Foundations of Statistical Physics

Aim: Given a Hamiltonian H and an initial condition, predict long-time behavior of a large number of interacting particles.

Examples:

(a) Consider the classical Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i \neq j} \frac{e^2}{|\vec{x}_i - \vec{x}_j|}$$

with the initial condition, $\vec{p}_i(t=0) = \vec{0}$ and $\vec{x}_i(t=0) = \vec{x}_{i0}$

Calculate $\langle \vec{p}_1^{\,2} \rangle = \int_t^{t+T} \vec{p}_1^{\,2}(t)\, dt \,/\, T$

$t \gg \frac{L}{v}$ where v is some characteristic velocity.

(b) Consider the quantum Hamiltonian of spin-1/2 spins

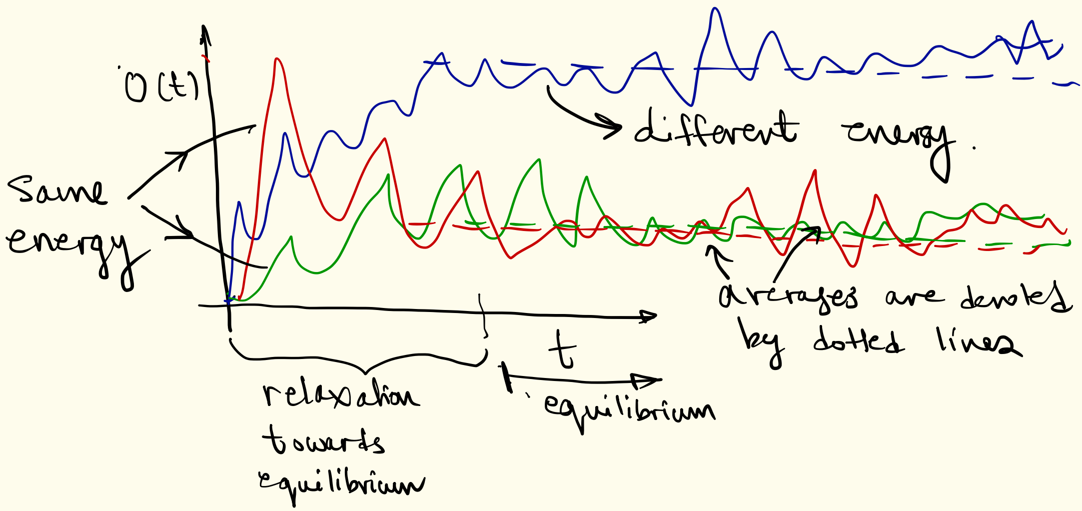
$$\hat{H} = -\sum_i \sigma_i^z \otimes \sigma_{i+1}^z + h_x \sum_i \sigma_i^x + h_z \sum_i \sigma_i^z$$

where σ_i^α are Pauli matrices and the initial state $|\psi(t=0)\rangle = |\uparrow \uparrow \cdots \uparrow\rangle$ (all spins pointing along $\hat{z}$ direction).

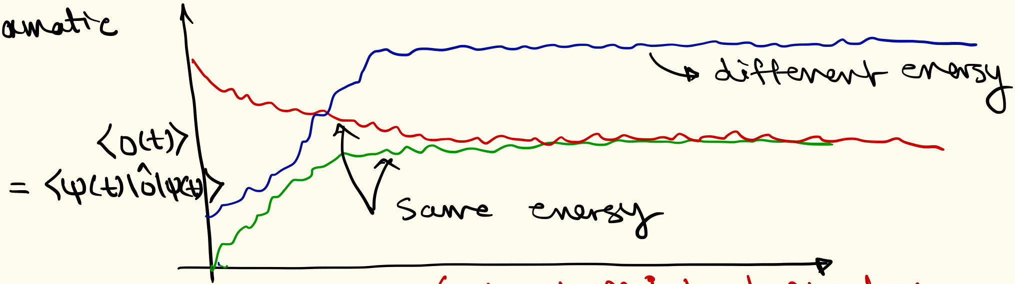
Calculate $\langle \sigma_i^z (t \to \infty) \rangle$

On the face of it, this is a very hard problem because one might think that $\langle \vec{P}_1^{\,2} \rangle_{t\to\infty}$ in (a) or $\langle \sigma^2 \rangle_{t\to\infty}$ depends on the precise initial conditions. Since there are infinitely many possible initial conditions, this seems like a hopeless problem.

Remarkably, the actual (i.e. experimentally observed) behavior seems much more simpler. With some exceptions, one typically finds that all initial conditions that have identical value for <u>conserved quantities</u> lead to identical long-time behavior. For example, if energy is the only conserved quantity, then $O(t)$ for some $O(p,q)$ may look like:



Quantum mechanically, the contrast is even more dramatic



$\Rightarrow$ in QM, averaging happens 'automatically' due to quantum fluctuations.

Why do conservation laws play such an important role? The reason is that sufficiently generic systems are <u>ergodic</u> and over long time explore <u>all</u> states accessible to them. (the three famous exceptions to this statement are classical glasses, many-body localized quantum systems, and systems that exhibit spontaneous symmetry breaking). Due to this democratic exploration of the phase space / Hilbert space, conservation laws act as the only constraint on long-time expectation value of observables. The 'memory' of the initial state is lost ('scrambled') by the chaotic dynamics.

Classically ergodicity implies equality of the following three quantities:

(i) $\int_t^{t+T} O(t)\, dt \,/\, T$ for $t > t_{eq.}$ and T large.

(ii) $\langle O(t) \rangle$ for fixed $t > t_{eq.}$ where $\langle \; \rangle$ is taken over all initial conditions with the same energy E as in (i).

(iii) $\langle O \rangle$ where $\langle \; \rangle$ is taken over all phase-space points with energy E. Explicitly,

$$\langle O \rangle = \frac{\displaystyle\int_{E < H(p,q) < E+\delta E} O(p,q)\, dp\, dq}{\displaystyle\int_{E < H(p,q) < E+\delta E} dp\, dq}$$

The section of phase-space with fixed energy is called <u>Microcanonical Ensemble</u> and the averaging in (iii) is sometimes called microcanonical averaging. Clearly (iii) is much easier to calculate than (i) or (ii).

Quantum mechanically, one analogue of a microcanonical ensemble is a single eigenstate at energy E, which we denote by $|E\rangle$.

In this case, ergodicity implies the equality of following three quantities:

(i) $\langle E|\hat{O}|E\rangle$

(ii) $\int_t^{t+T} \langle\psi_0|\hat{O}(t)|\psi_0\rangle\, dt \,/ T$ for $t > t_{eq}$.

where $\langle\psi_0|\hat{H}|\psi_0\rangle = E$.

(iii) $\langle\psi_0|\hat{O}|\psi_0\rangle$ averaged over all $|\psi_0\rangle$ that satisfy $\langle\psi_0|\hat{H}|\psi_0\rangle = E$

Finally one can also define a quantum microcanonical ensemble that is closer in definition to the classical one as:

$$\rho_{MC} = \frac{\sum_i |E_i\rangle\langle E_i|}{N}$$

$\rightarrow$ eigenstates.

where $E < E_i < E + \delta E$

The equality

$$\mathrm{Trace}[\rho_{MC}\,\hat{O}] = \langle E|\hat{O}|E\rangle,$$

if it holds is referred to as 'Eigenstate Thermalization'.

The concept of entropy

Given some probability distribution $\rho(p,q)$, it's entropy is defined as $S = -\int dp\, dq\ \rho(p,q) \log \rho(p,q)$.

S is a measure of ignorance associated with ρ: if ρ is sharpy peaked at a few values S is small, and if ρ is a flat distribution, then S is maximal.

Quantum mechanically, given a density matrix $\hat{\rho}$, $S = -\text{trace}[\hat{\rho} \log \hat{\rho}]$.

The most interesting property of S is that

(i) For an isolated system it stays constant with time (Sethna prob. 5.7)

(ii) For a subsystem of an isolated system, it increases with time due to scrambling of information (2nd law of thermodynamics). We will discuss this more later.

For the classical microcanonical ensemble, let's define $\Omega(E)$ by

$$\Omega(E)\,\delta E = \int_{E < H(p,q) < E+\delta E} dp\,dq$$ [what about units? we will return to it later]

= phase space volume of thin-shell with energy E.

$$\Rightarrow \rho(p,q) = \frac{1}{\Omega(E)\,\delta E} \quad \text{if } E < H(p,q) < E+\delta E$$

$$= 0 \quad \text{otherwise}$$

(Note that with this definition, ρ is already normalized).

$$\Rightarrow S_{MC} = -\int dp\,dq\, \rho(p,q) \log \rho(p,q)$$

$$= + \int_{\substack{E < H(p,q) \\ < E+\delta E}} dp\,dq\, \frac{1}{\Omega(E)\,\delta E} \log[\Omega(E)\,\delta E]$$

$$= \log[\Omega(E)\,\delta E] = \log[\Omega(E)] + \log(\delta E)$$

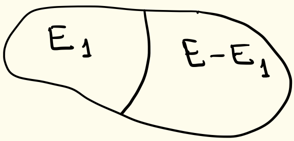
Quantum mechanically $S_{MC} = \log$ (number of eigenstates between E and $E+\delta E$).

The QM definition implies that S can at most be extensive because # of eigenstates between E and $E+\delta E$ can at most grow exponentially with system size.

The concept of temperature and the laws of thermodynamics

Zeroth Law

Consider bringing two initially isolated systems in contact so that they can exchange energy now:



# of states of total system at energy

$$\Omega(E) = \int dE_1 \, \Omega_1(E_1) \, \Omega_2(E-E_1)$$

$$= \int dE_1 \, e^{S_1(E_1) + S_2(E-E_1)}$$

Since both S_1, S_2 are extensive, $\Omega(E)$ can be evaluated using saddle point approx:

$$\Omega(E) = e^{S_1(E_1^*) + S_2(E - E_1^*)}$$

where E^*_1 is the maximum of the f^n $S_1(E_1) + S_2(E - E_1)$ and therefore satisfies,

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{V_1} = \left.\frac{\partial S_2}{\partial E_2}\right|_{V_2}$$ where V_1, V_2 are volumes of two systems.

The temperature is defined as $\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V$

$$\Rightarrow \qquad \frac{1}{T_1} = \frac{1}{T_2}$$

$\Rightarrow$ systems in equilibrium have the same temperature.

First Law

Lets do work on the system by changing its volume a little bit by applying pressure P. The energy changes by $-PdV$. The change in entropy is :

$$\delta S = S(E - PdV, V + dV) - S(E, V)$$

$$= \left.\frac{\partial S}{\partial E}\right|_V - PdV + \left.\frac{\partial S}{\partial V}\right|_E dV$$

$$= \frac{1}{T} - PdV + \left.\frac{\partial S}{\partial V}\right|_E dV$$

After equilibrium is reached, entropy will again be stationary $\Rightarrow$ $\delta S = 0 \Rightarrow \left.\frac{\partial S}{\partial V}\right|_E = +\frac{P}{T}$

$\Rightarrow$ In equilibrium,

$$dS = \left.\frac{\partial S}{\partial E}\right|_V dE + \left.\frac{\partial S}{\partial V}\right|_E dV$$

$$= \frac{dE}{T} + \frac{P}{T} dV$$

$$\Rightarrow \boxed{dE = TdS - PdV}$$

It's worth emphasizing that dE, dS etc. refer to differences between different equilibrium states, unlike δS above which referred to deviation from equilibrium.

Second Law

The number of accessible states in equilibrium are more than the # of states with same energy in any non-equilibrium state.

$$\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geq 0$$

$$\Rightarrow \frac{\partial S_1}{\partial E_1} \delta E_1 + \frac{\partial S_2}{\partial E_2} \delta E_2 \geq 0$$

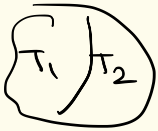
$$\Rightarrow \quad \frac{1}{T_1}\,\delta E_1 + \frac{1}{T_2}\,\delta E_2 \geq 0$$

but $\delta E_2 = -\delta E_1 \Rightarrow \delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0$

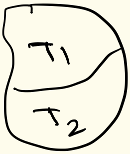
if $T_1 < T_2 \Rightarrow \delta E_1 \geq 0$ i.e. heat flows from 2 to 1.

Microscopic Origin of Second Law

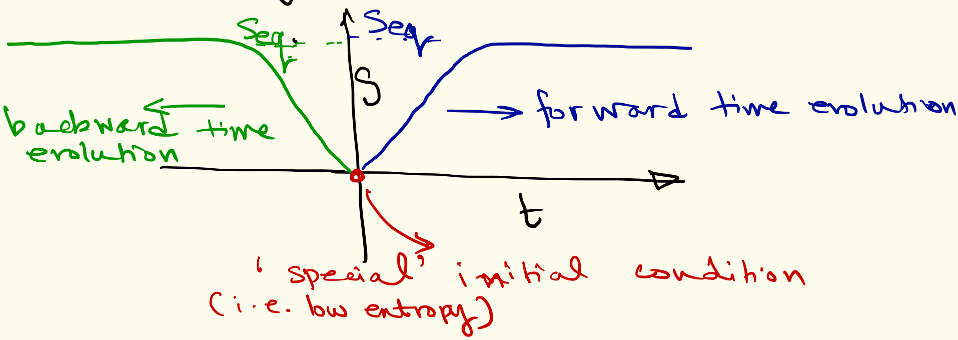
Both Newton's law and Schrodinger equation for time-independent Hamiltonians are time-reversal symmetric. This seems in contradiction with the second-law. Lets clarify this. The reason entropy increases is because the initial conditions that naturally arise in experiments tend to have a low entropy. For example, in the example just considered the system



is by construction a low entropy state if $T_1 \neq T_2$. Once entropy reaches its maximum possible value, it does not decrease (atleast not until a very long time cf. Poincare recurrence). But if it's not at its maximum possible value, then there are many more pathways to go to a higher entropy state than a lower entropy state. More crucially, lets evolve the state



for $T_1 \neq T_2$ backwards in time. One will find that the entropy will again increase with time. Therefore, second law is fundamentally about initial conditions.



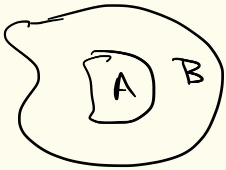
Second Law : Equilibrium Vs Non-Equilibrium

In thermodynamics, entropy is typically defined <u>only</u> at equilibrium. In this context, second law refers to the statement that as a system at equilibrium with entropy S_0 is perturbed and finally reaches a different equilibrium state with entropy S_1, then $S_1 > S_0$ assuming no work is done on the system.

However, one can define entropy even out of equilibrium using the definition $S = -\mathrm{Tr}\, \rho \log \rho$. To do ~~this~~, first let's remind ourselves that were the system described by ρ closed, then entropy is constant. Therefore to make sense of second-law, one has to consider non-closed systems.

As an example, consider a QM system that starts in a state $|\psi_0\rangle$ at $t=0$ and $|\psi_t\rangle = e^{-iHt}|\psi_0\rangle$. Clearly $S = -\mathrm{Tr}\, \rho_t \log \rho_t = 0$ for all time t. where $\rho_t = |\psi_t\rangle\langle\psi_t|$.

However now consider a smaller subsystem of the total system:

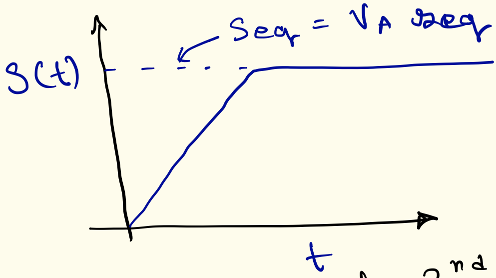


$A \cup B$ = total system

Define $\rho_A(t) = \mathrm{Trace}_B\, |\psi_t\rangle\langle\psi_t|$.

and $S_A(t) = -\mathrm{Tr}\, \rho_A(t) \log \rho_A(t)$

One finds that $S_A(t)$ grows with time and saturates at a value $V_A\, s_{eq}$ where s_{th} exactly corresponds to the equilibrium thermal entropy density



This is a manifestation of 2^{nd} law. Again the initial condition has low entropy.

One can define a similar quantity classically as well. Consider the phase-space p.d.f. $\rho(\{p\},\{q\},t)$ for all particles evolving under Newtonian dynamics. From this, one can define a 'partial' phase-space p.d.f. $\rho_A(\{p_1 \cdots p_{N_A},\, q_1 \cdots q_{N_A}\},t)$ of just N_A particles out of total N via

$$\rho_A = \int dp_{N_A+1} \cdots dp_N\, dq_{N_A+1} \cdots dq_N\, \rho(\{p\},\{q\},t)$$

Defining $S_A(t) = -\int dp_1 \cdots dp_{N_A}\, dq_1 \cdots dq_{N_A}\, \rho_A \log \rho_A$

One again expects that it will grow with time and then saturate to $N_A\, s_{eq}$ for most initial conditions that are easy to prepare in a lab.