

Time Average:

$$\bar{X} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} X(s) ds$$

$$\bar{X} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} X(s) ds$$

$X(t)$

First postulate of Statistical Mechanics:

$$\bar{X} = \langle X \rangle$$

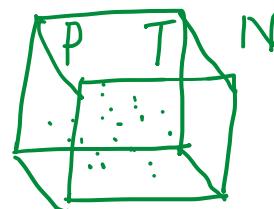
Time average = Ensemble average

Ensemble Average:

$$\langle X \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N p_i x_i$$

Macrostate of a System:

M ( $N, P, T$ )  
 ↓  
 Macrostate State  
 Variables

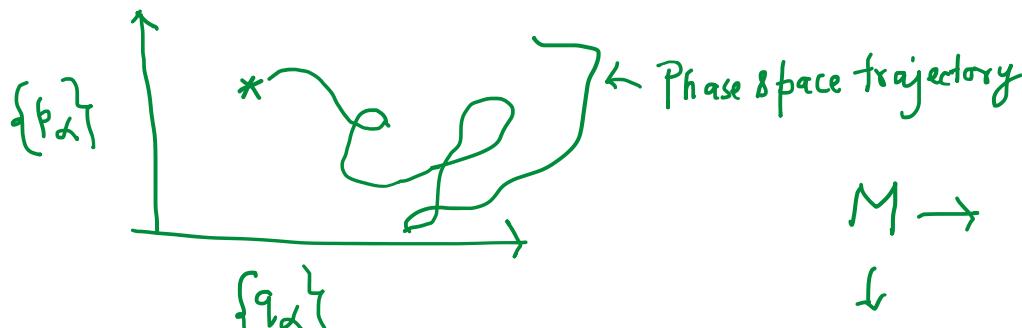
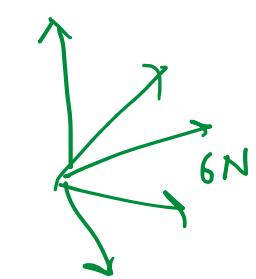


Phase Space  $\sim 6N$  dimensional space

Microstate  $\rightarrow$  position and the momentum co-ordinates of all the constituents

$$\frac{3N \rightarrow \text{position}}{3N \rightarrow \text{momenta}} = \frac{6N}{6N}$$

$$\sim 10^{24}$$



$M \rightarrow 1$  microstate

another copy of  $M \rightarrow 1$  microstate



An ensemble

$\dots dV$   
such macro states

$N_M$  no. of macrostates  $\sim N_M$  no. of microstates  
(mental copies of)

$\sqrt{N^0} \rightarrow$  No. of microstates

$\rightarrow 3N$  momenta co-ordinates

$P(\underline{P}, \underline{q}) \rightarrow 3N$  position co-ordinates

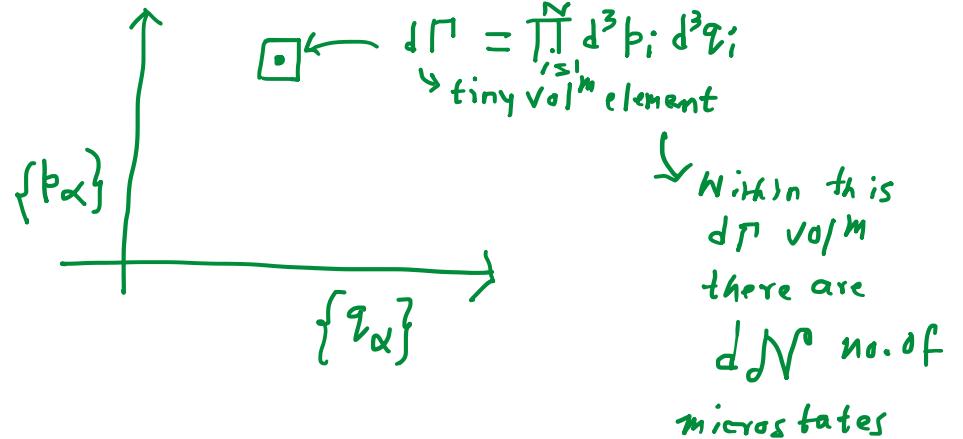
$\underline{P} = P_1, P_2, \dots$   
 $\underline{q} = q_1, q_2, \dots$

Gibbs Ensemble  $\rightarrow$

Ensemble density

$$P(\underline{p}, \underline{q}) = \frac{dN^{\alpha}}{N^{\alpha} d\Gamma}$$

Lim  
 $N \rightarrow \infty$



$$\int P(\underline{p}, \underline{q}) d\Gamma = \frac{dN}{N} = \frac{N}{N} = 1$$

Probability / density  $f^n$

How this prob. density  $f^n$  evolve in time?

ensemble density

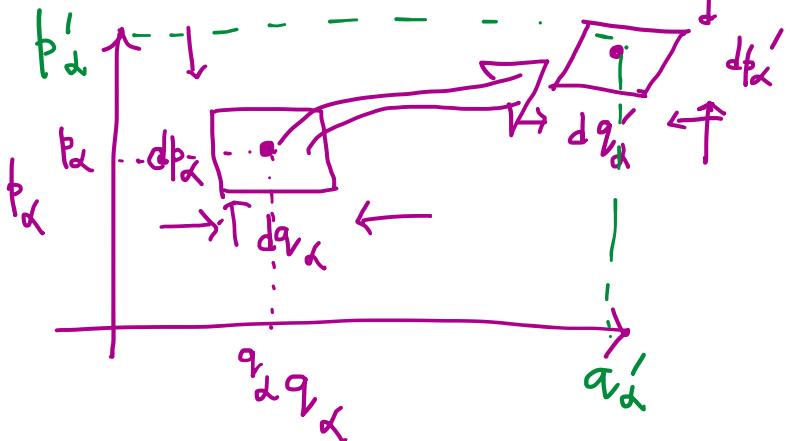
$$\langle X \rangle = \int x P(x) dx$$

$$\langle O(\underline{p}, \underline{q}) \rangle = \int O(\underline{p}, \underline{q}) P(\underline{p}, \underline{q}, t) d\Gamma$$

↓  
Ensemble average

in general it depends on time

Time evolution of  $p(\underline{p}, \underline{q}, t)$  is given by "Liouville's theorem"



$$dq'_\alpha = dq_\alpha + \left( \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} \right) dq_\alpha dt + O(\dots)$$

Derivative of  
the velocity with  
respect to the separation  
multiplied by the separation

$$dp'_\alpha = df_\alpha + \left( \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right) dp_\alpha dt + O(\dots)$$

$d\Pi$  (at time  $t$ )

$d\Pi'$  (at time  $t+dt$ )

→ Distorted

$$\begin{aligned} q'_\alpha &= q_\alpha + \dot{q}_\alpha dt + O(dt^2) \\ p'_\alpha &= p_\alpha + \dot{p}_\alpha dt + O(dt^2) \end{aligned}$$

$$d\Pi = df_\alpha dq_\alpha$$

$$d\Pi' = df'_\alpha dq'_\alpha$$

$$\begin{aligned} d\Pi' &= df_\alpha dq_\alpha \left[ 1 + \left( \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} \right) \right. \\ &\quad \left. + \left( \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right) dt \right] \\ &\quad + O(\dots) \end{aligned}$$

$$d\Gamma' = \underbrace{dp_\alpha dq_\alpha}_{d\Gamma} \left[ 1 + \left\{ \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right\} dt + O(dt^2) \right]$$

$$d\Gamma = \prod_i d\vec{p}_i d\vec{q}_i$$

Hamilton's equation of motion

$$\frac{\partial H}{\partial p_\alpha} = \dot{q}_\alpha \quad \frac{\partial H}{\partial q_\alpha} = -\dot{p}_\alpha$$

$$d\Gamma' = d\Gamma \left[ 1 + \left( \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha} - \frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha} \right) dt \right]$$

Phase Space volume is conserved Under Hamiltonian dynamics

$$\prod_\alpha dp_\alpha dq_\alpha = \prod_\alpha dp'_\alpha dq'_\alpha$$

~ Density does not change ~ Incompressible fluid

$$\vec{\nabla} \cdot \vec{v} = 0$$

↓ Divergence of velocity field is zero.

$$P(\underline{p}', \underline{q}', t + dt) = P(\underline{p}, \underline{q}, t)$$

$$\rightarrow P(\underline{p}', \underline{q}', t + dt) = P(\underline{p} + \dot{\underline{p}} \cdot dt, \underline{q} + \dot{\underline{q}} dt, t + dt)$$

$$= P(\underline{p}, \underline{q}, t) + \left[ \sum_{\alpha} \left( \dot{p}_{\alpha} \frac{\partial p}{\partial p_{\alpha}} + \dot{q}_{\alpha} \frac{\partial p}{\partial q_{\alpha}} \right) + \frac{\partial p}{\partial t} \right] dt$$

Recall

$$\frac{df(\underline{p}, \underline{q}, t)}{dt} = \frac{\partial f}{\partial t} + \sum_{\alpha} \left( \frac{\partial f}{\partial p_{\alpha}} \cdot \dot{p}_{\alpha} + \frac{\partial f}{\partial q_{\alpha}} \cdot \dot{q}_{\alpha} \right)$$

Total derivative  
of the function  $f$

Partial derivative

Streamline derivative

$$\frac{dp}{dt} = 0 \rightarrow \text{Like incompressible fluid}$$

$$\boxed{\frac{\partial p}{\partial t} + \left[ \sum_{\alpha} \left( \dot{p}_{\alpha} \frac{\partial p}{\partial p_{\alpha}} + \dot{q}_{\alpha} \frac{\partial p}{\partial q_{\alpha}} \right) \right] = 0}$$

$$\frac{\partial P}{\partial t} + \sum_{\alpha} \left[ \left( \frac{\partial P}{\partial p_{\alpha}} \right) \dot{p}_{\alpha} + \left( \frac{\partial P}{\partial q_{\alpha}} \right) \dot{q}_{\alpha} \right] = 0$$

$$\{A, B\} = \sum_{\alpha} \left( \frac{\partial A}{\partial q_{\alpha}} \frac{\partial B}{\partial p_{\alpha}} - \frac{\partial B}{\partial q_{\alpha}} \frac{\partial A}{\partial p_{\alpha}} \right)$$

↓ Poisson Bracket

$$\frac{\partial P}{\partial t} + \sum_{\alpha} \left\{ \frac{\partial P}{\partial p_{\alpha}} \left( - \frac{\partial H}{\partial q_{\alpha}} \right) + \left( \frac{\partial P}{\partial q_{\alpha}} \right) \left( \frac{\partial H}{\partial p_{\alpha}} \right) \right\}$$

$$\dot{p}_{\alpha} = - \frac{\partial H}{\partial q_{\alpha}}$$

$$\dot{q}_{\alpha} = \frac{\partial H}{\partial p_{\alpha}}$$

$$\frac{\partial P}{\partial t} + \{P, H\} = 0$$

$$\text{or } \frac{\partial P}{\partial t} = - \{P, H\} = \{H, P\}$$

$$\boxed{\frac{\partial P}{\partial t} = \{H, P\}}$$

Liouville's theorem  
or equation.

What is equilibrium in this perspective?

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}$$

$$\rho = \rho(H)$$

If the phase space density a function of the Hamiltonian

$$\frac{\partial \rho}{\partial t} = 0$$

$\hookrightarrow \rho$  has no explicit time dependence

$$\{\rho, H\} = \{\rho(H), H\}$$

$$= \sum_{\alpha} \left( \left( \frac{\partial \rho}{\partial H} \right)_{\rho'} \frac{\partial H}{\partial q_{\alpha}} \frac{\partial H}{\partial p_{\alpha}} - \left( \frac{\partial \rho}{\partial H} \right)_{\rho'} \frac{\partial H}{\partial p_{\alpha}} \frac{\partial H}{\partial q_{\alpha}} \right)$$

$$= 0$$

$$= \rho' \{H, H\}$$

$$\langle O(\underline{p}, \underline{q}) \rangle = \int d\underline{p} \rho(\underline{p}, \underline{q}, t) O(\underline{p}, \underline{q})$$

time-independent if

$$\rho(\underline{p}, \underline{q}, t) = \rho(\underline{p}, \underline{q}) \equiv \rho(H) \rightarrow \text{is a f'n of } H$$

Definition of equilibrium

$$P_{eq} = P(H)$$

$$L(p_i, q_i)$$

$$\{L, H\} = 0$$

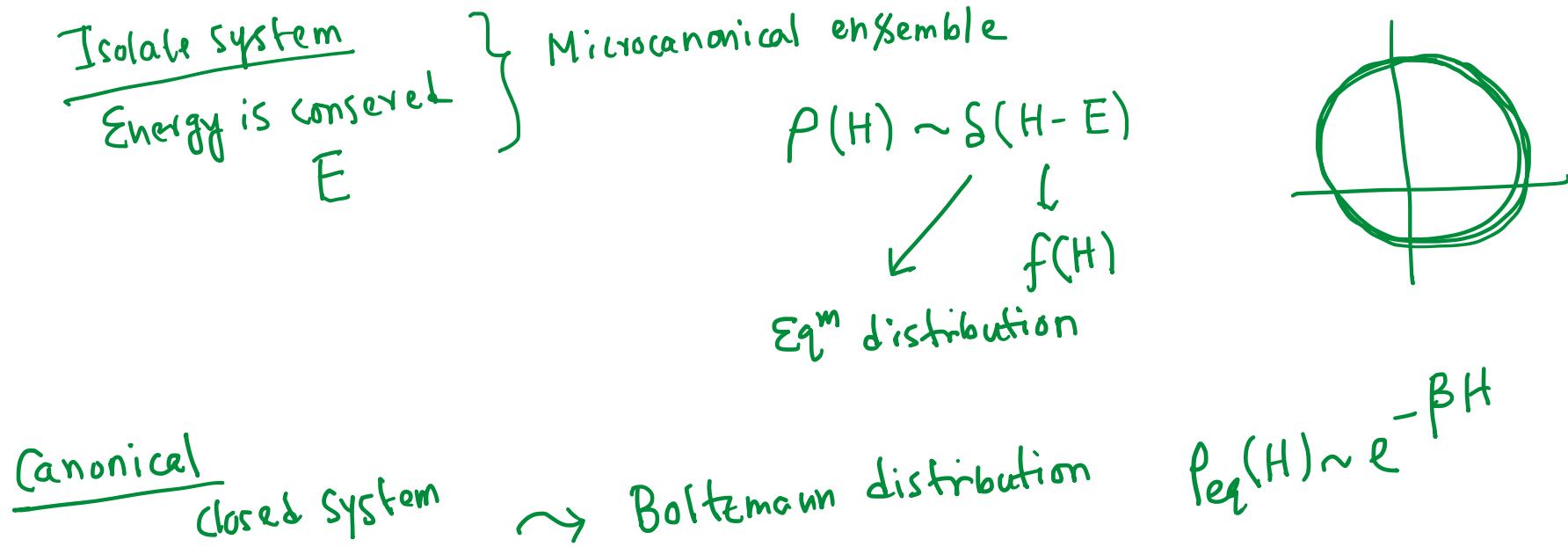
Say for a system  $\downarrow$  Angular momentum  
is also conserved

$$\begin{aligned} \frac{dL(p_i, q_i)}{dt} &= 0 \\ &= \sum_{\alpha} \left( \frac{\partial L}{\partial p_{\alpha}} \dot{p}_{\alpha} + \frac{\partial L}{\partial q_{\alpha}} \dot{q}_{\alpha} \right) \\ &= \sum_{\alpha} \frac{\partial L}{\partial p_{\alpha}} \left( -\frac{\partial H}{\partial q_{\alpha}} \right) + \frac{\partial L}{\partial q_{\alpha}} \frac{\partial H}{\partial p_{\alpha}} \\ &= 0 \end{aligned}$$

$$P_{eq}(H, L)$$

$$P_{eq}(H(p_i, q_i), L(p_i, q_i))$$

$$\begin{aligned} \{P_{eq}, H\} &= P_1' \{H, H\} + P_2' \{L, H\} \\ &= 0 \end{aligned}$$



$$\beta = \frac{1}{k_B T}$$