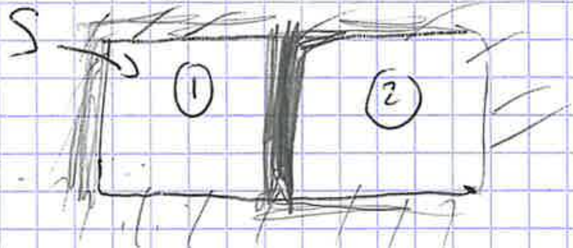
Chap IV : Non isolated systems
⇒ Relaxing constraints between 2 sub-systems

①

Motivations : Realistic cases ; Irreversibility

I) Thermal contacts

We consider an isolated system seperated from the rest (still macroscopic)



E = energy of S fixed

i) $S = S_1 \cup S_2$

with $S_i = \{E_i, N_i, V_i\}$

$V = V_1 + V_2$
$N = N_1 + N_2$

ii) Suppose we replace the wall by a diathermal one and wait until an equilibrium is reached.

Initially in i) : $E = E_1 + E_2$ with E_1, E_2 fixed

step ii) : $E = E_1 + E_2 + \underbrace{E^{int}_{1\leftrightarrow 2}}_{\text{interaction energy}}$

E fixed → extern^{nl}
E_1, E_2 internal

→ We assume short range interaction.

Therefore neglecting $E^{int}_{1\leftrightarrow 2} \ll E_1, E_2$ amounts to neglect a surface effect compared to a volume

$E^{int}_{1\leftrightarrow 2} \sim N^{2/3}$ while $E_1, E_2 \sim N$

$\frac{E^{int}_{1\leftrightarrow 2}}{E_1} \sim N^{-1/3}$ → negligeable $N \gg 1$ if N macroscopic

→ We need $E^{int}_{1\leftrightarrow 2} \neq 0$ ⇒ It governs the time it takes to reach a new equilibrium

Step i : $S^* = S_1^* + S_2^* = k_B \ln \Omega_1 + k_B \ln \Omega_2$ (extensivity of entropy)

After step ii) : what is S^*?

# of microstates accessible in ii)

We fix E_1. For E_1 fixed $\Omega_{1\otimes 2}(E; E_1) = \Omega_1(E_1)\,\Omega_2(\underbrace{E-E_1}_{E_2})$

However E_1 is not fixed

$$\Omega_{1\otimes 2}(E) = \sum_{E_1} \Omega_1(E_1)\,\Omega_2(E-E_1)$$

replace $\delta E \sum_{E_1} \to \int dE_1$

$$= \sum_{E_1} \delta E_1 \, \rho_1(E_1)\,\rho_2(E-E_1)\,\delta E$$

$$= \int dE_1 \, \rho_1(E_1)\,\rho_2(E-E_1)\,\delta E$$

In $\underline{C}$ limit

$$\underline{\Omega_{1\otimes 2} = \int \frac{dE_1}{\delta E}\, \Omega_1(E_1)\,\Omega_2(E-E_1)}$$

However $\Omega_{1/2} = \exp \frac{S^*_{1/2}}{k_B}$ ← microcanonical entropy

$$\Omega_{1\otimes 2} = \int \frac{dE_1}{\delta E} \exp\Big[\underbrace{\frac{1}{k_B} S_1^*(E_1, V_1, N_1) + \frac{1}{k_B} S_2^*(E-E_1, V_2, N_2)}_{\frac{1}{k_B} S^*_{1,2}(E, V, N; E_1)}\Big]$$

$S^*_{1,2}$ corresponds to some microcanonical entropy of the whole system at fixed E_1

We know that $S^*_{1,2} \propto N \gg 1$ (extensivity)

We can thus evaluate the integral using a saddle point approx

<u>Mathematical apparte</u>: Saddle pt approx

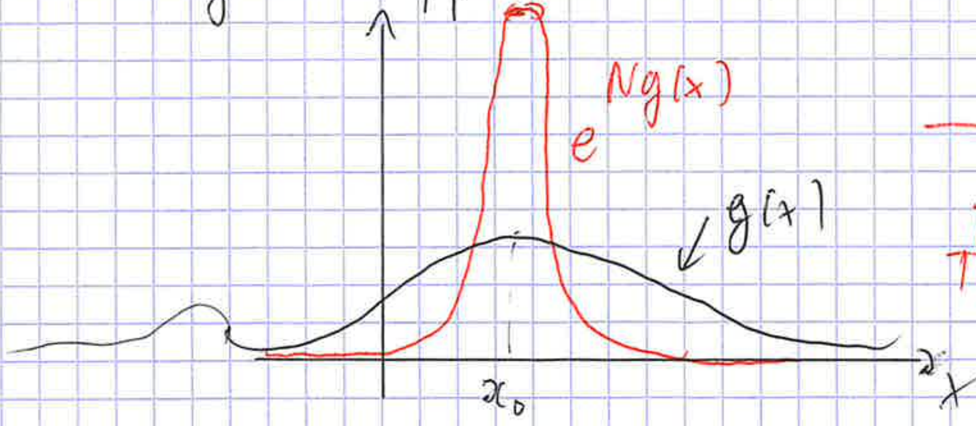
$$I_N = \int_{-\infty}^{+\infty} dx \; e^{N g(x)}$$ where $N \gg 1$ and g has one maximum in $x = x_0$

Taylor expansion: $g(x) \simeq g(x_0) + (x-x_0)\underbrace{g'(x_0)}_{0} + \frac{1}{2}(x-x_0)^2 g''(x_0) + \dots$

$$I_N \simeq \int_{-\infty}^{+\infty} dx \; e^{N g(x_0)} \, e^{\frac{N}{2}(x-x_0)^2 g''(x_0)}$$

→ say that $\boxed{N g''(x_0) = \sigma^{-2}}$

Why this approx works?



— $e^{Ng(x)}$ is a highly peaked function around x_0
The larger N, the more peaked is $e^{Ng(x)}$

The integral we need to evaluate is a Gaussian of variance $(g''(x_0)N)^{-1}$ $\Rightarrow$ mean deviat°: $(Ng''(x_0))^{-1/2}$

$$\underline{I_N \simeq \sqrt{\frac{2\pi}{N|g''(x_0)|}}\, e^{Ng(x_0)} \left(1+ \ldots\right)} \quad \|$$

If $g(x)$ is maximum in $x = x_0$, $g''(x_0) < 0$

Let us therefore apply this approx to our case

To do so, we look for extrema of $S^*_{1,2}(E,V,N;E_1)$

$$\frac{\partial S^*_{1,2}}{\partial E_1} = 0 \Leftrightarrow \frac{\partial S_1^*}{\partial E_1}(E_1,V_1,N_1) = \frac{\partial S_2^*}{\partial E_2}(E-E_1,V_2,N_2)$$

We recognize our microcanonical temperature $(T^*)^{-1} = \frac{\partial S^*}{\partial E}$

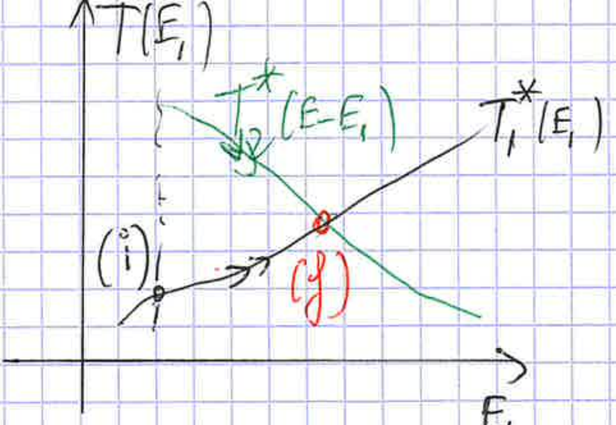
$$\frac{\partial S^*_{1,2}}{\partial E_1} = 0 \Leftrightarrow \frac{1}{T_1^*(E_1)} = \frac{1}{T_2^*(E-E_1)} \Leftrightarrow \underline{T_1^* = T_2^* = T_f^*} \quad \|$$

The extremum corresponds to a state where both microcanonical temperature are equal → like in thermo

→ This further confirms our previous identification between microcanonical def and thermodynamical ones

Confirms $S^* = k_B \ln \Omega \xleftrightarrow[\text{alike}]{\text{and}} S_{\text{thermo}}$

Give



If we start with $T_1^* < T_2^*$
the final state corresponds
to $T_f > T_1$ and $T_f < T_2$
$\mathcal{S}_1$ has received some energy
and $\mathcal{S}_2$ has lost ______

Give the example

Does the extremum we found is a maximum?

$$\frac{\partial^2 S^*_{1,2}}{\partial E_1^2} = \frac{\partial^2 S_1^*}{\partial E_1^2} + \frac{\partial^2 S_2^*}{\partial E_1^2}$$

In thermodynamics, we identified $C_v^{th} = \frac{\partial E}{\partial T} = \left(\frac{\partial T}{\partial E}\right)^{-1} > 0$

Let us define $C_v^* = \left(\frac{\partial T^*}{\partial E}\right)^{-1}$ by analogy $\left(\begin{matrix}E \text{ increases} \\ \text{with } T \\ \sim \text{valid}\end{matrix}\right)$

$$\left(C_v^*\right)^{-1} = \frac{\partial T^*}{\partial E} = -T^{*2}\frac{\partial (T^*)^{-1}}{\partial E} = -T^{*2}\frac{\partial^2 S^*}{\partial E^2}$$

$$\Leftrightarrow C_v^* = -\frac{1}{(T^*)^2}\left(\frac{\partial^2 S^*}{\partial E^2}\right)^{-1} = -\frac{\left(\frac{\partial S^*}{\partial E}\right)^2}{\left(\frac{\partial^2 S}{\partial E^2}\right)} > 0$$

Therefore $\left(\frac{\partial^2 S}{\partial E^2}\right) < 0 \rightarrow$ comes also from concavity

reverse the argument

$\hookrightarrow$ valid for short-range interactions

It follows that $\frac{\partial^2 S^*_{12}}{\partial E_1^2} < 0 \Rightarrow$ Maximum!

Like thermo || The system with a larger T^* provides energy to the system with lower T^*

Coming back to the integral

$$\Omega_{1,2} \simeq \frac{e^{S^*_{1,2}(E,V,N;E_1^*)}}{\delta E} * \sqrt{\frac{2\pi k_B}{\left|\frac{\partial^2 S^*_{1,2}}{\partial E_1^2}\right|}}$$

Fluctuations?

$$\left.\frac{\partial^2 S_{1+2}^*}{\partial E_1^2}\right|_{E_1=E_1^*} = \frac{\partial^2 S_1^*}{\partial E_1^2} + \frac{\partial^2 S_2^*}{\partial E_1^*} = -\frac{1}{(T_f^*)^2}\left(\frac{1}{C_{v,1}^*} + \frac{1}{C_{v,2}^*}\right)$$

$$\text{var}(E_1) = (\sigma_{E_1})^2 = \frac{k_B}{\left|\frac{\partial^2 S_{1+2}^*}{\partial E_1^2}\right|} = k_B (T_f^*)^2 \left[\frac{1}{C_{v,1}^*} + \frac{1}{C_{v,2}^*}\right]^{-1}$$

Give a physical meaning to C_V

RQ: Imagine we have $S_1^* \ll S_2^*$ (a small and a large one)

Then $C_{v,1}^* \ll C_{v,2}^* \Rightarrow \text{var}(E_1) \approx k_B (T_f^*)^2 C_{v,1}$

Thm

⇒ Assessment: When a constraint is relaxed ~~[illegible]~~ in a isolated system, the latter evolves toward a macroscopic equilibrium state which maximizes its entropy

(we recover the entropy equivalence of the fundamental principle

RQ: $C_v \propto N \rightarrow \sigma(E_1) \propto \sqrt{N}$ (for $N_1 \sim N_2 \sim N$)

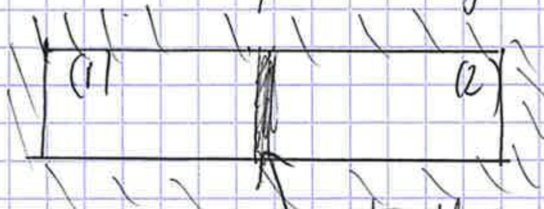
Therefore $\frac{\sigma(E_1)}{E_1^{mc}} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \longrightarrow 0$

Thm: In the $N \to \infty$ limit (thermo limit), fluctuations are negligible

→ This can be viewed as a consequence of the central limit thm

II) Sliding wall with volume exchange. (Joule expansion)

2 systems ① and ② separated by a piston



Initial: $(E_1, V_1, N_1) \parallel (E_2, V_2, N_2)$

Final: [Relax the piston and allow the wall to move
[Assumes also <u>diathermal wall</u>

Same treatment as I) : $S^*_{1,2}(E, V, N; E_1, V_1) = S_1^*(E_1, V_1, N_1) + S_2^*(E-E_1, V-V_1, N_2)$

The two internal variables E_1, V_1 can fluctuate

At equilibrium $\frac{\partial S^*_{1,2}}{\partial E_1} = 0$ & $\frac{\partial S^*_{1,2}}{\partial V_1} = 0$

$$\frac{\partial S_1^*}{\partial E_1} = \frac{\partial S_2^*}{\partial E_2} \qquad \frac{\partial S_1^*}{\partial V_1} = \frac{\partial S_2^*(E-E_1^*, V-V_1^*)}{\partial V_2}$$

We introduced $p^* = T^* \frac{\partial S^*}{\partial V}$ microcanonical pressure

Thus the final eq. state is characterized by

$$T_1^* = T_2^* \quad \text{and} \quad p_1^* = p_2^*$$

Convexity of $S^*_{1,2}$ ensures $\frac{\partial^2 S}{\partial V^2} < 0 \rightarrow \frac{\partial p^*}{\partial V} < 0$

Pressure is decreasing when V ↗

→ Also in line with our thermodynamical intuition

compressibility

$$\rightarrow \underset{\text{isotherm}}{K_T} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T > 0$$

Iso compressibility

Ex: pressure of a perfect gas

We have seen that for uncorrelated particles (perfect gas)

$$\Omega \propto V^N \quad \text{with } \Omega = \#\text{ of accessible microstates}$$

$$S^* = N k_B \ln V + k_B f(E,N)$$

$$\Rightarrow \frac{p^*}{T^*} = \frac{N k_B}{V} \Rightarrow \boxed{p^* V = N k_B T^*}$$

This result is remarkable as it does not depend on details

$$\text{As } \frac{1}{T^*} = \frac{\partial S^*}{\partial E} = \frac{3 N k_B}{2E} \Rightarrow \boxed{p^* = \frac{2}{3}\frac{E}{V}}$$ Also valid for a quantum gas

Ex: Permeable wall

Let us consider the same two subsystems but with a permeable wall which is maintained fixed.

$$S^*_{1,2}(E,V,N;E_1,N_1) = S^*_1(E_1,V,N_1) + S^*(E-E_1,V-V_1,N-N_1)$$

$$\text{Equilibrium: } \frac{\partial S^*_{1,2}}{\partial E_1} = 0 \quad \text{and} \quad \frac{\partial S^*_{1,2}}{\partial N_1} = 0 \rightarrow \frac{\mu_1^*}{T_1^*} = \frac{\mu_2^*}{T_2^*}$$

$$\Leftrightarrow T_1^* = T_2^* \quad \text{and}$$

$$\Leftrightarrow T_1^* = T_2^* \quad \text{and} \quad \mu_1^* = \mu_2^*$$

Exo: Check that the system with the lower μ gains particles from the other one

III) Arbitrary extensive variable

Consider an isolated system with some arbitrary extensive variable named X

Previously $X = E$ or $X = N$

We introduce $\omega(x,E) = \{\#\text{ of microstates} \mid X = x\}$

$$\hookrightarrow S^*(x,E) = k_B \ln \omega(x,E) \rightarrow p^*(x,E) = \frac{\omega(x,E)}{\Omega(E)}$$

The most likely value x^* is given by $\frac{\partial S^*}{\partial x}(x = x^*) = 0$

i.e. by the maximum of $S^*(x,E)$

$\frac{\partial S^*}{\partial x}(\underset{x}{\overset{\shortparallel}{x^*}}, E) = 0 \Rightarrow$ The entropy of the system is given by $S^*(E) \simeq S^*(E, x = x^*)$ up to some subextensive corrections

The deviations from $x = x^*$ are given by

$\sqrt{\overline{\Delta x^2}} \propto \sqrt{N} \Rightarrow$ Therefore, in the thermodynamic limit the extensive variable X takes a well-defined value

Again, this is a consequence of the central-limit theorem: Huge difference between the microscopic random values and deterministic value in the thermodynamic limit $(N \to \infty)$

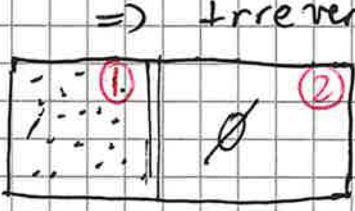
IV) Irreversibility

4.1) Where does it come from?

The results we discussed above are quite illustrative and consequences of the Boltzmann principle: An isolated system, when a constraint $X = x$ is released, will tend toward a new macrostate where X takes a value $x = x^*$ that maximizes the entropy $\Rightarrow$ an isolated system always tend to maximize its entropy $\Rightarrow$ this implies at the macro. level some arrow of time $\Rightarrow$ The laws of nature (at the macroscopic scale) are not time reversal invariant.

$\Rightarrow$ Irreversibility sets in

Ex:



$V_1 = V_2 = \frac{V}{2}$ $\Rightarrow$

At $t = 0$ $N_1 = N$ At t large $\overline{N_1} \simeq \frac{N}{2}$

What is the proba of having all particles back to the left?

Proba of having N_1 atoms in the left: $P(N_1) = \frac{C_N^{N_1}}{2^N} = \frac{1}{2^N} \frac{N!}{N_1!\,(N-N_1)!}$

$$\frac{\min(P^*)}{\max(P^*)} = \frac{P^*(N)}{P^*(\frac{N}{2})} = \frac{\left(\frac{N}{2}!\right)^2}{N!} \simeq \frac{1}{2^N}$$

For $1\,\text{cm}^3$ of a perfect gas $N \sim 10^{20} \to \frac{\min(P^*)}{\max(P^*)} \sim 2^{-10^{+20}}$

$\Rightarrow$ Never happens!

⑨

=> This result should be constrasted with the microscopic eqs of motion which are reversible

Rq: We have argued about irreversability of the process by comparing the initial and final states. We said nothing how we go from one to the other

In particular: how do we go from microscopic reversible eqs to macroscopic irreversibles ones → large litterature to derive it!

=> Sinai pb is interesting.

macroscopic irreversibility => arrow of time

4.2) Gibbs paradox (see TD 4.2)

2 perfect gas at same T^* and p^*
we remove the wall, what happen

Two cases : (a) : (1) and (2) contains particles of the same kind
(b) : ———————— of ≠ kinds

In (b), mixing => $\Delta S > 0$

In (a) due to irreversibility, $\Delta S = 0$

let us check it:

$$S^* = k_B \ln \phi_{indis} = k_B \ln\left(\frac{\phi_{dis}}{N!}\right) \simeq N k_B\left(\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{mE}{3\pi\hbar^2}\right)^{3/2}\right)\right)$$

$$\simeq \frac{5}{2} N k_B + N k_B \ln\left(\frac{V}{N} c\right) \text{ when } c = \Lambda_T^{-3}$$

Same T^*, p^* => $p^* V_1 = N_1 k_B T^*$ and $p^* V_2 = N_2 k_B T^*$) initial

$$\Rightarrow p^*(V_1 + V_2) = (N_1 + N_2) k_B T^*$$

$$\frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{V_1 + V_2}{N_1 + N_2} = \frac{V}{N} = \frac{k_B T^*}{p^*}$$

$$\Delta S = S_{final} - S_{init}$$

Case (b) $\Rightarrow \Delta S^{dis}_{mixture} = N_1 k_B \ln\left(\frac{V_1+V_2}{N_1} c_1\right) + N_2 k_B \ln\left(\frac{V_1+V_2}{N_2} c_2\right)$

$$- N_1 k_B \ln\left(\frac{V_1}{N_1} c_1\right) - N_2 k_B \ln\left(\frac{V_2}{N_2} c_2\right)$$

$$= N_1 k_B \ln\left(\frac{N_1+N_2}{N_1}\right) + N_2 k_B \ln\left(\frac{N_1+N_2}{N_2}\right) > 0$$

we could have obtained this result by counting the microstates

$$\Delta S = k_B \ln\left(\frac{(N_1+N_2)!}{N_1!\, N_2!}\right) \approx \Delta S_{mixture}.$$

Case (a) If the atoms are identical, the final state is different we have a single gas in a volume $V = V_1 + V_2$

$$\Delta S^{indis}_{mix} = (N_1+N_2) k_B \ln\left(\frac{V_1+V_2}{N_1+N_2} c\right) - N_1 k_B \ln \frac{V_1}{N_1} c - N_2 k_B \ln \frac{V_2}{N_2} c$$

$$= 0$$

4.3) About Maxwell demon?

If I have some time