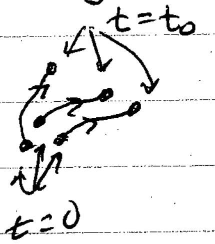
Liouville's theorem

The concept of density matrix will soon be expanded beyond the particular example of the microcanonical ensemble. It can also be generalized to non-equilibrium situations. $\rho(q_i, p_i, t)$
We therefore want to see what general condition ρ must satisfy in order that $\frac{\partial \rho}{\partial t} = 0$, ie steady-state

Consider an initial density ρ of points in phase space. As the systems represented by these initial points evolves in time, their trajectories give the density $\rho(t)$ at later times. Think of the points in ρ like particles in a fluid.



The probability density ρ must obey a local conservation equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$$

Where $\vec{v}$ is the "velocity" vector of the probability "current" $\rho\vec{v}$, that tells how the points in ρ flow in phase space.
$\vec{v}$ is the $6N$ dimensional vector $(\dot{q}_1, \dots, \dot{q}_{3N}, \dot{p}_1, \dots \dot{p}_{3N}$

and
$$\vec{\nabla} \cdot (\rho \vec{v}) = \sum_{i=1}^{3N} \left[\frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \right]$$

$$= \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \rho \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \rho}{\partial p_i} \dot{p}_i + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right]$$

$$\vec{\nabla}\cdot(\rho\vec{v}) = \sum_i \left[\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i\right] + \rho\left[\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right]$$

use $\dot{q}_i = \frac{\partial H}{\partial p_i}$ $\quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$

$$\Rightarrow \frac{\partial\dot{q}_i}{\partial q_i} = \frac{\partial H}{\partial p_i \partial q_i} \qquad \frac{\partial\dot{p}_i}{\partial p_i} = \frac{-\partial H}{\partial q_i \partial p_i}$$

so $\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i} = 0$

and

$$\vec{\nabla}\cdot(\rho\vec{v}) = \sum_i \left\{\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right\}$$

$$= [\rho, H]$$

defines the "Poisson braket"

so

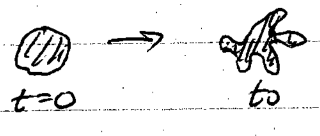
$$\frac{\partial\rho}{\partial t} + [\rho, H] = 0$$

or $$\frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N}\left\{\frac{\partial\rho}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial\rho}{\partial p_i}\frac{dp_i}{dt}\right\} = \underset{\uparrow}{\frac{d\rho}{dt}} = 0$$

total time derivative

$\frac{d\rho}{dt}$ is also called the convective derivative. It is how ρ changes in time if one moves along with "particles" (ie the systems on their trajectories)

$\frac{d\rho}{dt} = 0 \Rightarrow$ density in phase space is ~~independent of~~ constant in time as it flows - like an incompressibly fluid.



density of points at to = density at t:

Equilibrium requires a stronger condition, namely $\frac{\partial \rho}{\partial t} = 0$, so that ensemble averages will not vary in time.

$$\frac{\partial \rho}{\partial t} = 0 \quad \Rightarrow \quad [\rho, \mathcal{H}] = 0$$

$$[\rho, \mathcal{H}] = \sum_i \left[\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right]$$

we see that $[\rho, \mathcal{H}] = 0$ if $\rho(q_i, p_i)$ denpends on q_i, p_i only via the function $\mathcal{H}[q_i, p_i]$, ie $\rho = \rho(\mathcal{H}(q_i, p_i))$. Then $\frac{\partial \rho}{\partial q_i} = \frac{\partial \rho}{\partial \mathcal{H}} \frac{\partial \mathcal{H}}{\partial q_i}$, $\frac{\partial \rho}{\partial p_i} = \frac{\partial \rho}{\partial \mathcal{H}} \frac{\partial \mathcal{H}}{\partial p_i}$

$$[\rho, \mathcal{H}] = \sum_i \left[\frac{\partial \rho}{\partial \mathcal{H}} \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial \mathcal{H}} \frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right] = 0$$

so $\rho(q_i, p_i)$ must be constant on constant energy surfaces, if ρ is to describe equilibrium.

We already saw one example

microcanonical ensemble $\quad \rho(q_i, p_i) \sim \delta(\mathcal{H}(q_i, p_i) - E)$

another choise later will be

canonical ensemble $\quad \rho(q_i, p_i) \sim e^{-\mathcal{H}[q_i, p_i]/k_B T}$

Microcanonical Ensemble and Entropy

We saw that the microcannonical ensemble, at energy E, assigned equal weight to all systems on the surface in phase space of constant energy $\mathcal{H}[q_i, p_i] = E$.

To count the number of such states on the energy surface we define the "density of states"

$$g(E) \equiv \int \frac{dq_i\, dp_i}{h^{3N}} \quad \delta(\mathcal{H}[q_i, p_i] - E)$$

where h is a constant with units of $q_i p_i$.
h^{3N} represents the volume of phase space occupied by one "state". Classically, h is totally arbitrary so our thermodynamic results should not depend on it. Quantum mechanically, we will see that h turns out to be Planck's constant.

At this stage, the factor $\frac{1}{h^{3N}}$ is introduced so that $g(E)$ has the units of $1/\text{energy}$.

We can now define the number of states in a shell of thickness Δ about the energy surface E.

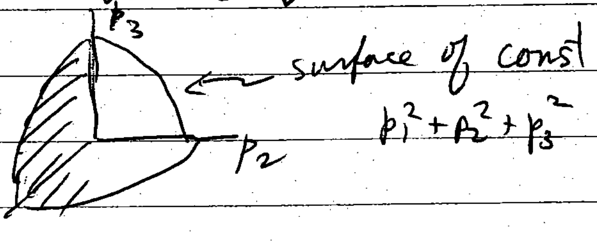
$$\Omega(E, V, N) = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} dE'\, g(E')$$

Ω is a pure number. Again, Δ is arbitrary, but

$\frac{E}{N} < \Delta \ll E$

assumed to be [illegible]. It can be thought of as representing the finite accuracy with which one knows E. Our thermodynamic results should not depend on Δ. [both h and Δ are introduced so that ~~the~~ ~~dimension of~~ Ω is a dimensionless pure number that we can think of as being the ~~[illegible]~~ number of microscopic states occupied in the microcanonical ensemble at E]

Example: Compute Ω for the ideal gas of non interacting particles, confined to a volume V



$$\mathcal{H} = \sum_i \frac{p_i^2}{2m}$$

$$g(E) = \int \frac{d^3 r_i}{h^{3N}} \int d^3 p_i \; \delta\left(\sum_i \frac{p_i^2}{2m} - E \right)$$

$$= \frac{V^N}{h^{3N}} \int d^3 p_i \; \delta\left(\sum_i \frac{p_i^2}{2m} - E \right)$$

The surface of constant energy is just the surface of a sphere in 3N dimensional momentum space given by the coords $p_{1x}, p_{1y}, p_{1z}, \dots p_{Nx}, p_{Ny}, p_{Nz}$
The radius of the sphere is $\sqrt{2mE}$

Let $\mathbb{P} \equiv \sqrt{\sum_i p_i^2}$ be the length of the momentum vector in the 3N dimensional momentum space

Then $\prod_{i=1}^{N} d^3p_i = d\mathbb{P}\, \mathbb{P}^{3N-1}\, d\Omega_{3N}$

↑ differential solid angle in 3N dimensional space

$$g(E) = \frac{V^N}{h^{3N}} \int d\Omega_{3N} \int_0^\infty d\mathbb{P}\, \mathbb{P}^{3N-1}\, \delta\left(\frac{\mathbb{P}^2}{2m} - E\right)$$

$$= \frac{V^N}{h^{3N}} \underbrace{S_{3N}}_{\text{area of unit sphere in 3N-dim space}} \int_0^\infty d\mathbb{P}\, \mathbb{P}^{3N-1} \frac{\delta(\mathbb{P} - \sqrt{2mE})}{\underbrace{(\mathbb{P}/m)}_{\text{from converting the } \delta\text{-function}}}$$

$$= \frac{V^N}{h^{3N}} S_{3N}\, m\, (2mE)^{\frac{3N-2}{2}}$$

From Appendix C of Pathria (equ C.76) or elsewhere, one has the area of unit sphere in d-dim space

$$S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$

where $\Gamma(n) = (n-1)!$ for integer n

Γ is the Gamma function

So $$S_{3N} = \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}$$

$$g(E) = \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}\, m\, \frac{(2mE)^{\frac{3N}{2}}}{2mE}$$

$$\boxed{g(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \frac{1}{E}}$$

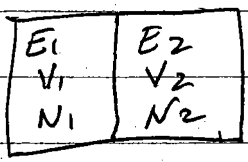
$$\Omega(E) = \int_{E-\frac{\Delta}{2}}^{E+\Delta/2} dE' \, g(E') \approx g(E)\Delta$$

$$\boxed{\Omega(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \frac{\Delta}{E}}$$

For large N, $\Omega(E)$ is a <u>very</u> rapidly increasing function of E! $\sim E^{\frac{3N}{2}-1}$

We will now argue that $\Omega(E)$ is related to the entropy of the system.

Consider two subsystems separated by a wall



$E_T = E_1 + E_2$ energy conserved

let $g_1(E_1)$ is density of states of system 1 with energy E_1
$g_2(E_2)$ is density of states of system 2 with energy E_2

Now suppose the wall is thermally conducting so that energy can be transfered between the two systems. $\Rightarrow$ E_1 can vary but $E_T = E_1 + E_2$ is fixed. What will be the value of E_1 when the system comes to equilibrium?

The density of states of the combined system will be

$$g_T(E_T) = \int_0^{E_T} dE_1\, g_1(E_1)\, g_2(E_T - E_1)$$

Now if
$$\Omega_T(E_T) \approx g_T(E_T)\Delta$$
$$\Omega_1(E_1) = g_1(E_1)\Delta$$
$$\Omega_2(E_2) = g_2(E_2)\Delta$$

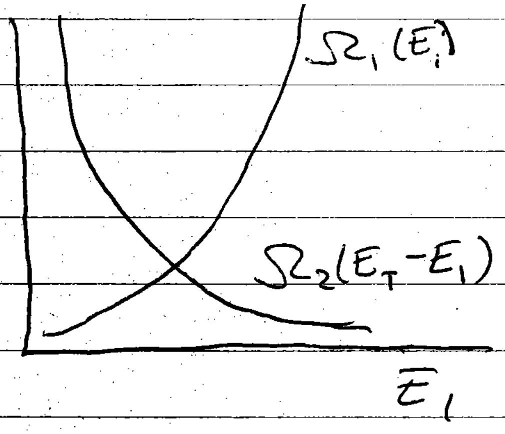
Then the above can be written as

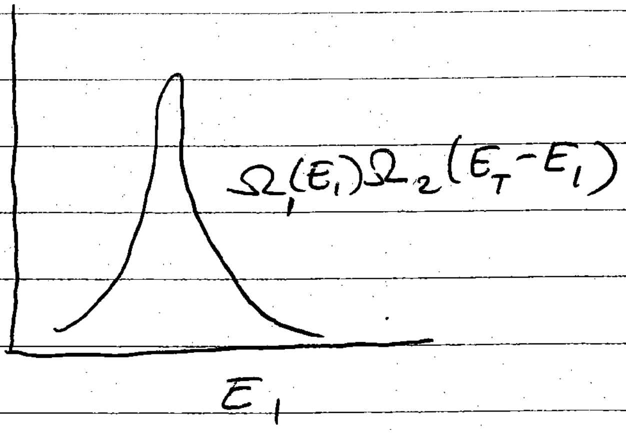
$$\Omega_T(E_T) = \int \frac{dE_1}{\Delta}\, \Omega_1(E_1)\, \Omega_2(E_T - E_1)$$

The integrand is the number of states with total energy E_T that also have system 1 with energy E_1

Consider the behavior of the integrand
$\Omega_1(E_1)$ is a rapidly increasing function of E_1
$\Omega_2(E_2)$ is a rapidly increasing function of E_2
$\Rightarrow \Omega_2(E_T - E_1)$ is a rapidly <u>decreasing</u> function of E_1

$\Rightarrow$ the product $\Omega_1(E_1)\Omega_2(E_T - E_1)$ has a sharp maximum at some particular value of E_1





In the microcanonical ensemble, all states with total energy E_T are equally likely. But the value of E_1 that one is most likely to find as the energy of system 1 is the particular value that maximizes $\Omega_1(E_1)\Omega_2(E_T-E_1)$. That is, there are more states with this particular value of $\bar{E}_1$ than with any other value of E_1, and since all microscopic states are equally likely, this value of $\bar{E}_1$ is the most likely. Moreover, since $\Omega_1(E_1)$ is rapidly increasing in E_1 and $\Omega_2(E_T-E_1)$ is rapidly decreasing in E_1, the maximum is extremely sharp. So one is almost certain to find the maximizing value of E_1 (the probability to find any other value of E_1 will vanish as the size of the systems get infinitely large)

What condition determines this maximizing value of E_1?

$$\frac{\partial}{\partial E_1}\left[\Omega_1(E_1)\Omega_2(E_T-E_1)\right] = 0$$

$$\Rightarrow \left(\frac{\partial \Omega_1(E_1)}{\partial E_1}\right)\Omega_2(E_T-E_1) + \Omega_1(E_1)\left(\frac{\partial \Omega_2(E_T-E_1)}{\partial E_1}\right) = 0$$

$$\left(\frac{\partial \Omega_1(E_1)}{\partial E_1}\right)\Omega_2(E_T-E_1) - \Omega_1(E_1)\left(\frac{\partial \Omega_2(E_T-E_1)}{\partial E_2}\right) = 0$$

$$\Rightarrow \frac{1}{\Omega_1}\frac{\partial \Omega_1(E_1)}{\partial E_1} = \frac{1}{\Omega_2}\frac{\partial \Omega_2(E_T-E_1)}{\partial E_2}$$

$$\Rightarrow \quad \frac{\partial}{\partial E_1}\left(\ln \Omega_1\right) = \frac{\partial}{\partial E_2}\left(\ln \Omega_2\right)$$

But from thermodynamics we know that the equilibrium value of E_1 will be determined by the condition

$$\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} = \frac{1}{T_2}$$

Therefore, following Boltzmann, we identify

$$S(E) \propto \ln \Omega(E)$$

as the entropy.

Since the relation between thermodynamics + mechanics should be fundamental, Boltzmann postulated that the proportionality constant in the above should be a universal number, and not depend on the particular system. This constant is Boltzmann's constant k_B.

$$\boxed{\underset{\substack{\uparrow \\ \text{entropy}}}{S(E)} = k_B \ln \underset{\substack{\uparrow \\ \text{\# states} \\ \text{with energy } E}}{\Omega(E)}}$$

$S(E)$ is a monotonic increasing function of E as it should be.