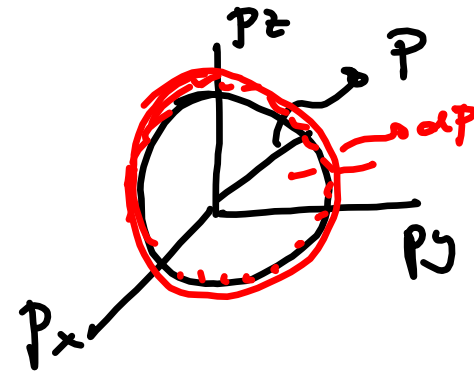


$$9/6 \quad \vec{p} = (p_x, p_y)$$

Single free particle in volume V (with $p \leq P$)

$$E = \frac{p^2}{2m}$$



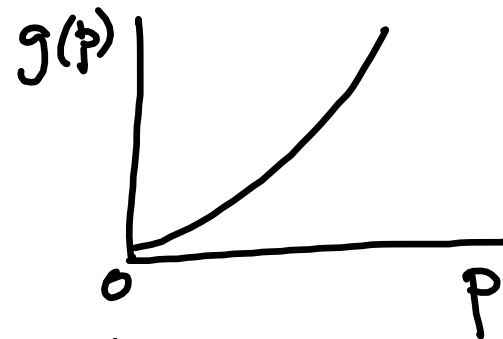
$$\Sigma(P) \approx \frac{1}{h^3} \int_{p \leq P} \dots \int d^3q d^3p =$$

$$= \frac{V}{h^3} \frac{4}{3} \pi P^3 \quad \# \text{ of available microstates.}$$

Let's find $g(p) dp$: the # of microstates with momentum in the interval $p - p + dp$.

$$g(p) dp = \frac{d\Sigma(p)}{dp} dp \approx \frac{V 4\pi p^2}{h^3} dp$$

density of states
 density of states

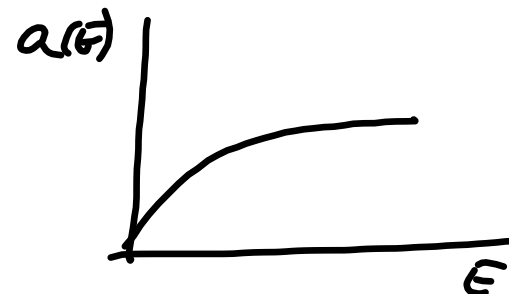


Also as a function of E we can find $a(E)$ (density of states as a function of E):

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

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

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



1D Simple Harmonic oscillator:

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

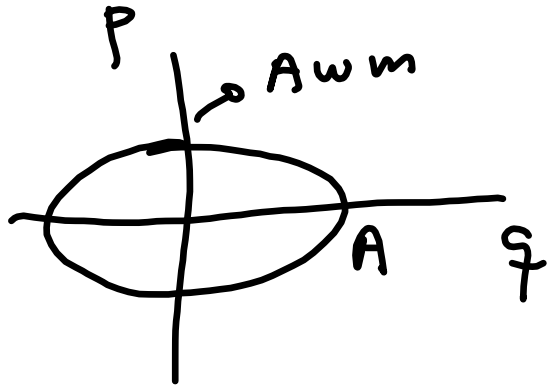
$$m \ddot{q} = -kq \Rightarrow q = A \cos(\omega t + \phi)$$

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

$$E = \frac{1}{2} m \omega^2 q^2 + \frac{p^2}{2m} = \frac{1}{2} \omega^2 m A^2 = \text{constant} \quad \omega = \sqrt{\frac{k}{m}}$$

To obtain the constant \bar{E} surface in phase space (q, p) divide ① by $\frac{1}{2} m \omega^2 A$:

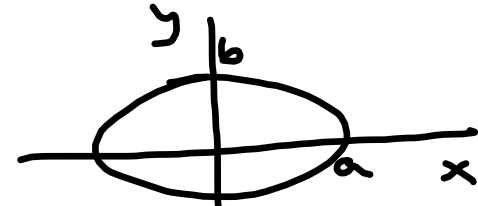
$$\frac{q^2}{A^2} + \frac{p^2}{A^2 \omega^2 m^2} = 1$$



$$\text{Area} = A^2 \omega m \pi$$

$$\text{In terms of } \bar{E} = \frac{1}{2} m \omega^2 A^2 \Rightarrow$$

$$\boxed{\text{Area} = \frac{2\bar{E}}{m\omega^2} \omega m \pi = 2\bar{E}\pi/\omega}$$



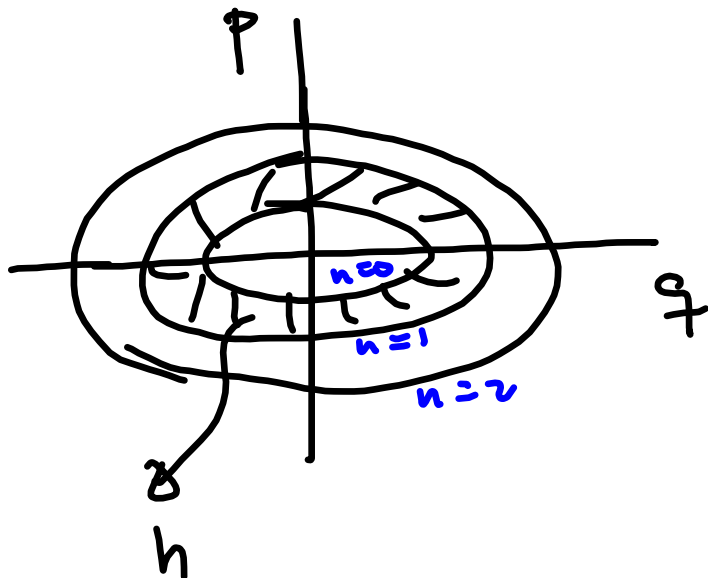
$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$$

$$\text{Area} = \pi a b$$

If we know that the oscillator has energy in the interval $(E - \frac{\Delta}{2}, E + \frac{\Delta}{2})$ then the accessible volume in phase space is

$$\begin{aligned}
 \omega &= \int_{\dots} \int dq dp = \frac{2\pi}{\omega} (E + \frac{\Delta}{2}) - \frac{2\pi}{\omega} (E - \frac{\Delta}{2}) = \\
 E - \frac{1}{2}\Delta &\leq H(p, q) \leq E + \frac{1}{2}\Delta &= \boxed{\frac{2\pi\Delta}{\omega}} &\text{classical}
 \end{aligned}$$

For a quantum mechanical oscillator we know that $E_n = (n + \frac{1}{2}) \hbar \omega \quad n = 0, 1, \dots$



$$\Delta = E_{n+1} - E_n = \hbar \omega$$

Area between 2 consecutive levels is

$$\frac{2\pi}{\omega} (E_{n+1} - E_n) = \frac{2\pi}{\omega} \hbar \omega = h$$

If $E \gg \Delta \gg \hbar \omega$ then the number of classical eigenstates per ΔE is approximately $\frac{\Delta}{\hbar \omega}$ (classical uncertainty in E)

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

volume of ω_0 in phase space \rightarrow quantum separations

For N harmonic oscillators $\omega_0 = h^N$
 (consistent with $\omega_0 = h^N$)

$$h \cong \Delta p_i \Delta q_i$$

Quantum states and phase space:

h defines a minimum volume due to the uncertainty principle.

q and p cannot be specified without uncertainty: $\Delta q \Delta p \Big|_{\min} \sim h$

\therefore for $2N$ dimensions in phase space the minimum volume is h^N .

Liouville's theorem and entropy:

We know that $S = k \ln \Gamma$ (Boltzmann)

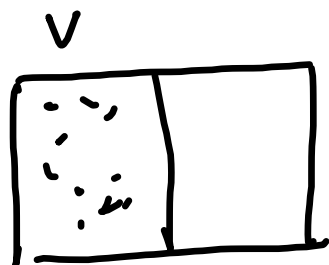
Γ \rightarrow # of accessible microstates.

We also found that $\Gamma = \frac{\omega}{\omega_0}$ \rightarrow allowed volume
 ω_0 \rightarrow unit cell volume.

$\therefore S = k \ln (\omega/\omega_0)$ (Gibbs)

What happens with S_B and S_G in an irreversible process?

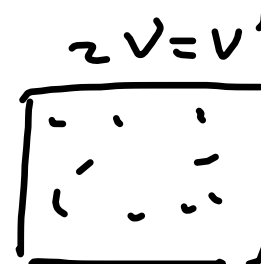
Consider the free expansion of a gas:



$$S_0 = k \ln \Gamma$$

$$\Delta E = 0$$

$$\Delta W = 0$$

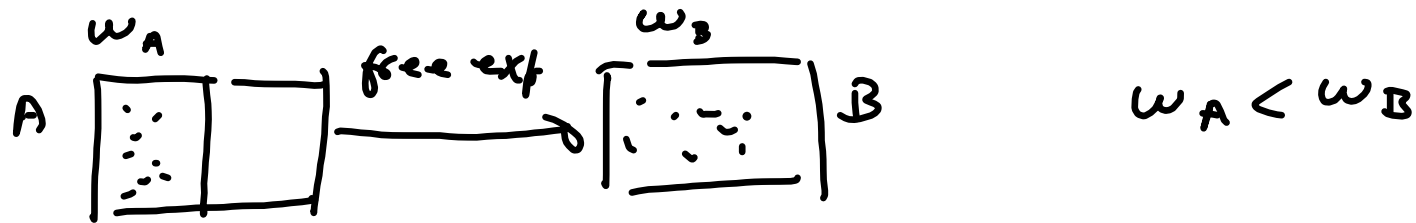


$$S_f = k \ln \Gamma'$$

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

\Rightarrow if $V' = 2V$
 (use any reversible
 process because
 S is a state
 function)

But what happens with Liouville's theorem?



Liouville forces $S(A) \leq S(B)$
 because if we start with system B Liouville prevents going to A because $\omega(B) > \omega(A)$
 we only could do it if in B we knew the fraction of states that came from A. But we do not know it. In the free expansion we look in formation about the system.

Increase in entropy means decrease in available information (we will come back to this later).

Use Boltzmann's expression always.
Use Gibbs for reversible processes.

Ch. 3: Canonical Ensemble.

From $\Omega(N, V, E)$ or $\Gamma(N, V, E; D)$ we can obtain S and all thermodynamical properties.

But it is very hard to control E in the lab.

It is much easier to control T . So

we want to find a formulation in which

T , N and V are the parameters and

E would be obtained as a thermodynamic average $E \rightarrow \langle E \rangle$.

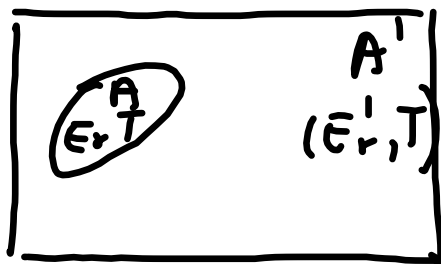
We want to construct a formalism in which E can range from 0 to ∞ and we need to determine the probability that the system will have a certain energy E_r . That probability will be called P_r .

Two ways of finding E :

- 1) System + reservoir in equilibrium at temp. T . Study the statistic of the energy exchange.
- 2) Consider the system as a member of an ensemble with (N, V, T) in which energy

Σ is shared by N copies of the system and study the distribution of \mathcal{E} among the possible \mathcal{E}_r states.

1) System in equilibrium with a reservoir:



$$T = T' \text{ (equilibrium)}$$

$$N \text{ and } N' \text{ are fixed}$$

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

$$A' \gg A$$

$A' + A = A^{(0)}$ isolated system with equal probability of being in any of its accessible states.

If we specified the energy of A as E_r
 we know that A' has energy $E_r' = E^{(0)} - E_r$.

Since $E_r + E_r' = E^{(0)}$

Notice that $E_r \ll E^{(0)}$ because $A' \gg A$.

Then

$$\frac{E_r}{E^{(0)}} = \frac{E^{(0)} - E_r'}{E^{(0)}} = 1 - \frac{E_r'}{E^{(0)}} \ll 1.$$

The probability of E_r for A will be maximum
 when A' is in a state E_r' with maximum
 $\Omega'(E_r')$.

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

Let's expand $\Omega'(E'_r)$ about $E'_r \equiv E^{(0)}$:

Consider $\ln \Omega'$:

$$\ln \Omega'(E'_r) = \underbrace{\ln \Omega'(E^{(0)})}_{\text{constant}} + \underbrace{\frac{\partial \ln \Omega'}{\partial E'}}_{\beta'} \Big|_{E'=E^{(0)}} (-E_r) + \dots$$

$$= C - \beta' E_r \equiv C - \beta E_r =$$

$$= C - \frac{1}{kT} E_r$$

$$\therefore P_r \propto e^{-\beta E_r}$$

because $\beta = \beta'$
at equilibrium.

But $0 \leq P_r \leq 1$ because P_r is a probability

Then
$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

Canonical probability distribution.

(all possible states of A)

2 - Ensemble approach:

N systems $(1, 2, \dots, N)$ sharing energy E .

All systems have the same number of particles

N is fixed.

E_r $r = 0, 1, \dots$ are the energy levels of the systems.

n_r : # of systems in the ensemble with energy E_r at a given time t .

$\{n_r\}$ is a "distribution" that satisfies:

$$\textcircled{1} \left\{ \begin{array}{l} \sum_r n_r = N \\ \sum_r n_r E_r = \Sigma = N U \end{array} \right. \quad r: 0, 1, \dots \text{ (energy levels)}$$

→ average energy for the ensemble.