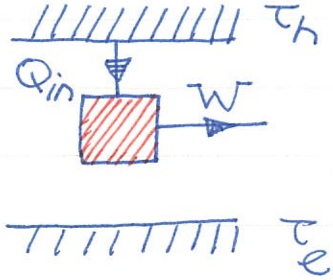
HH0026 The Second Law of Thermodynamics

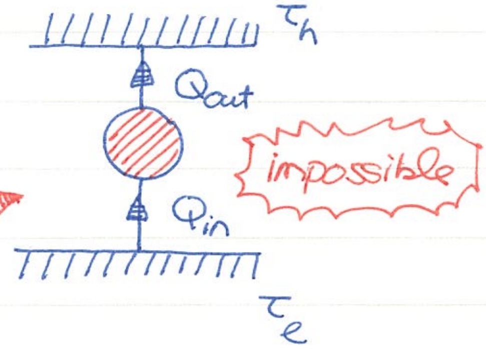
The 2^{nd} law has various forms. One of the earliest forms can be stated in Carnot's language easily.



$\boxed{Q_{in} = W}$

It's impossible to have a perfect heat engine like this!

Or, equivalently,



Let's try to re-state the 2^{nd} law in modern language.

> For an isolated system, its entropy never decreases and it remains constant during a reversible process.
> That is to say, $\Delta\sigma \geq 0$

Let's go back to the case of a "perfect" refrigerator.

$$Q_{out} = Q_{in} = Q \longrightarrow \Delta\sigma = \frac{Q_{out}}{\tau_h} - \frac{Q_{in}}{\tau_e} = Q\left(\frac{1}{\tau_h} - \frac{1}{\tau_e}\right) < 0$$

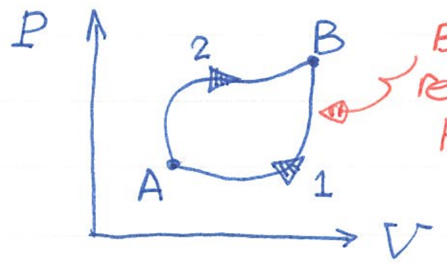
The important point is to include the refrigerator and BOTH thermal reservoirs as an isolated system.

Now that the 2^{nd} law is stated in terms of entropy. Let's try to understand the mysterious entropy.

① Clausius : He proved a theorem from Carnot's heat engine

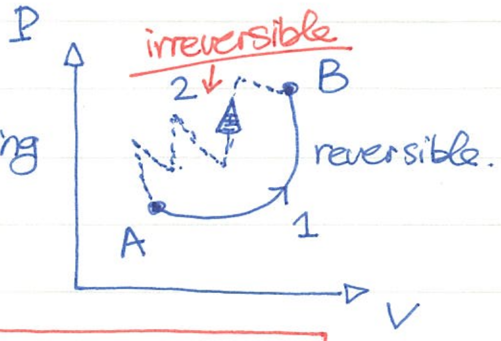
$$\boxed{\oint \frac{dQ}{\tau} \leq 0 \quad \text{in an arbitrary cycle}}$$

The equality holds for reversible process. It allows us to show that entropy is a state function.



Both are reversible paths!

$$\boxed{\int_1 \frac{dQ}{\tau} = \int_2 \frac{dQ}{\tau} \equiv \sigma(B) - \sigma(A)}$$

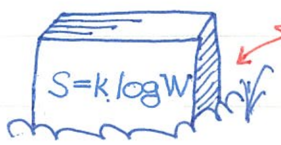


Now consider an irreversible path. According to Clausius' theorem,

$$\int_2 \frac{dQ}{\tau} - \underbrace{\int_1 \frac{dQ}{\tau}}_{= \Delta\sigma = \sigma(B) - \sigma(A)} \leq 0 \quad \Rightarrow \quad \boxed{\sigma(B) - \sigma(A) \geqslant \int_2 \frac{dQ}{\tau}}$$

For an isolated system, it does not exchange heat with the external world, i.e. $dQ = 0$ In consequence, $\Delta\sigma \geq 0$

Ø Boltzmann: He introduced the milestone relation to define entropy $\boxed{\sigma = \log g}$ OR



on real tomb

The above definition is used in Kittel's textbook and I shall say no more. But, the definition only works for thermal equilibrium states. It is a great breakthrough. But, can we have an even better definition for entropy?

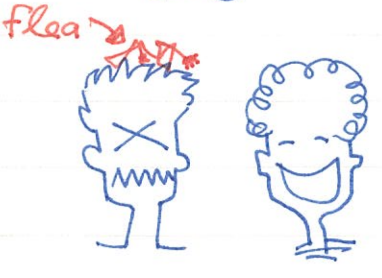
Ø Shannon: He beautifully relates the entropy to the information capacity and comes up with

$$\boxed{\sigma = \langle -\log P_s \rangle = -\sum_s P_s \log P_s}$$

Consider the following "hopping-flea problem". At the beginning,

$$P_A(t=0)=1 \text{ and } P_B(t=0)=0$$

t=0

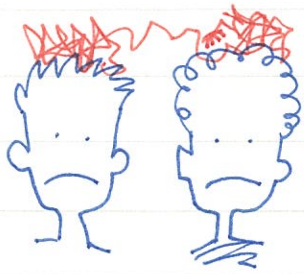


A B

Write down the master eq.

$$\boxed{P_A(t+\Delta t) = P_A(t)\,(1-\gamma\Delta t) + P_B(t)\cdot\gamma\Delta t}$$

$t\to\infty$



Taking the continuous limit $\Delta t\to 0$, the master eq. becomes:

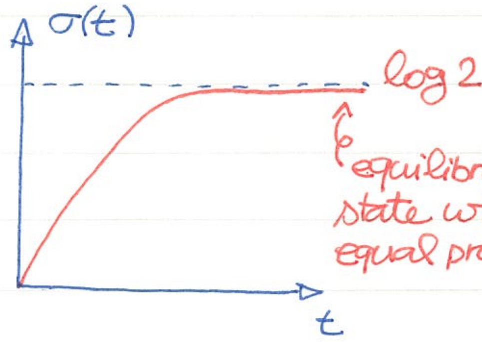
$$\frac{dP_A}{dt} = -\gamma(P_A-P_B) \qquad \text{Similarly,} \qquad \frac{dP_B}{dt} = \gamma(P_A-P_B)$$

Because the probability is conserved, $P_A+P_B=1$, one can find the solutions

$$\boxed{\begin{aligned} P_A(t) &= \frac{1}{2}+\frac{1}{2}e^{-2\gamma t} \\ P_B(t) &= \frac{1}{2}-\frac{1}{2}e^{-2\gamma t} \end{aligned}}$$

$P_A=P_B=\frac{1}{2}$ as $t\to\infty$.

One can plot the Shannon entropy. It's quite interesting to see that $\sigma(t)$ increases with time as predicted by the 2nd law. As $t\to\infty$, this simple system reaches its equilibrium with $g=2$. In this limit, the Shannon entropy coincides with Boltzmann's proposal $\sigma=\log g=\log 2$, YES!



equilibrium state with equal prob.!

(2) Von Neumann: OK, all previous proposals are somehow "classical". How about adding in some quantum flavor? In quantum world, a system is described by density matrix operator ρ (not just a wave function),

$$\boxed{\rho \equiv \sum_n P_n\,|\psi_n\rangle\langle\psi_n|} \quad \text{with } \sum_n P_n = 1$$

If only $P_0 = 1$ and the other $P_{n\neq 0} = 0$, the density matrix op. takes the simple form

$$\underbrace{\rho = |\Psi_0\rangle\langle\Psi_0|}$$

We call it a pure state

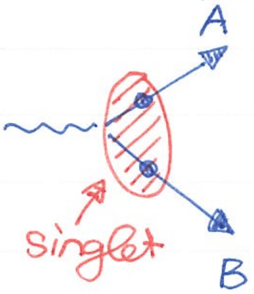
If more than one $P_n \neq 0$, the system cannot be described by a single wave function. $\longrightarrow$ It's called a mixed state.

The entropy proposed by von Neumann takes the form.

$$\boxed{\sigma = -\,\mathrm{tr}\,(\rho \log \rho)} \longrightarrow \underbrace{\sigma = -\sum_n P_n \log P_n}$$

if ρ is a diagonal matrix.

Quantum mechanics brings out interesting stuffs ☺ Consider a decay process generating a pair of spin-$\frac{1}{2}$ particles. Let's say their spins are in a singlet.



$$|\Psi\rangle = \frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle$$

One can construct the total density operator

$$\boxed{\begin{aligned}\rho_{AB} = |\Psi\rangle\langle\Psi| &= \frac{1}{2}|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + \frac{1}{2}|\downarrow\uparrow\rangle\langle\downarrow\uparrow| \\ &\quad - \frac{1}{2}|\uparrow\downarrow\rangle\langle\downarrow\uparrow| - \frac{1}{2}|\downarrow\uparrow\rangle\langle\uparrow\downarrow|\end{aligned}}$$

OR, it can be written in matrix form

$$\rho_{AB} = \begin{array}{c|cccc} & \uparrow\uparrow & \uparrow\downarrow & \downarrow\uparrow & \downarrow\downarrow \\ \hline \uparrow\uparrow & & & & \\ \uparrow\downarrow & & & & \\ \downarrow\uparrow & & & & \\ \downarrow\downarrow & & & & \end{array} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Straightforward to diagonalize the matrix ρ_{AB} and obtain $P_n = 1, 0, 0, 0$

$$\longrightarrow \boxed{\sigma_{AB} = -\sum_n P_n \log P_n = 0} \;//$$

The pair as a whole has <u>ZERO</u> entropy. But since they are flying apart, it is sensible to define density matrix operators ρ_A, ρ_B for the subsystems.

$$\rho_A \equiv tr_B \, \rho_{AB} = \sum_b \langle b | \rho_{AB} | b \rangle$$ $|b\rangle = |\uparrow\rangle, |\downarrow\rangle$ here.

$$= \frac{1}{2} |\uparrow\rangle\langle\uparrow| + \frac{1}{2} |\downarrow\rangle\langle\downarrow| \doteq \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$$

The corresponding entropy is $\boxed{\sigma_A = -\sum_a p_a \log p_a = \log 2.}$ It makes sense if only particle A is measured – its spin can be up or down with equal probability.

Similarly, one can compute $\rho_B \equiv tr_A \, \rho_{AB}$, giving $\sigma_B = \log 2$. It is quite remarkable to notice that there exists an inequality

$$\boxed{\sigma_A + \sigma_B \geqslant \sigma_{AB}}$$ true, even for general cases.

How can we understand this? Simple. σ_A arises because only partial measurement on particle A – some information is lost. Same for σ_B. The inequality tells us, even if we try to perform all partial measurements, we still do not have full understanding of the composite system. Hum, be careful about the weird quantum world!

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