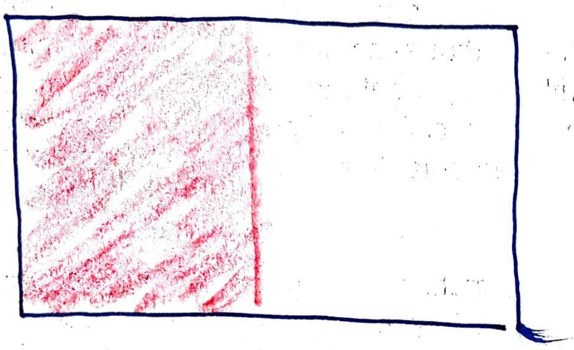
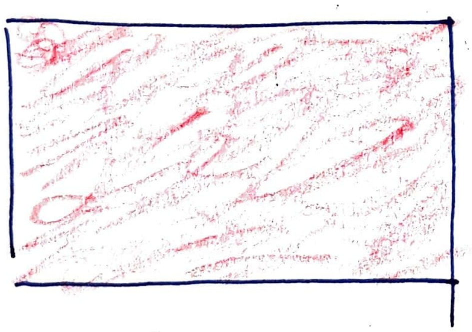
Macroscopic Irreversibility

(adiabatic expansion in Isolated system)

non eq initial state...



... equilibrium state



never return to a state similar to initial state

$$\Delta S = N k_B \ln \frac{V_{fin}}{V_{in}} > 0$$

Definitions to start with..

- Classical mechanical system
- Isolated ⇒ Total energy is conserved
- Hamiltonian system

⇒ prototype N particles

$$\begin{cases} \dot{\vec{q}}_i = \dfrac{\partial H}{\partial \vec{p}_i} \\ \dot{\vec{p}}_i = -\dfrac{\partial H}{\partial \vec{q}_i} \end{cases} \qquad i = 1, N \qquad 6N \text{ degrees of freedom}$$

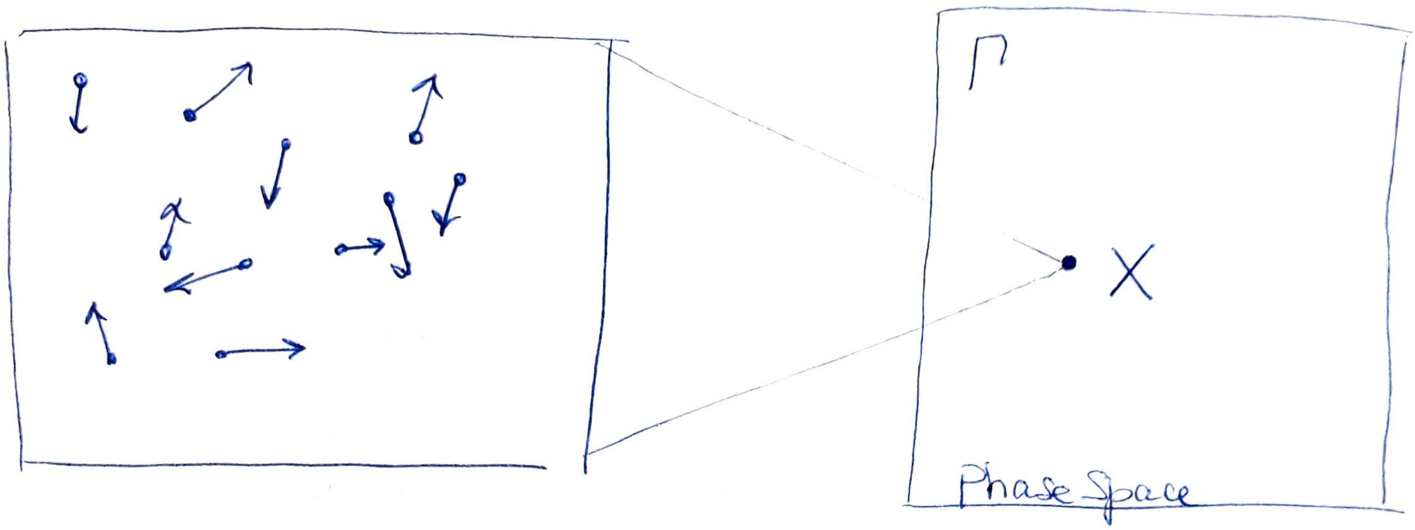
- Phase space: the space in which the single point representing the system evolves

- the Mecanical state of the system is a 6N dimentional point

$$X = (\{\vec{q}_i\}, \{\vec{p}_i\}) =$$

$$= \underbrace{(q_1^x\, q_1^y\, q_1^z\, q_2^x\, q_2^y\, q_2^z \cdots q_N^z;\ p_1^x\, p_2^x \cdots p_N^z)}_{6N}$$

This point represent a single macroscopic state for N particle



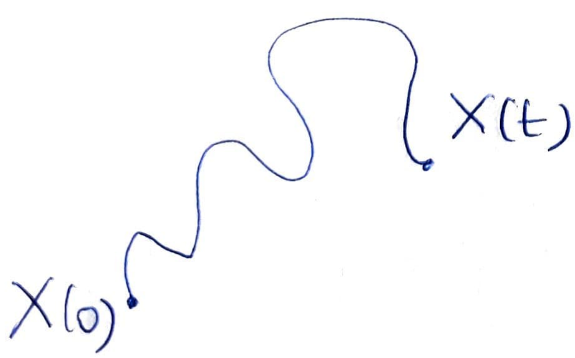
If the energy is conserved

$$\underbrace{H(q, p)}_{6N} = E$$

therefore a 6N-1 variety is selected

i.e. the Available Phase Space

X moves in the Available Phase Space



An observable is a function of the mechanical state X

$f(X)$

whicke evolves in time because X evolves

example the total Kinetic Energy (which is not conserved for a system of interacting particles)

$$K(t) = \sum_i^N \frac{P_i^2(t)}{2m}$$

this is a function of only ~~coor~~ momenta.

The position of the barycenter

$$\vec{R}(t) = \sum_i \frac{m_i \vec{q}_i(t)}{\sum_i m_i}$$

for a system of particle in a vessel this position has non trivial motion

→ problem what is the motion of R in the presence of reflecting walls?

the time average of an observable is defined as

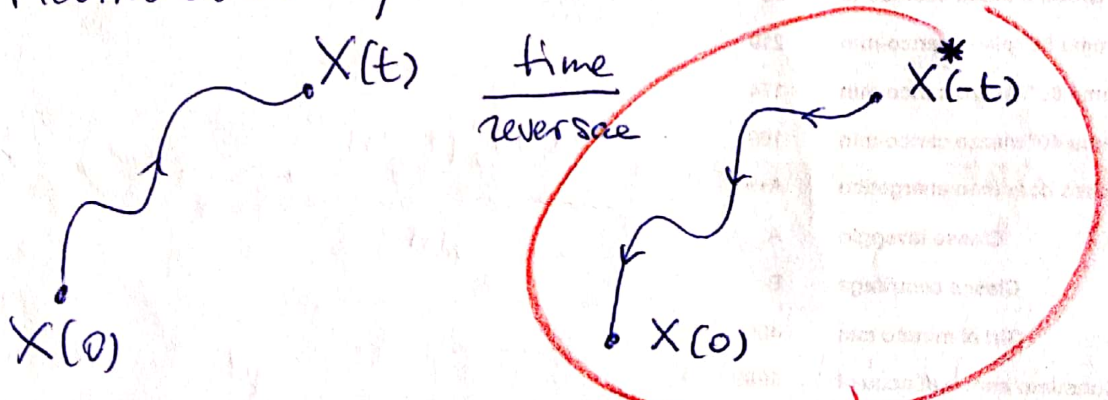
$$\overline{(f(x))}_T = \frac{1}{T}\int_0^T dt' \, f(x(t'))$$

and eventually we take $T \to \infty$

Microscopic reversibility

$$\begin{cases} \dot{q} = \dfrac{\partial H}{\partial p} \\ \dot{p} = -\dfrac{\partial H}{\partial q} \end{cases} \qquad \begin{matrix} t \to -t \\ p \to -p \end{matrix} \qquad \begin{cases} -\dot{q} = \dfrac{\partial H}{\partial(-p)} \\ -(-\dot{p}) = -\dfrac{\partial H}{\partial q} \end{cases}$$

Hamilton eq are invariant



Quantum Mechanics (H$\cancel{(t)}$)

$t \to -t$

$\psi \to \psi^*$

Warning

$X^*(-t) \neq X(t)$ because of $p \to -p$
but the final point is $X(0)$

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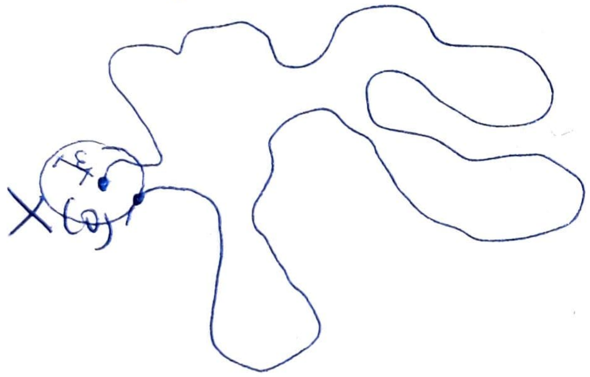
Poincare's recursion time

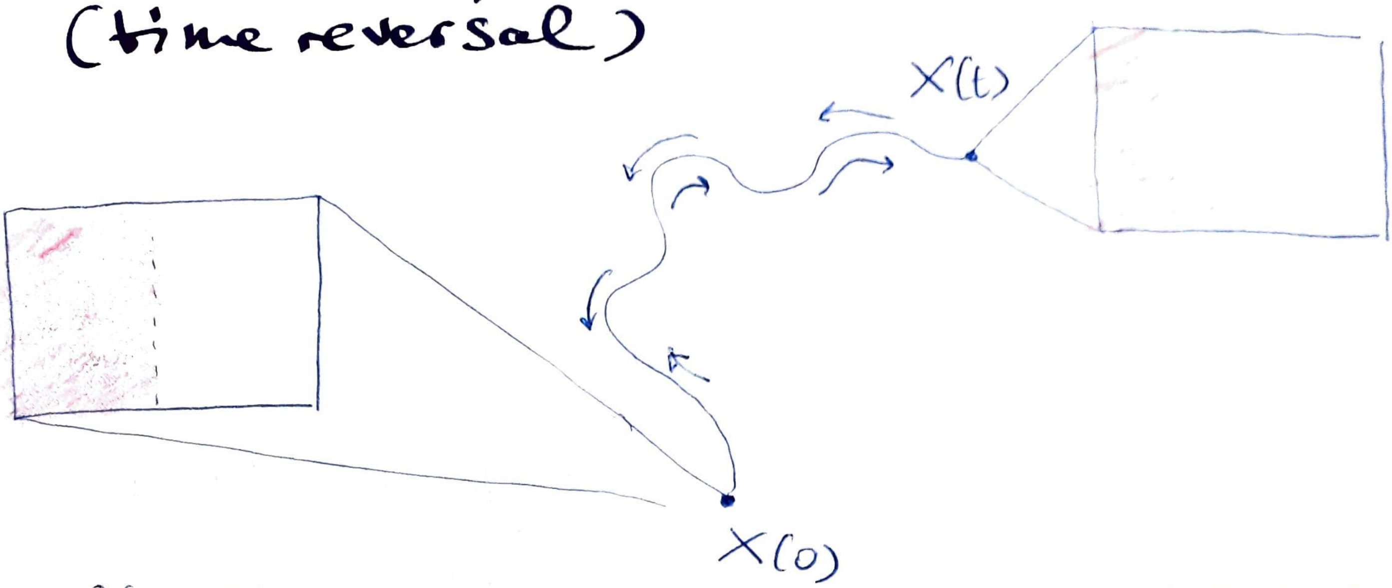
for a Finite System having
finite Volume
finite Energy
there exist a time θ_ε such that

$$|X(\theta_\varepsilon) - X(0)| < \varepsilon$$

for any small ε



Loschmidt paradox
(time reversal)



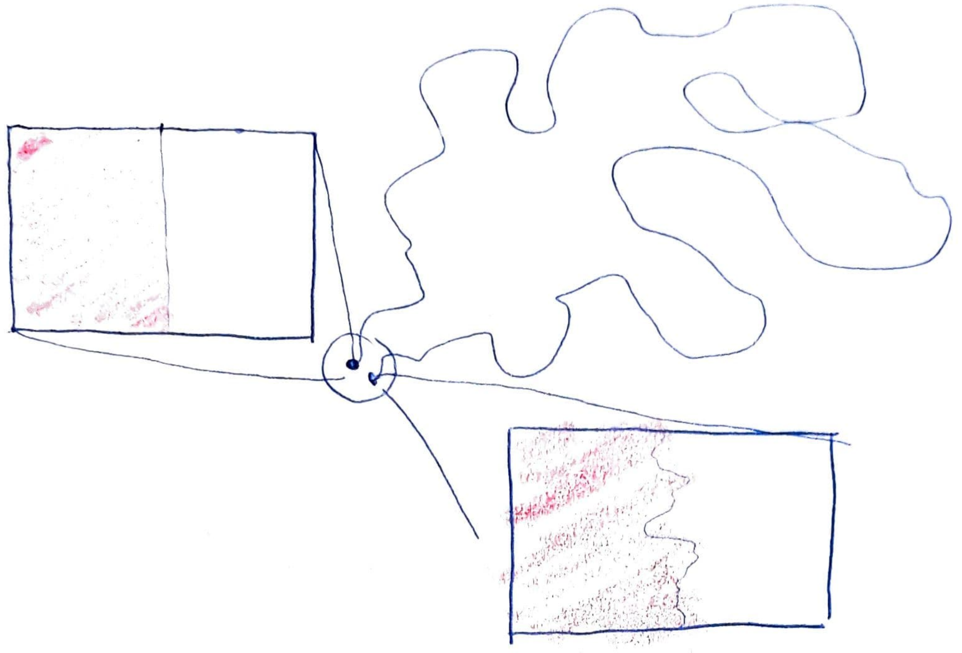
after time reversal which is an ISOENERGETIC transformation

$X(t) \longrightarrow X(0)$ and then it is possible

via an ISOENERGETIC TRANSFORMATION

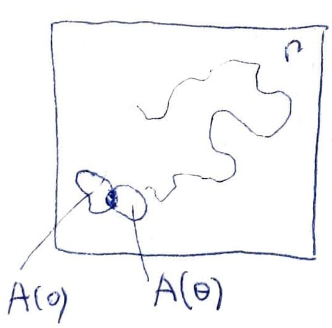
to return into a ~~single~~ higly improbable initial state

Zermelo's paradox (time recursion)



after recursion time a mechanical system will return asymptotically near an initial unprobable state

(Poincaré's theorem: a FINITE system evolving in a FINITE "volume" Γ the motion is almost periodic



for any finite set of initial states $A(0)$

$\exists \theta$ such that:

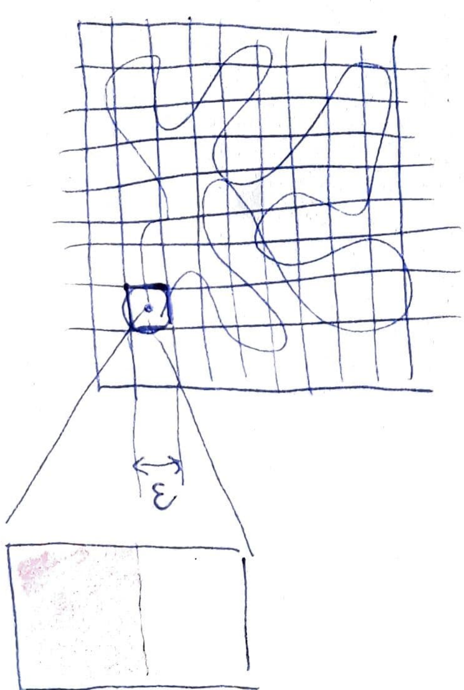
$$A(\theta) \cap A(0) \neq \emptyset$$

Resolution of paradoxes

- Recurrence (Zermelo)

for a large system say N particle the recurrence time is exp(N)

this basically occurs because the mechanism of proofing the Poincare's theorem gives that Θ is the time needed to visit all available states for the system after a discretization of phase space in ε-spheres has been made



$\longrightarrow$ Postponed calculation of Θ

Time Reversal (Loschmidt)

transformation

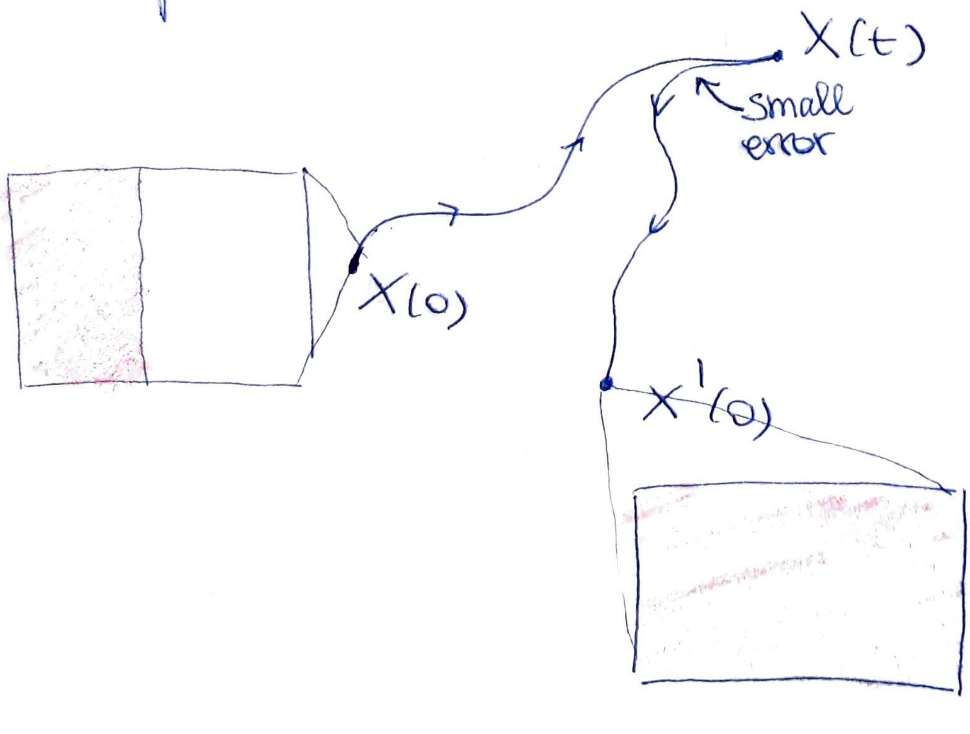
$$\begin{cases} q_i \to q_i \\ p_i \to -p_i \\ t \to -t \end{cases}$$

IS ISOENERGETIC $V(q) \to V(q)$ $T(p) = T(-p)$

but not <u>ISOENTROPIC</u>

we should exactly change all $q_i \to \bar{q}_i$ all $\bar{p}_i \to -\bar{p}_i$

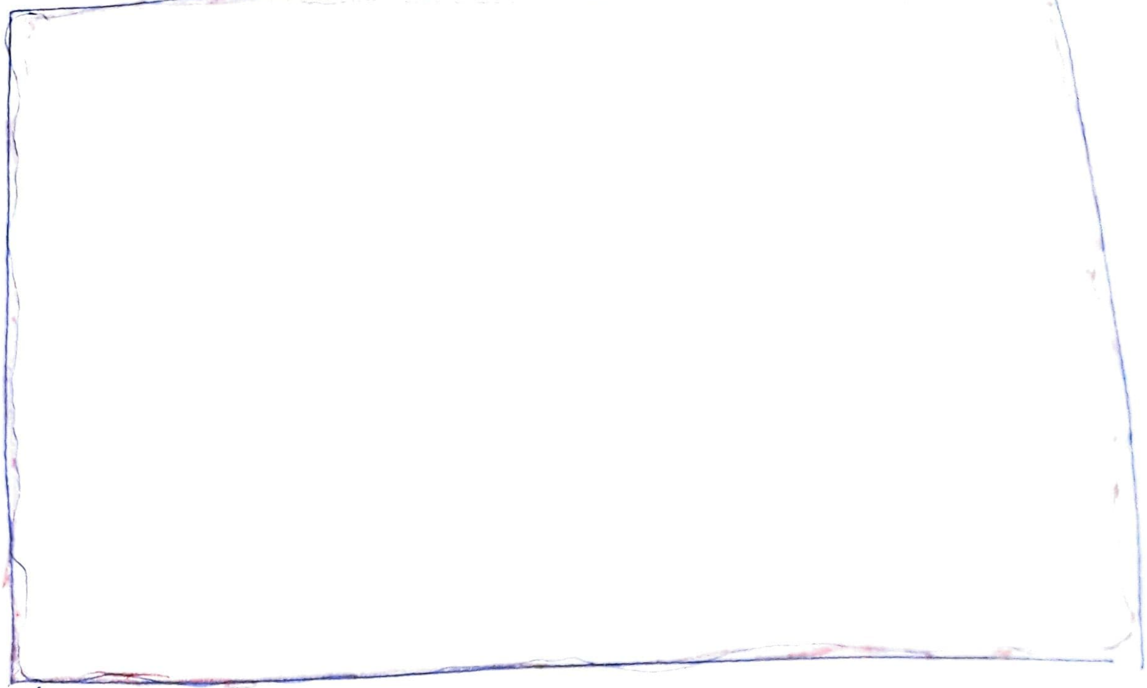
a small ISOENERGETIC error mad in this transformation will propagate exponentially (see <u>chaos</u>) and the system will never return to its unprobable initial state



why we see a system in equilibrium while its microscopic constituents moves randomly

Concentrate on observables

say $f(X)$ an observable then $f(X(t))$ should depend on time however the "volume" of the phase space for which $f(X(t)) \neq f_{eq}$ where f_{eq} is some constant value is exponentially small compared to the volume where $f(X(t)) = f_{eq}$,



available phase space

states where $f(X) \neq f_{eq}$

even if we start in the red region the suddenly we enter the white region and f indicates equilibration

of course this property in principle depends on f