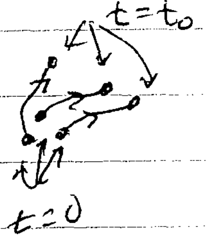
Liouville's theorem

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 $(\dot{q}_1, \ldots, \dot{q}_N, \dot{p}_1, \ldots \dot{p}_N$

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

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

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

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

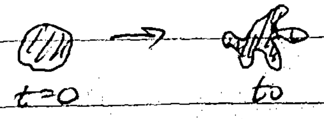
$$\frac{\partial\rho}{\partial t} + [\rho, H] = 0$$

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

another choise later will be

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

Microcanonical Ensemble and entropy

We saw that the microcanonical ensemble, at energy E, assigned equal weight to all systems on the surface of constant $\mathcal{H}[q_i, p_i] = E$ in phase space. In order not to deal with the singular nature of the δ-function that defines this surface, we generalize it slightly to consider all systems within ~~a finite over~~ an energy shell of finite width about E, ~~$E<\mathcal{H}[q_i,p_i]<E+\Delta$~~

$$E < \mathcal{H}[q_i, p_i] < E + \Delta.$$

where Δ is small but finite. Physically this is reasonable since in a real thermodynamic system there will always be some small uncertainty in the value of E. But we want to take Δ such that none of our thermodynamic results will depend on the particular value of Δ chosen, in the thermodynamic limit $N \to \infty$. This requires $\frac{E}{N} < \Delta \ll E$, ie Δ is bigger than the average energy per particle, but much less than the total energy.

Define the number of states in the energy shell as

$$\Omega(E, V, N) \equiv \frac{1}{h^{3N}} \int\limits_{E<\mathcal{H}[q_i,p_i]<E+\Delta} dq_i \, dp_i$$

where h is a constant introduced to make Ω dimensionless. h has units of $q_i p_i$ and

h^{3N} represents the volume of phase space occupied by one "state". Classically, h is totally arbitrary, and so thermodynamic results should not depend on it. Quantum mechanically we will see that h should be taken as Planck's constant.

Example we compute Ω for the ideal gas of non-interacting particles, confined to a volume V

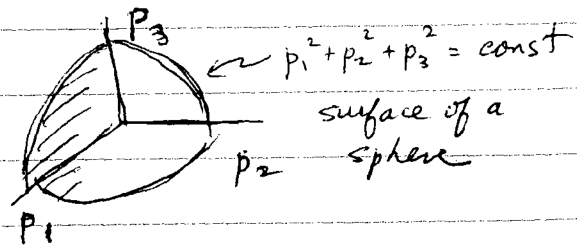
$\mathcal{H} = \sum_i \frac{p_i^2}{2m}$ indep of position of particle

⇒ each particle equally likely anywhere in space

⇒ factor V^N from $\int dq_i$ part of phase space integral

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

⇒ constant energy surface is ~~a sphere~~ the surface of a sphere in 3N dimensional momentum space given by the coordinates $\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N$. Radius of this sphere is $\sqrt{2mE}$.



From appendix C of Pathria, the area of the surface of a sphere, of radius r, in n-dimensional space is

$$A_n(r) = \frac{2\pi^{n/2}\, r^{n-1}}{\Gamma(n/2)}$$ (eqn C.7b

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

So the surface of the sphere of constant energy in momentum space has area given by, $n = 3N$, $r = \sqrt{2mE}$

$$\frac{2\pi^{3N/2}\,(2mE)^{\frac{3N-1}{2}}}{\left(\frac{3N}{2}-1\right)!}$$

The width of the shell in momentum space that corresponds to an energy width of Δ is

$$\Delta r = \frac{dr}{dE}\,\Delta = \frac{m\Delta}{\sqrt{2mE}}$$

~~putting the~~

putting the pieces together we get for the number of states

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

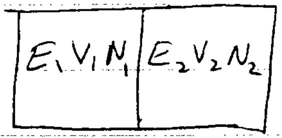
$$= \frac{V^N}{h^{3N}}\,\frac{2\,(2\pi mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}\,\frac{(2mE)^{-1/2}}{(2mE)^{1/2}}\,m\Delta$$

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

Note: for large N, $\Omega(E)$ is a very rapidly increasing function of E! $\sim E^{3N/2}$

We now argue that Ω is directly related to the entropy of the system.

Consider two subsystems separated by a wall



$E_T = E_1 + E_2$

$\Omega_1(E_1)$ is number of states of system 1 with energy between E_1 and $E_1+\Delta$

$\Omega_2(E_2)$ is number of states of system 2 with energy between E_2 and $E_2+\Delta$

$\Omega_T = \Omega_1(E_1)\,\Omega_2(E_2)$ are the number of states of the combined system

Now if the wall is made thermally conducting, so that energy may be exchanged between the two systems, what will determine the equilibrium values of E_1 and E_2

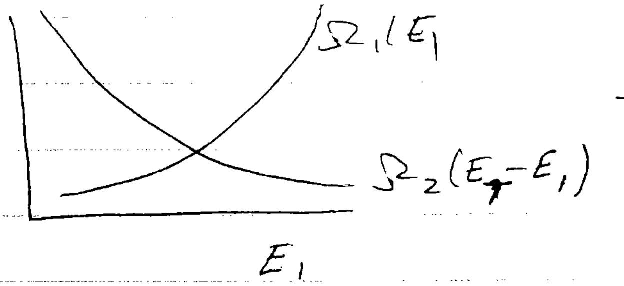
$$\underset{\uparrow}{\Omega_T}(E_T;E_1) = \Omega_1(E_1)\,\Omega_2(E_T-E_1) \qquad \text{since } E_2 = E_T - E_1$$

number of states for total energy E_T and system 1 with E_1

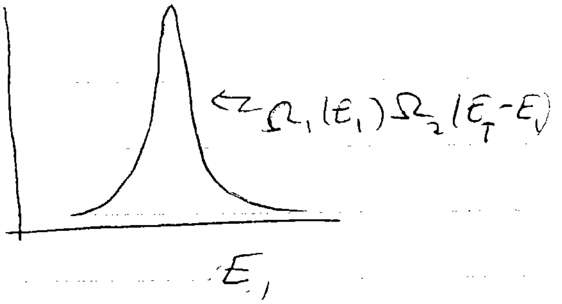
Since any value of $E_1 < E_T$ is allowed, we have

$$\Omega_T(E_T) = \int_0^{E_T} dE_1\, \Omega_1(E_1)\,\Omega_2(E_T-E_1)$$

Now $\Omega_1(E_1)$ and $\Omega(E_2)$ are both very rapidly increasing functions of energy. $\Rightarrow \Omega_2(E_T - E_1)$ is a rapidly decreasing function of E_1



$\Rightarrow$



$\Rightarrow \Omega_T(E_T; E_1) = \Omega_1(E_1)\Omega_2(E_T - E_1)$ is strongly peaked at some particular E_1

Now since, in the absence of any other information, we assume that all states with total energy E_T are equally likely, and $\Omega(E_T; E_1)$ gives the number of states where system 1 has energy E_1, we see that in equilib the most likely value of E_1 will be where $\Omega(E_T; E_1)$ has its strong peak, ie at the max of $\Omega(E_T; E_1)$. This is given by

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

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

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

$$\Rightarrow \quad \frac{\partial}{\partial E_1} \ln[\Omega_1(E_1)] = \frac{\partial}{\partial E_2} \ln[\Omega_2(E_2)] \qquad E_2 = E_T - E_1$$

But from thermodynamics we know equilib will occur when $\frac{1}{T_1} = \frac{1}{T_2}$, where $\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1}$ and $\frac{1}{T_2} = \frac{\partial S_2}{\partial E_2}$

Therefore, following Boltzmann, we can identify

$$S \propto \ln \Omega$$

Since the relation between thermodynamics & mechanics should be fundamental, Boltzmann postulated that the proportionality constant in the above should be a universal number k_B - Boltzmanns Constant

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

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

Ideal gas

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

for large N, use Stirling formular $\ln N! = N\ln N - N$

$$S(E,V,N) = k_B \ln \Omega$$

$$= k_B \left\{ N \ln\left[\frac{V}{h^3}(2\pi m E)^{3/2} \right] - \left(\tfrac{3N}{2}-1\right)\ln\left(\tfrac{3N}{2}-1\right) + \left(\tfrac{3N}{2}-1\right) + \ln(\Delta/E) \right\}$$

$$\cong k_B \left\{ N \ln\left[\frac{V}{h^3}\frac{(2\pi m E)^{3/2}}{\left(\frac{3N}{2}\right)^{3/2}} \right] + \ln\left(\tfrac{3N}{2}\right) + \tfrac{3N}{2} - 1 + \ln(\Delta/E) \right\}$$

$$\simeq N\left\{ \frac{3}{2}k_B + k_B \ln\left[\frac{V}{h^3}\left(\frac{4}{3}\pi m \frac{E}{N}\right)^{3/2} \right] \right\}$$

where the remaining terms $\ln\left(\frac{3N}{2}\right) - 1 + \ln(\Delta/E)$ are all negligible compared to the above as $N \to \infty$ (recall we took $\frac{E}{N} < \Delta \ll E$, so $-\ln N \le \ln\frac{\Delta}{E} \le 0$ is small compared to the terms $\propto N$)

$$\boxed{S(E,V,N) = N\left\{ \frac{3}{2}k_B + k_B \ln\left[\frac{V}{h^3}\left(\frac{4}{3}\pi m \frac{E}{N}\right)^{3/2} \right] \right\}}$$

note, our result does not depend on Δ as we desired.

with the above, we recover the expected

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{\partial}{\partial E}\left(N k_B \frac{3}{2} \ln E\right) = \frac{3}{2} N k_B \frac{1}{E}$$

$$\Rightarrow \quad E = \frac{3}{2} N k_B T$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{\partial}{\partial V}\left(N k_B \ln V\right) = N k_B \frac{1}{V}$$

$$\Rightarrow \quad pV = N k_B T$$

so far so good!

But there is a problem – S above is <u>not</u> extensive. If we take $E \to 2E$, $V \to 2V$, $N \to 2N$, we do <u>not</u> get $S \to 2S$.

(1) $$S(E,V,N) = \frac{3}{2} k_B N + k_B N \ln\left[\frac{V}{h^3}\left(\frac{4}{3}\pi m \frac{E}{N}\right)^{3/2}\right]$$

the $\ln V$ term in above spoils the desired extensivity

Compare the above to our earlier result for the ideal gas, obtained from combining $pV = N k_B T$ and $E = \frac{3}{2} N k_B T$ with the Gibbs-Duhem relation

(2) $$S(E,V,N) = \frac{N}{N_0} S_0 + k_B N \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{E}{E_0}\right)^{3/2}\left(\frac{N}{N_0}\right)^{-5/2}\right]$$

this version is extensive – it scales proportionate to N. here V_0, E_0, N_0 constants. ⌐ we have an extra factor N^{-1} in the log

Note: The Gibbs-Duhem relation was derived assuming S was extensive. Hence it should not be surprising that our expression (2) for S is extensive.

What is the physical reason why the expression (1) fails to be extensive?