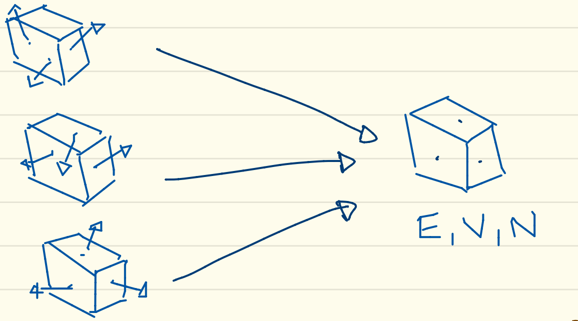
STATISTICAL MECHANICS NOTES

FOUNDATIONS

Paulo Bedaque

STATISTICAL MECHANICS

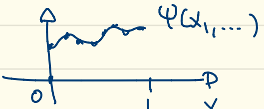
The object of stat. mech. is to study systems with a large number of degrees of freedom focusing on macroscopic properties only:



$\underbrace{\hspace{3cm}}$ microscopic states (specified by $\mathbf{r}_i, \mathbf{p}_i$, $i = 1, \ldots, N$)

$\underbrace{\hspace{3cm}}$ macroscopic state (specified by E, V, N only)

Concentrating on macroscopic properties simplifies the problem tremendously. In fact, just storing the information describing the ground state of $N = 20$ particles is, and it'll always be impossible:



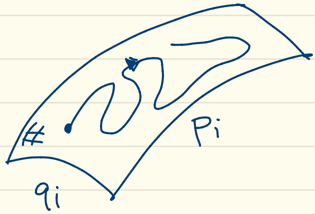
$\underbrace{\hspace{2cm}}$ 10 points per dimension for a rough representation of Ψ

$$\text{memory} \simeq (10)^{3N} \underbrace{8}_{\substack{\text{8 bytes} \\ \text{per real number}}} \simeq 10^{61} \text{ bytes}$$

$$\simeq \frac{10^{12} \text{ bytes}}{\underbrace{0.4 \text{ Kg}}_{\substack{\text{1 TByte / pound} \\ \text{(2016 Technology)}}}} \quad \underbrace{10^{49} \times 0.4 \text{ Kg}}_{\gg \text{ mass of the galaxy}}$$

STATISTICAL MECHANICS

hamiltonian dynamics



phase space
(in the case of a gas w/ N molecules, $i=1,\dots,3N$ and the phase space has $6N$ dimensions)

evolution governed by Hamilton eqs.:

$$\frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}$$

$$\frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i} \quad \Longrightarrow \quad q_i(t),\ p_i(t)$$

$$q_i(t=0) = q_i^0$$

$$p_i(t=0) = p_i^0$$

evolution is deterministic

idealization of the measurement process

result of solving Hamilton eqs. w/ initial condition q_i^0, p_i^0

$$\bar{f} = \lim_{T\to\infty} \frac{1}{T} \int_{\zeta}^{\zeta+T} dt\, f(q(t),p(t)) = \underbrace{\tilde{f}(q_i^0,p_i^0)}_{\text{some function of the initial condition}}$$

result of measuring f (function of p's and q's (like $K=\sum_i \frac{p_i^2}{2m}, \dots$)

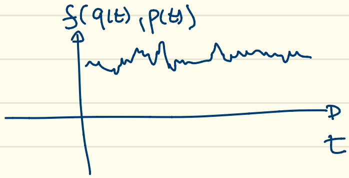
duration of the measurement

time the measurement starts

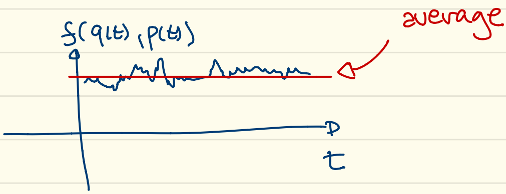
This is an idealization. In reality, the measurement last a finite time T which is much larger than the microscopic scales. For instance,

STATISTICAL MECHANICS

Suppose f is the pressure on a wall containing a gas. The quantity $f(q(t), p(t))$ fluctuates like:

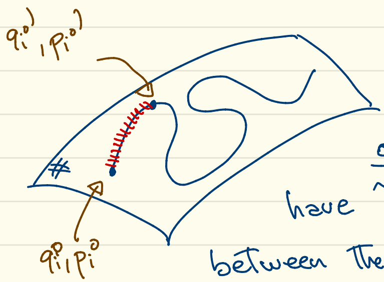


But any real, macroscopic apparatus can't measure this and, instead, averages $f(q(t), p(t))$ over a (finite) time:



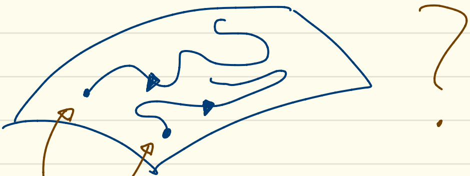
The limit $T \to \infty$ is just a mathematical idealization of this averaging out of fluctuations.

Now, back to the analysis of $\tilde{f}$. The function $\tilde{f}(q_i^0, p_i^0)$ is not really a function of the initial condition but only of the trajectory. That is, if we choose another initial point $q_i^{0'}, p_i^{0'}$ on the trajectory of q_i^0, p_i^0, we will have $\tilde{f}(q_i^0, p_i^0) = \tilde{f}(q_i^{0'}, p_i^{0'})$ since the difference between the two trajectories (shown in red in the figure) is negligible compared to the infinite extend of the trajectories.



STATISTICAL MECHANICS

Now, it could be that two different trajectories give different values for $\bar{f}$.



Two different initial conditions, two different trajectories, two different values of $\bar{f}$

It turns out that, for the systems we are interested in, that does not happen. They will have the property that any trajectory passes through every point in phase space. This is called the "ergodic property".

well, every point with the same value of the energy (and total momentum, and angular momentum) as the initial point. After all, those are quantities conserved by the hamiltonian flow.

actually, "almost" any, in the measure theory sense.

It's really difficult to prove that a realistic system has the ergodic property, even if by proof we mean a

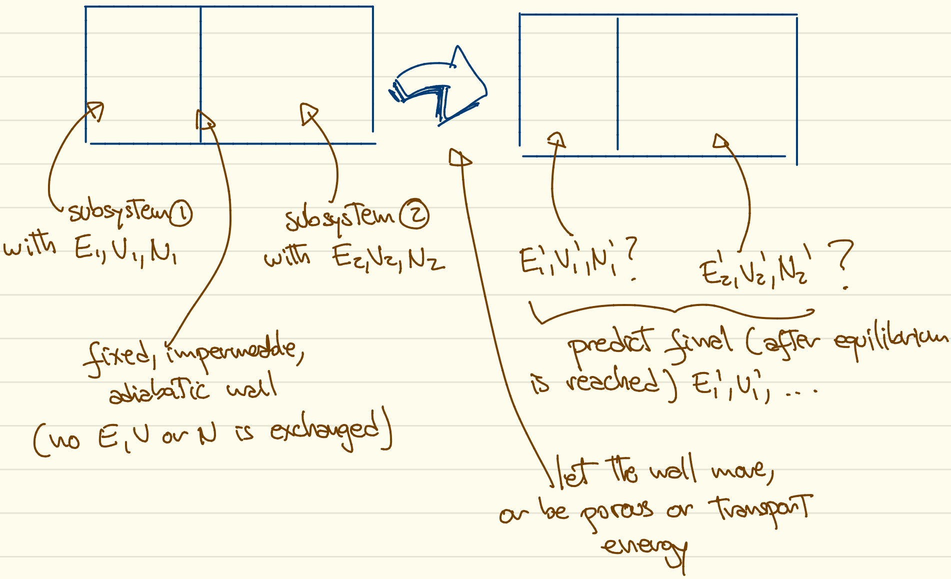
STATISTICAL MECHANICS

physicist proof. In a couple of cases a rigorous proof is available (look up "Sinai billiards / stadium"). So, we will make the assumption that the systems we are interested in are ergodic, that is, we will make the "ergodic hypothesis". On the other hand it is easy to find systems that are <u>not</u> ergodic. Any conserved quantity restricts the trajectories to lie on a submanifold of the phase space. If the only conserved quantities are the ones resulting from the standard symmetries (energy, momentum, ...) we can wonder about the validity of the ergodic hypothesis within the restricted subspace with constant energy, momentum, ... There are systems with so many other conserved quantities that this subspace is one dimensional (they are called "integrable systems"). For them the ergodic hypothesis is not true. In between integrable and ergodic systems there are intermediate kinds (mixing, ...).

more on this soon.

STATISTICAL MECHANICS

An important insight is that every thermodynamical problem can be phrased as:



Since every microstate is equally probable, the final macroscopic state will be the one corresponding to the largest number of microstates:

$$\underbrace{\Gamma(E_1', V_1', N_1', E_2', V_2', N_2')}_{\#\text{ states of composite system}} = \underbrace{\Gamma_1(E_1', V_1', N_1')}_{\#\text{ of microstates of subsystem ①}} \underbrace{\Gamma_2(E_2', V_2', N_2')}_{\#\text{ of microstates of subsystem ②}}$$

Take the case the wall allows exchange of energy but not volume or particle number. Then:

STATISTICAL MECHANICS

$$E_1 + E_2 = E_1' + E_2'$$
$$V_1 = V_1', \quad V_2 = V_2'$$
$$N_1 = N_1', \quad N_2 = N_2'$$

$$\Gamma(E_1', E_2') = \Gamma_1(E_1')\,\Gamma_2(E - E_1')$$ (drop the explicit $V_1, V_1', \dots$)

Now:

maximum of Γ (keeping total E fixed) $\Longleftrightarrow \frac{1}{\Gamma_1}\frac{d\Gamma_1(E_1')}{dE_1'} - \frac{1}{\Gamma_2(E_2')}\frac{d\Gamma_2(E_2')}{dE_2'} = 0$

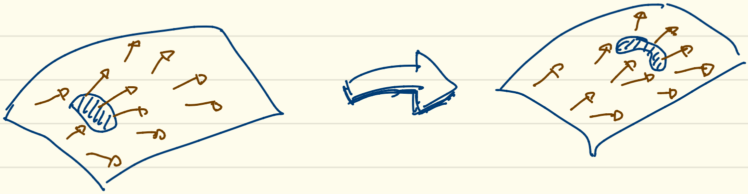
So, knowing $\Gamma_1(E_1)$ and $\Gamma_2(E_2)$ we can predict the final state. It's convenient to use the entropy

$$S = k_B \ln \Gamma$$

instead of Γ. Notice S is extensive ($S = S_1 + S_2$) as long as the subsystems are large enough so boundary effects are negligible.

<u>How can entropy grow?</u> There's an apparent paradox in saying the entropy is maximized (within the constraints of the problem). That's because, using Hamiltonian eqs., we can show S is a constant.

Let $\rho(q, p, t=0)$ be an initial distribution of identical systems (an ensemble). As the hamiltonian flow evolves in time every element of the ensemble is carried with it and the distribution evolves to $\rho(q,p,t) = \rho(q(t), p(t))$.



Since the number of systems in the ensemble is fixed ρ obeys the continuity equation:

$$\frac{d\rho}{dt} + \nabla\cdot(\rho \mathbf{v}) = 0$$

Hamiltonian flow $(\dot{q}_i, \dot{p}_i)$

or

$$0 = \frac{\partial \rho}{\partial t} + \underbrace{\sum_{i=1}^{3N} \frac{\partial}{\partial q_i}(\rho\, \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho\, \dot{p}_i)}_{\nabla\cdot(\rho \mathbf{v})}$$

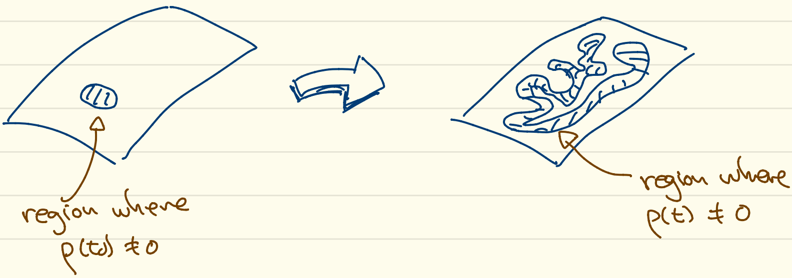
$$= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left[\underbrace{\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i}_{\nabla\rho\cdot\mathbf{v}} + \underbrace{\rho\frac{\partial \dot{q}_i}{\partial q_i} + \rho\frac{\partial \dot{p}_i}{\partial p_i}}_{\rho\,\nabla\cdot\mathbf{v}}\right]$$

$$= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left[\underbrace{\frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}}_{\{\rho,\mathcal{H}\}} + \rho\underbrace{\left(\frac{\partial^2 \mathcal{H}}{\partial q_i\partial p_i} - \frac{\partial \mathcal{H}}{\partial p_i\partial q_i}\right)}_{=0}\right]$$

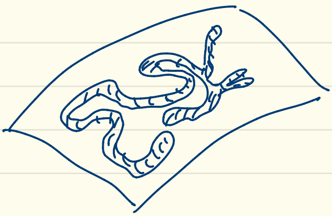
$$= \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} \equiv \frac{d}{dt}\rho \quad \left(\text{derivative along the flow}\right)$$

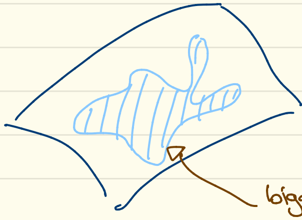
This result is known as the Liouville theorem. It implies that the density of elements on the ensemble does not change as it evolves along the Hamiltonian flow (of course, it changes at any fixed position in phase space). As the number of systems in the ensemble is fixed, the Liouville theorem implies that the volume of the phase space occupied by the ensemble is fixed.
So the entropy (log of the volume) cannot change either. How can the entropy grow if the microscopic equations of motion show that it does not? Also, everyday experience shows that entropy grows. Heat goes from hot to cold objects, cooked eggs cannot be uncooked, ..., not the other way around.

A resolution to this apparent paradox is to notice that, for systems for which stat. mech. works, the hamiltonian flow takes nice looking, civilized ensembles $\rho(t_0)$ into convoluted intestine-looking shapes



The average of smooth observables $f(q,p)$ do not distinguish between the average perfomed with the true $\rho(t)$ or the "coarse grained" one $\tilde{\rho}(t)$:





$$\bar{f} = \int dq\,dp\; f(q,p)\,\rho(q,p,t) \simeq \int dq\,dp\; f(q,p)\,\tilde{\rho}(q,p,t)$$

For all practical purposes, the entropy grows, as long as we only look at observables that are very smooth. Macroscopic observables don't care about the precise position of the particles and tend to be smooth in phase space. Systems whose Hamiltonian flow have this property are called "mixing". It's easy to show that ergodic systems are mixing (first, of course, we'd have to define the mixing property more rigorously) but mixing systems are not necessarily ergodic. A good way to visualize the mixing property is through an analogy. Consider a bucket of water (analogue to the phase space) where we put one drop of ink ($\rho(t_0)$). Suppose now we shake the bucket and the water moves (analogue of the Hamiltonian flow). After a while we end up with lightly colored water (the distribution $\tilde{\rho}(t)$). If we could examine water at a fine scale we would find water molecules or ink molecules but, from far away, we see colored water.

What we discussed was (a very cursory version) of one way of justifying the principles of equilibrium stat. mechanics. There are others. The last word has not been said yet.