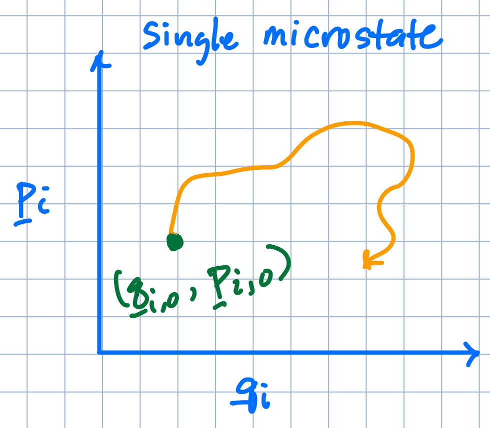
Lecture 15 – The Microcanonical Ensemble

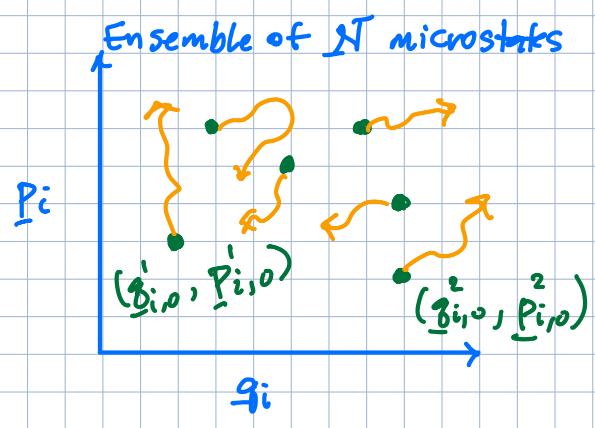
A. Microstates and Ensembles

In our discussion of dynamics, we became acquainted with the concept of the phase space. For a system with N particles, phase space is a $6N$-dimensional space where the coordinates are the $3N$ generalized coordinates q_i and $3N$ generalized momenta p_i $(i \in [1, 3N])$

For a given set of initial conditions $q_i(t=0) = q_{i,0}$ and $p_i(t=0) = p_{i,0}$, we will move with some trajectory in this very high dimensional space. We call a single system a microscopic state or microstate.

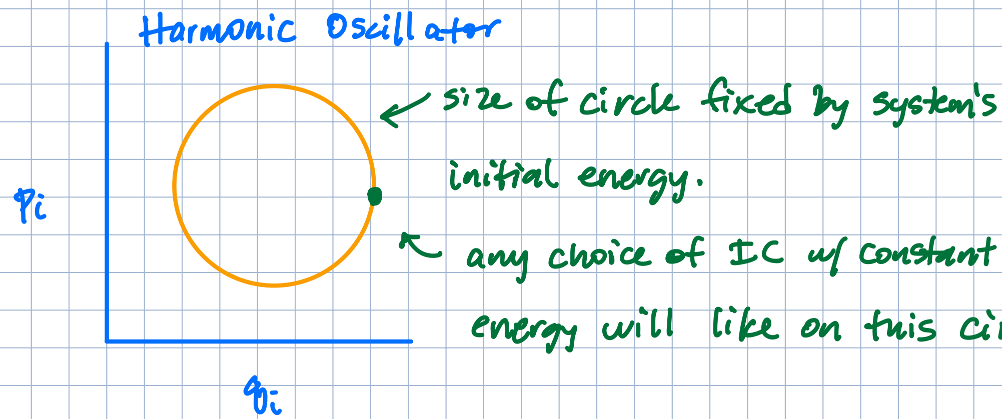
The key insight of Josiah W. Gibbs is that instead of thinking about trying to compute the dynamics of microstates, we should focus on ensembles of microstates. An ensemble is a collection of different microstates with different initial conditions.





B. The Ergodic Hypothesis

At first, this seems like it only complicates things. Instead of trying to solve the dynamics of one I.C., we are now trying to solve for the dynamics of N ICs! But think back to the harmonic oscillator for a moment. There the phase space trajectory was periodic. If I picked a different initial condition, I was going to get a very similar trajectory.



So, the trajectory of a single microstate is the same as if I picked an ensemble that corresponds to all of the possible initial conditions! (This has the constraint of having constant energy, but I could always define a different energy and get a new circle if needed.) This idea is called the Ergodic Hypothesis. It says that the dynamics of a single microstate will visit every possible state, given a long enough time. This is one of the fundamental postulates of statistical thermodynamics.

In thermodynamics, we are going to be interested in average quantities. So, for example, we might want the average pressure. If we have a very long trajectory of a single microstate, we could get this average,

$$\overline{M} = \lim_{T\to\infty} \frac{1}{T}\int_0^T M(\underline{x}(t))\,dt \qquad \underline{x} = (\underline{p}_i, \underline{q}_i) \quad i \in [1, 3N]$$

Can we do this? Yes, we can now with computers. One needs to solve the equations of motion for the system. This is molecular dynamics. But, the founders of stat thermo couldn't do this. They wanted to be able to do something! The Ergodic hypothesis of Gibbs says that we don't have to. Instead, we can do an ensemble average,

$$\langle M \rangle = \int_{\Gamma} M(\underline{X})\, \rho(\underline{X})\, d\underline{X}$$

probability density of point $\underline{X}$.

phase space volume

$$\Gamma = \int d\underline{X}$$

In other words,

$$\langle M \rangle = \overline{M}$$

Ensemble average = time average.

This is a mathematical expression of the Ergodic hypothesis.

C. Phase Space Probability Density

Because of the E.H., we now see that if we know the probability density of microstates in phase space, we can compute ensemble averages. How do we get this probability density?

Suppose we have $\mathcal{N}$ microstates. Let $D(\underline{X})$ be the number of microstates per phase space volume, so that

$$\mathcal{N} = \int_{\Gamma} D(\underline{X})\, d\underline{X}$$

The probability density must then be normalized to 1, so that

$$\rho(\underline{X}) = \frac{1}{\mathcal{N}} D(\underline{X}) = \frac{D(\underline{X})}{\int_{\Gamma} D(\underline{X})\, d\underline{X}}$$

This is a formal definition of the probability density of microstates in phase space. It seems very "mathy." We have just kicked the can down the road. How can I compute $\mathcal{N}$ or $D(\underline{X})$ or $\rho(\underline{X})$?

D. Microcanonical Ensemble

I am going to assume a certain kind of ensemble of microstates. In this ensemble I will have N particles in a box of volume V. The total system energy will be a constant E. Let's see if we can find the probability density of the microstates $\rho(\underline{X})$ in this ensemble.

My phase space integral for the NVE-ensemble, or the microcanonical ensemble, is given by

$$\Sigma(N,V,E) = \int_{\Gamma} \delta(H(\underline{X}) - E)\, d\underline{X}$$

Dirac delta function

size of hypersurface.

$\propto$ # of microstates

$$= \int_{q_1}\int_{q_2}\cdots\int_{q_{3N}}\int_{p_1}\int_{p_2}\cdots\int_{p_{3N}} \delta(H(q_1, q_2, \ldots, q_{3N}, p_1, p_2, \ldots, p_{3N}) - E)\, dq_1\, dq_2 \cdots dq_{3N}\, dp_1\, dp_2 \cdots dp_{3N}$$

Using this, the probability density is given by

$$\rho_{NVE}(\underline{X}) = \frac{1}{\Sigma}\,\delta(H(\underline{X}) - E) = \begin{cases} 1/\Sigma & \text{if energy} = E \\ 0 & \text{if energy} \neq E \end{cases}$$

In other words, there is a uniform probability of microstates in the microcanonical ensemble. This is the second postulate in statistical thermodynamics. It is sometimes called the principle of equal a priori probabilities.

E. Quantum Correction to the Number of Microstates

There is a problem with our probability density that we just wrote down. It is continuous. We really want a PMF! The probability of a microstate is infinitely small for a continuous probability density. We will see in a minute that the connection to thermo-dynamics means that this infinitely small probability makes some macroscopic quantities infinitely large. This is obviously wrong.

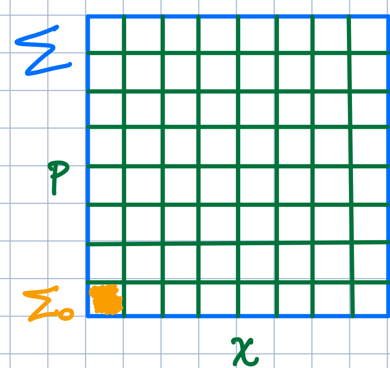
This isn't that hard of a problem to solve. We will just define some minimum volume of phase space to be our smallest "chunk" that counts as a microstate. Then we can get a discrete number of states by dividing.

$\Sigma(N,V,E)$: size of phase space

$\Sigma_o(N,V,E)$: minimum volume of Phase Space.

$\Omega(N,V,E)$: number of microstates

$$\Omega = \frac{\Sigma}{\Sigma_o}$$



But what is Σ_o? From a classical mechanics perspective, it is arbitrary. We just need something there. The fact that it is arbitrary is a sign our theory (classical mechanics) is incomplete. But, we know Qunatum Mechanics! In QM we know that there is an uncertainty principle. Uncertainty says that

$$\sigma_x \sigma_p \geq h/4\pi$$

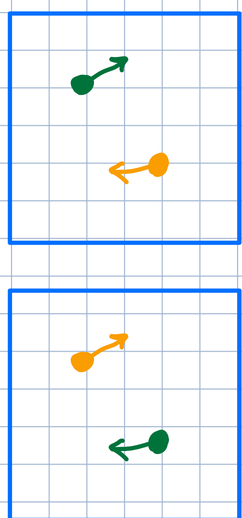
Using this principle (math not shown) one can say that a single dimension of x and p give a volume of h in phase space.

So, for N particles in three dimensions, we get a factor of h^{3N},

$$\Sigma_0 \propto h^{3N}$$

F. Gibbs Paradox

There is one more problem with our counting of microscopic states. We are overcounting the number of states because of possible permutations between particles. Suppose we have a two particle gas:



particle 1: $\underline{x}_1, \underline{p}_1$
particle 2: $\underline{x}_2, \underline{p}_2$

particle 1: $\underline{x}_1, \underline{p}_1$
particle 2: $\underline{x}_2, \underline{p}_2$

All I did here is swap the labels between particle 1 and particle 2, but these are the same microstate! However, our integral counts these as two states.

We need to "fix" our integral to not double count permutations that aren't really different states. We could redefine a new integral (hard). Instead, we can just divide by the number we are overcounting. This is the other piece that goes into Σ_0,

$$\Sigma_0 \propto N! \quad \leftarrow \text{Factor for overcounting.}$$

Putting this with the quantum correction gives,

$$\Sigma_0 = h^{3N} N! \qquad \Omega = \frac{1}{h^{3N} N!} \Sigma$$

Aside: The $N!$ term was initially missing in Gibbs formulation, and it made Entropy not extensive and broke mixing entropy. This was "Gibbs Paradox."

with this normalization factor we can write the PMF for the # of microstates like we wanted.

$$P(\underline{x}) = \begin{cases} 1/\Omega & \text{if } H(\underline{x}) = E \\ 0 & \text{otherwise} \end{cases}$$

Ω: # of microstates

Ω is also called the "density of states"

where

$$\Omega(N,V,E) = \frac{1}{h^{3N} N!} \int_{\Gamma} \delta(H(\underline{x}) - E)\, d\underline{x}$$