# 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 evolve in time, their trajectories give the density $\rho(t)$ at later times. Think of the points in ρ like particles in a fluid.
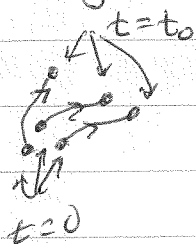
The probability density ρ must obey a local conservation equation

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

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

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

$$\vec{\nabla} = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots \frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \dots \right)$$

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

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

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

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

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

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

$$= [\rho, H] \quad \longleftarrow \text{ defines the "Poisson braket"}$$

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

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

$\uparrow$ total time derivative

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

$\dfrac{d\rho}{dt} = 0 \Rightarrow$ density in phase space is ~~independent of~~ <u>constant</u> in time as it flows — like an <u>incompressible</u> fluid.
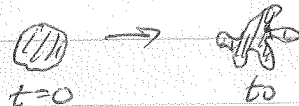
$(\!1\!) \longrightarrow$ $\quad$ density of points at t_0 = density at $t=0$
$t=0 \qquad\qquad\quad t_0$

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

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

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

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

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

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

We already saw one example

<u>microcanonical ensemble</u> $\rho(q_i, p_i) \sim \delta(H(q_i, p_i) - E)$

another choice later will be

<u>canonical ensemble</u> $\rho(q_i, p_i) \sim e^{-H(q_i, p_i)/k_B T}$

Microcanonical Ensemble and Entropy

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

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

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

$\nearrow$ (number of states) (per unit energy)

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 $1/$energy.

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

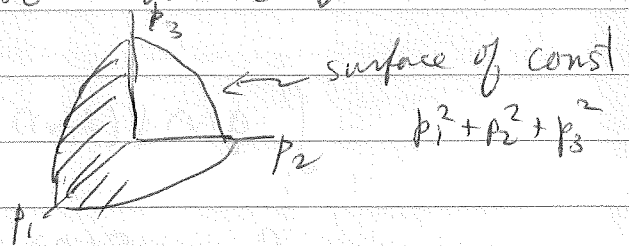$$\Omega(E, V, N) = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} dE' \, g(E')$$

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

$$\frac{E}{N} \lesssim \Delta \lesssim E$$

assumed to be small. 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 ~~total~~ 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

$$\mathcal{H} = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m}$$

surface of const $p_1^2 + p_2^2 + p_3^2$

$$g(E) = \prod_{i=1}^{N} \int \frac{d^3 r_i}{h^{3N}} \int d^3 p_i \; \delta\left(\sum_i \frac{|\vec{p}_i|^2}{2m} - E \right)$$

$$= \frac{V^N}{h^{3N}} \prod_{i=1}^{N} \int d^3 p_i \; \delta\left(\sum_i \frac{|\vec{p}_i|^2}{2m} - E \right)$$

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

Let $\mathbb{P} \equiv \sqrt{\sum_{i=1}^{N} |\vec{p}_i|^2}$ be the length of the momentum vector in the $3N$ dimensional momentum space ~~that~~

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

differential solid angle
in $3N$ dimensional space

$$g(E) = \frac{V^N}{h^{3N}} \int d\Omega_{3N} \int\limits_0^\infty d\mathbb{P} \, \mathbb{P}^{3N-1} \, \delta\left(\frac{\mathbb{P}^2}{2m} - E\right)$$

$$= \frac{V^N}{h^{3N}} \, S_{3N} \int\limits_0^\infty d\mathbb{P} \, \mathbb{P}^{3N-1} \, \frac{\delta\left(\mathbb{P} - \sqrt{2mE}\right)}{(\mathbb{P}/m)}$$

area of unit
sphere in $3N$-dim space

from converting the δ-function

$$\delta(f(x)) = \frac{\delta(X - X_0)}{f'(x_0)}$$
where $f(x_0) = 0$

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

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

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

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

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

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

For large N, $\Omega(E)$ is a very 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_1	E_2
V_1	V_2
N_1	N_2

$E_T = E_1 + E_2$ 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
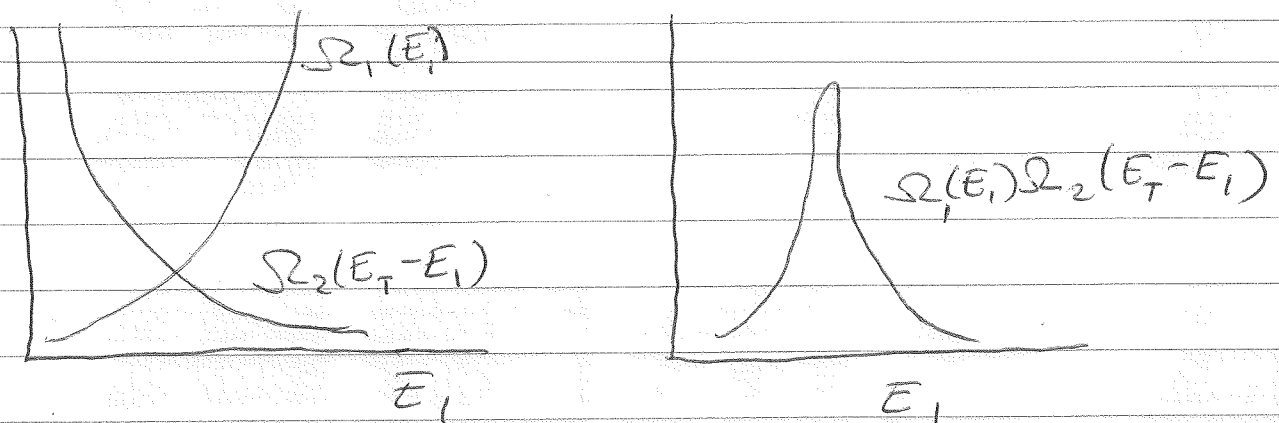
In the micro canonical ensemble, all states with total energy E_T are equally likely. But the value of E_1 that one is most likely to find as the energy of system 1 is the particular value that maximizes $\Omega_1(E_1)\Omega_2(E_T - E_1)$. That is, there are more states with this particular value of E_1 than with any other value of E_1, and since all microscopic states are equally likely, this value of 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 the maximizing value of E_1?

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

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

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

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

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

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.

$$\boxed{S(E) = k_B \ln \Omega(E)}$$

entropy   # states with energy E

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