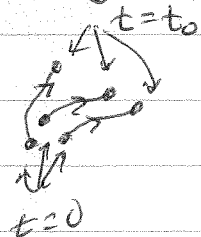


Liouville's theorem

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 $\frac{\partial \rho}{\partial t} = 0$, i.e. 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 $(\dot{q}_1, \dots, \dot{q}_N, \dot{p}_1, \dots, \dot{p}_N)$

and

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

$$\vec{\nabla} = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \dots \right) = \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \rho \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \rho}{\partial p_i} \dot{p}_i + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right]$$

$$\vec{\nabla} \cdot (f \vec{v}) = \sum_i \left[\frac{\partial f}{\partial g_i} \dot{g}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right] + f \left[\frac{\partial \dot{g}_i}{\partial g_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right]$$

use $\dot{g}_i = \frac{\partial H}{\partial p_i}$ $\dot{p}_i = -\frac{\partial H}{\partial g_i}$

$$\Rightarrow \frac{\partial \dot{g}_i}{\partial g_i} = \frac{\partial H}{\partial p_i \partial g_i} \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial H}{\partial g_i \partial p_i}$$

$$\text{so } \frac{\partial \dot{g}_i}{\partial g_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$$

and

$$\begin{aligned} \vec{\nabla} \cdot (f \vec{v}) &= \sum_i \left\{ \frac{\partial f}{\partial g_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial g_i} \right\} \\ &= [f, H] \end{aligned}$$

← defines the "Poisson bracket"

so

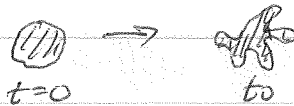
$$\frac{\partial f}{\partial t} + [f, H] = 0$$

$$\approx \frac{\partial f}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial f}{\partial g_i} \frac{dg_i}{dt} + \frac{\partial f}{\partial p_i} \frac{dp_i}{dt} \right\} = \frac{df}{dt} = 0$$

↑
total time derivative

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

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



density of points
at $t=0$ = density at $t=0$

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

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

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

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.

$$\rho = \rho(H(q_i, p_i)). \text{ Then } \frac{\partial \rho}{\partial q_i} = \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i}, \quad \frac{\partial \rho}{\partial p_i} = \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i}$$

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

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

We already saw one example

microcanonical ensemble $\rho(q_i, p_i) \sim \delta(H(q_i, p_i) - E)$

another choice later will be

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

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"

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

(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 $1/\text{energy}$.

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

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

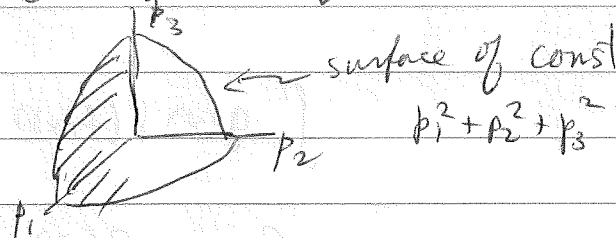
Ω is a pure number. Again, Δ is arbitrary, but

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

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~~ Ω is a dimensionless pure number that we can think of as being the ~~mode~~ 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

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



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

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

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

↑ differential solid angle
in $3N$ dimensional space

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

$$= \frac{V^N}{h^{3N}} S_{3N} \int_0^\infty dP P^{3N-1} \frac{\delta(P - \sqrt{2mE})}{(P/m)}$$

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

← from
converting the
 δ -function

$$\delta(f(x)) = \frac{\delta(x)}{f'(x)}$$

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

From Appendix C of Pathria (eqn 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

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

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

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

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

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

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

$$E_T = E_1 + E_2 \quad \text{energy conserved}$$

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 transferred 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 .

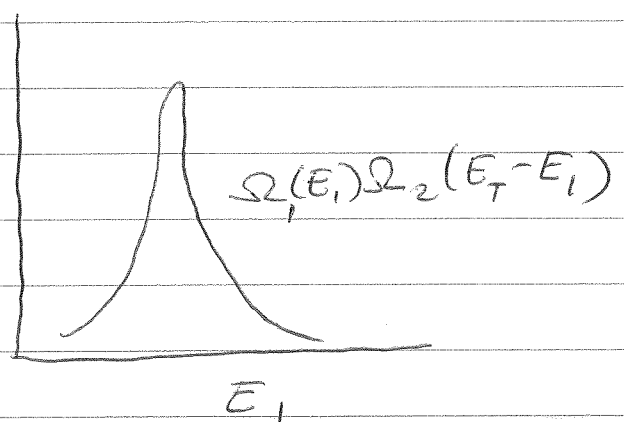
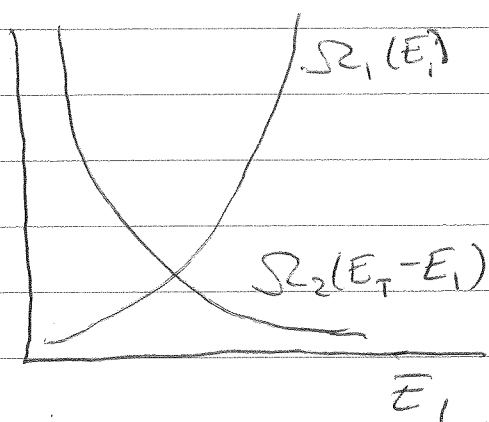
~~Then~~ Consider the behavior of the integrand

$\Omega_1(E_1)$ 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 decreasing 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 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 this maximizing value of E_1 ?

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

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

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

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

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

But from thermodynamics we know that ^{the} equilibrium value of E , 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 .

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

$\uparrow$ entropy $\uparrow$ # states with energy E

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