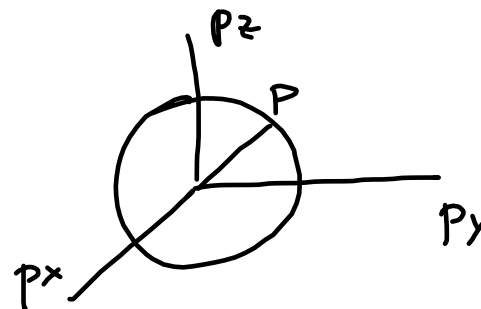


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Density of states:

Single particle in a volume $V=L^3$ with
 $p \leq P$ (momentum)

$$\sum_{\substack{\sigma \\ \# \text{ of states} \\ \text{allowed}}} \Omega(p) \sim \frac{1}{h^3} \int_{p \leq P} d^3q d^3p =$$



$$= \frac{V}{h^3} \frac{4}{3} \pi P^3 \quad \text{this is } \Omega(p) \text{ for } p \leq P.$$

$$\underline{g(p)} dp \cong \frac{\Delta N}{\Delta p} dp \equiv \frac{d\Omega(p)}{dp} dp = \frac{2}{h^3} V \frac{4}{3} \pi p^2 dp = \frac{4\pi V p^2}{h^3} dp$$

of states with
 momentum between p and $p+dp$

$g(p)$ is the density of states.

We see that $g(p) \propto p^2$.

In terms of $E = \frac{p^2}{2m}$ replacing in ① $p^2 = 2mE$

$$\Sigma(E) = \frac{V}{h^3} \frac{4\pi}{3} (2mE)^{3/2}$$

$$a(E) dE = \frac{\partial \Sigma(E)}{\partial E} dE = \frac{3}{2} \frac{V}{h^3} \frac{4\pi}{3} (2m)^{3/2} E^{1/2} dE$$

$$a(E) \propto E^{1/2}$$

↳ density of states.

Finding ω_0 :

1D simple harmonic oscillator.

$$H(q, p) = \frac{1}{2} k q^2 + \frac{p^2}{2m}$$

$$m \ddot{q} = -kq$$

$$q = A \cos(\omega t + \phi) \quad (1) \quad p = m \dot{q} = -m\omega A \sin(\omega t + \phi) \quad (2)$$

$$\omega = \sqrt{\frac{k}{m}} \Rightarrow H(q, p) = \frac{1}{2} \omega^2 m q^2 + \frac{p^2}{2m}$$

$$E = V + T = \frac{1}{2} \omega^2 m A^2 \cos^2(\omega t + \phi) + \frac{m^2 \omega^2 A^2 \sin^2(\omega t + \phi)}{2m}$$

①+②

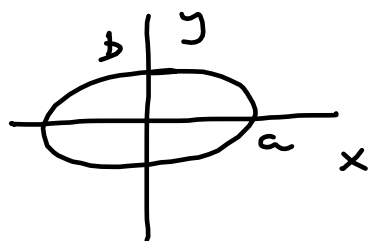
$$= \frac{1}{2} m \omega^2 A^2 \quad \text{constant of motion.}$$

Notice that

$$\underbrace{\frac{1}{2} m \omega^2 q^2}_V + \underbrace{\frac{p^2}{2m}}_T = \underbrace{\frac{1}{2} \omega^2 m A^2}_E$$

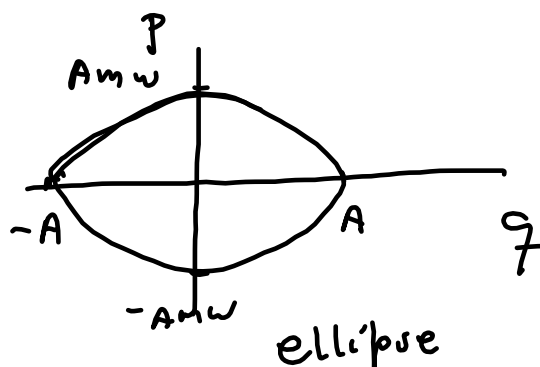
Dividing by E :

$$\frac{q^2}{A^2} + \frac{p^2}{A^2 m^2 \omega^2} = 1$$



$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$$

$$A = \pi a b$$



In terms of
 E :

$$\frac{q^2}{2E/m\omega^2} + \frac{p^2}{2Em} = 1$$

Area of ellipse:

$$A = \pi \sqrt{\frac{2E}{m\omega^2}} \sqrt{2Em} = \pi \frac{2E}{\omega}$$

Now in order to find the number of states for an oscillator with energy $E - \frac{\Delta}{2} \leq E \leq E + \frac{\Delta}{2}$ we need to find the area between the ellipses defined by $E + \frac{\Delta}{2}$ and $E - \frac{\Delta}{2}$.

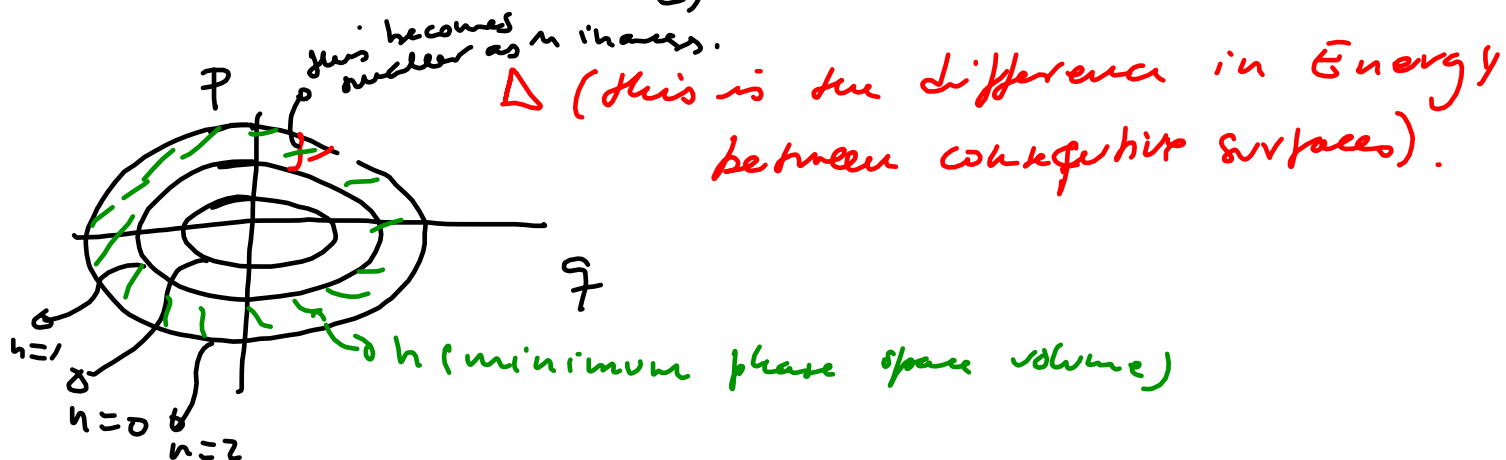
$$W = \int \dots \int dq dp = \frac{2\pi}{\omega} (E + \frac{\Delta}{2}) - \frac{2\pi}{\omega} (E - \frac{\Delta}{2}) =$$

Volume $E - \frac{1}{2}\Delta \leq E \leq E + \frac{1}{2}\Delta$

$$= \frac{2\pi}{\omega} \Delta$$

Now we need to find ω : 1) quantum mechanics
2) arbitrary small volume in phase space.

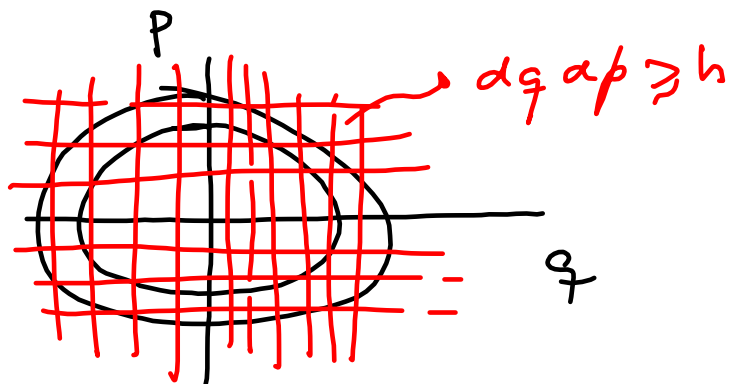
$$1) \text{ Q.M. } E_n = (n + \frac{1}{2}) \hbar \omega \quad n = 0, 1, 2, \dots$$



$$\begin{aligned}
 \text{Area between trajectories: } \frac{2\pi}{\omega} (E_{n+1} - E_n) &= \frac{2\pi}{\omega} \hbar \omega = \\
 &= 2\pi \frac{h}{2\pi} = h
 \end{aligned}$$

2) classically

$$n \text{ very large} \quad \Delta E \gg 2\pi \hbar$$



If $E \gg \Delta \gg \hbar \omega$ the # of eigenstates per

$$\Delta E \approx \frac{\Delta}{\hbar \omega}$$

$\hbar \omega \rightarrow$ eigenstate separation

$\Delta \rightarrow$ Area between the ellipses

$$\therefore \omega_0 = \frac{\frac{2\pi\Delta}{\omega}}{\frac{\Delta}{\hbar \omega}} = \frac{2\pi\Delta}{\omega \Delta} \hbar \omega = \hbar$$

ω_0
area per
eigenstate

\rightarrow # of states in ΔE

Now for N harmonic oscillators phase space has $2N$ dimensions.

$$\omega_0 = h^N \quad \text{consistent with} \quad \omega_0 = h^N \quad N = \# \text{ of degrees of freedom.}$$

Quantum States and phase space:

h defines a minimum volume due to the uncertainty principle.

q and p cannot be specified without uncertainty

$(\Delta q \Delta p)_{\min} \sim h$ best possible determination in phase space.

In general any pair of conjugate variables defines a phase space.

Liouville's theorem and entropy:

We know that $S = k \ln \Gamma$ (Boltzmann's)
 Γ # of accessible microstates.

But we showed that

$$\Gamma = \frac{\omega}{\omega_0}$$

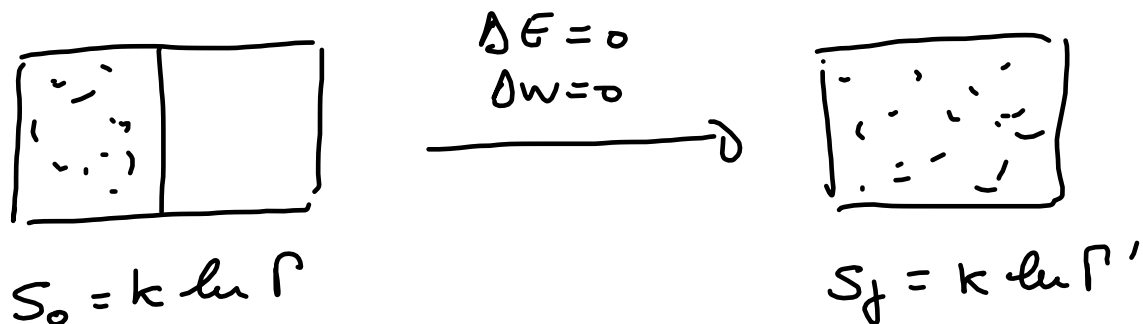
ω allowed volume in phase space
 ω_0 unit of volume. (Gibbs)

works in reversible processes or at equilibrium
 when $\Delta S = 0$ since $\omega = \text{constant}$ due to

Liouville's theorem,

What happens in an irreversible process?

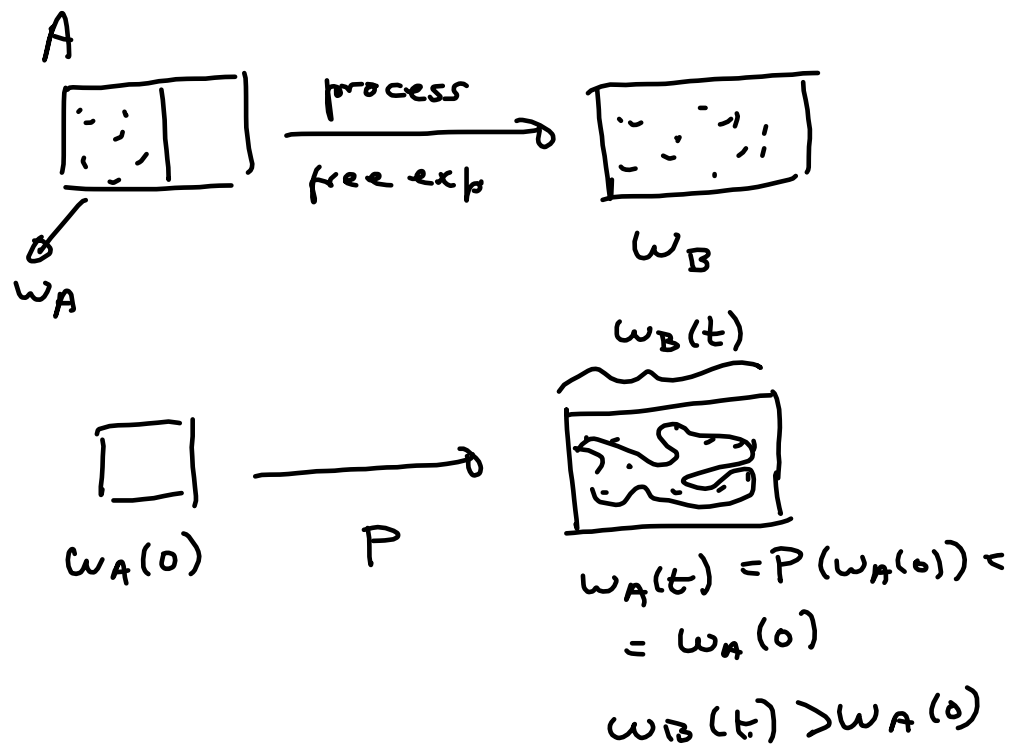
Free expansion:



We know that $S_f > S_0$ because for free reversible process (isothermal expansion of a gas)

$$\Delta S = Nk \ln \left(\frac{V'}{V} \right) = Nk \ln 2 \quad \text{if } V' = 2V.$$

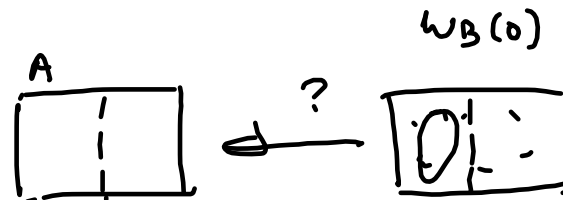
Then for free expansion $S_f > S_0$ but $w(f) = w(i)$.



Liouville tells us that

$$S_A \leq S_B$$

Why the process cannot occur in reverse?



In this case we would have to know the states in B that were from A, but we do not have that information.

Canonical Ensembles:

We obtained the microcanonical formalism in which:

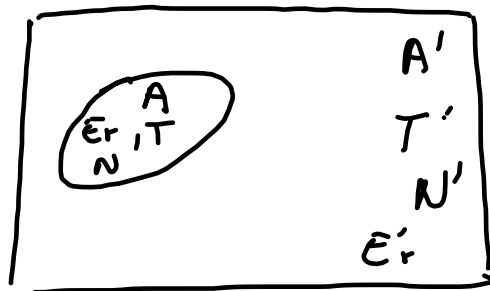
- E is fixed (unrealistic since is easier to fix T than E)
- We need to find $\Omega(E, N, V)$ (very hard to obtain).
- Then $S = k \ln \Omega$ gives all thermodynamics.

We would like to develop a way of predicting thermodynamical properties when we know (N, V, T) for a system.

There are 2 ways of solving this problem:

- 1) consider a system + a heat reservoir that controls the temperature. Study the statistics of the energy exchange between system and source.
- 2) Consider the system as a member of an ensemble with (N, V, T) in which a total energy $E = N\bar{E}$ is shared among the N copies of the system that form the ensemble and study the distribution of E among the energies E_i allowed to the system. (\bar{E} is the average energy of the ensemble)

1)



$$A' \gg A$$

in equilibrium $T = T'$

$$A^{(0)} = A + A'$$

isolated system
with $\bar{E} = E^{(0)}$
constant.

$$\bar{E}^{(0)} = \bar{E}_r + \bar{E}_r'$$

$$N^{(0)} = N + N'$$

Notice that

$$\bar{E}_r \ll \bar{E}^{(0)} \quad \text{because} \quad A \ll A'$$

$$\therefore \frac{\bar{E}_r}{\bar{E}^{(0)}} = \frac{\bar{E}^{(0)} - \bar{E}_r'}{\bar{E}^{(0)}} = 1 - \frac{\bar{E}_r'}{\bar{E}^{(0)}} \ll 1$$

If we specify the state of A as being \bar{E}_r then A' will have to be in any state of the $\Omega'(\bar{E}'_r)$ compatible with \bar{E}_r .

The larger $\Omega'(\bar{E}'_r)$ the most likely that A' will have \bar{E}'_r and correspondingly the most likely A will have energy \bar{E}_r . Then,

$$P_r \propto \Omega'(\bar{E}'_r) \equiv \Omega'(E^{(0)} - \bar{E}_r)$$

\Rightarrow probability of A having $E = \bar{E}_r$.

We will expand $\Omega'(E^{(0)} - \bar{E}_r)$ about $\bar{E}'_r = E^{(0)}$
 since A' has most of $E^{(0)}$ as \bar{E}_r about
 to zero.