ocean) whose temperature T is always fixed. The rate at which heat đQ is taken out of the reservoir is slow compared to the rate of equilibration. The system + reservoir forms the universe:

$$dS_{sys} + dS_{res} \geq 0$$

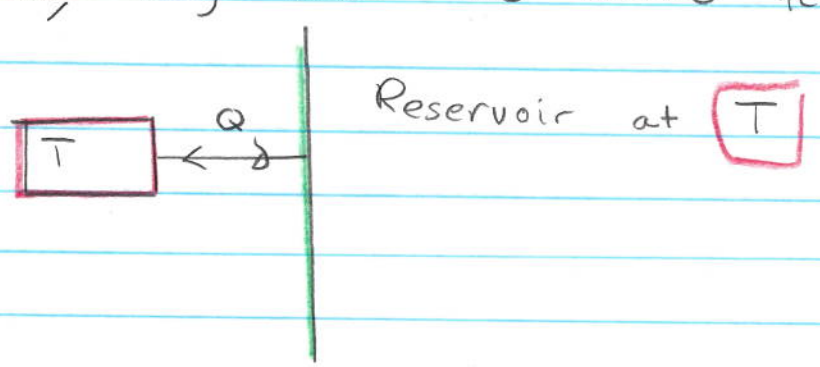
But, the reservoir has $dS_{res} = -\frac{Q}{T_0}$ (it is always in equilibrium) and so

$$\boxed{dS_{sys} \geq \frac{đQ}{T}}$$

heat added to system

temperature of reservoir

In the limit that the system and bath are in equilibrium, they have the same temperature:



Now heat can flow both ways (i.e. the heat transfer is reversible) without increasing the entropy of the universe

$$dS_{sys} + dS_{res} = 0$$

system + reservoir in equilibrium $\longrightarrow$ $dS_{sys} - \frac{đQ}{T} = 0$

$$\boxed{dS_{sys} = \frac{đQ_{rev}}{T}}$$

we put "rev" as a reminder that the reservoir and system are ...

... assumed to be in equilibrium, $\Delta S = 0$, so that heat can flow both ways, as opposed to an irreversible process where the heat flows one way, $\Delta S > 0$.

If there is more than one reservoir then we should generalize $\Delta S_{\text{sys}} \geq Q/T$. Say there are multiple reservoirs at temperature T_1, T_2, $\ldots T_N$ with heat transfers to the system Q_1, Q_2, $\ldots Q_N$. Then the appropriate generalization is

$$\Delta S_{\text{sys}} \geq \frac{Q_1}{T_1} + \frac{Q_2}{T_2} \ldots + \frac{Q_N}{T_N}$$

Sometimes this las expression is sometimes written

$$\Delta S_{\text{sys}} \geq \int \frac{\text{d}Q}{T}$$

But, I find the discrete case easier to interpret