Statistical meaning of entropy. The second law of thermodynamics

We have established that the change of the internal energy of a system is given by

$$dE = \delta W_{ext} + \delta Q$$

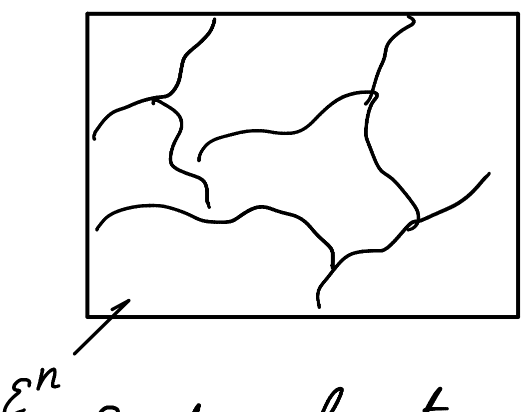
By considering a process in which the system is always in equilibrium with the environment (whose temperature may change) we established that

quasistatic process

$$\delta Q = T\,dS$$

where $S = \frac{E}{T} + \ln Z$ is the entropy.

Explore in more detail its statistical meaning.



Consider a macroscopic system, which we will split into subsystems, each containing very many particles
$\Rightarrow$ each subsystem is quasiisolated

Each subsystem is in equilibrium, we assume

$$Z_n = \sum_i e^{-\varepsilon_i^n/T} N(\varepsilon_i^n) \approx e^{-\frac{E_n}{T}} N(\varepsilon_i^n)$$

$N(\varepsilon_i^n)$ ← The degeneracy of the respective level

Take the log of that (Note: we don't need to know $N(\varepsilon_i^n)$ super accurately; log accuracy is needed)

$$\ln Z_n + \frac{E_n}{T} \approx \ln N(E_n)$$

Thus, $S_n \approx \ln N(E_n)$

The subsystems are not necessarily in equilibrium with each other. We define the total entropy

$$S = \sum_n S_n$$

$$S = \sum_n \ln N(E_n) = \ln \prod_n N(E_n) = \ln N$$

The full number of states for a given distribution of subsystems

$$S = -\ln w$$ ← <u>Boltzmann's entropy formula</u>

Relies on the microcanonical distribution (for a system with a given energy)

If the system may be in a state with very different energies

$$S = -\sum_i w_i \ln w_i \equiv -\mathrm{Tr}\,(\hat{\rho} \ln \hat{\rho})$$

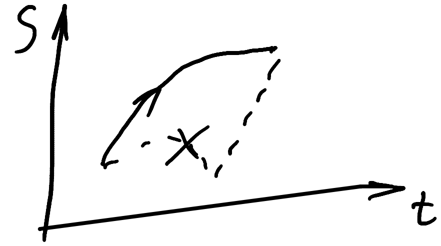
– in principle applies to non-equilibrium systems

Let's assume the system is out of equilibrium, in a state whose probability is w_1. After some time, it will come to its equilibrium state, whose probability is greater (by definition).

That means there will be equilibrium between all the subsystems we considered. Because $w_f > w_1$, the entropy in the equilibrium state is greater

[illegible] in the equilibrium [illegible] all the subsystems [illegible] the entropy in the equilibrium state is greater

This transition happens monotonously



If the system is in the equilibrium state initially, then it will remain there. So, in general

$\Delta S \geq 0$

– the second law of thermodynamics

It may be also used is a criterion of reversibility of a process. If a process is reversible, then the entropy is constant in it. If, however, the entropy grows, then the process is irreversible.

As an exampe, consider a process in which two systems at different temperatures

$$\delta S = \delta S_1 + \delta S_2 = \frac{\partial S_1}{\partial E_1} \delta E_1 + \frac{\partial S_2}{\partial E_2} \delta E_2 =$$

$$= \frac{\delta E_1}{T_1} + \frac{\delta E_2}{T_2} \geq 0$$

According to the energy conservation law, $\delta E = \delta E_1 + \delta E_2 = 0$

$$\delta S = \delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0$$

Th[illegible] that if $T_1 < T_2$, then $\delta E_1 \geq 0$

$\delta S = \delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

This means that if $T_1 < T_2$, then $\delta E_1 \geq 0$

if $T_1 > T_2$, $\delta E_1 \leq 0$

→ Heat flows from the hotter body to the colder one, and this is a <u>consequence of the second law</u>

What if the system is not closed?

Consider a system whose external macroscopic parameters may be changed. For open, but thermally isolated systems $\delta S \geq 0$.

In general, one may say $\delta S \geq \frac{\delta Q}{T}$, when a system is allowed to exhange heat. For quasistatic processes $\delta S = \frac{\delta Q}{T}$. This inequality says that there may be an additional increase of entropy due to transitioning to a more probable state.

This means that for an open system a reversible process means $\delta S = \frac{\delta Q}{T}$. For irreversibe processes, $\delta S > \frac{\delta Q}{T}$

$$\delta E \leq T \delta S + \delta W_{ext}$$