

Macrostates M are usually described by a small number of state functions, e.g. T, P, N .

A large # of microstates μ correspond to a given macrostate M .

→ Consider ensembles of microstates, many copies of a given macrostate described by different microstates.

$dN(\vec{p}, \vec{q}, t)$ = # microstates in infinitesimal volume
 $d\Gamma = \prod_{i=1}^N d^3p_i d^3q_i$ around pt. (\vec{p}, \vec{q})

If total number of microstates in ensemble is $N \gg 1$, then the phase space density $\rho(\vec{p}, \vec{q}, t)$ is:

$$\rho(\vec{p}, \vec{q}, t) d\Gamma = \lim_{N \rightarrow \infty} \frac{dN(\vec{p}, \vec{q}, t)}{N}$$

$\rho(\vec{p}, \vec{q}, t)$ is normalized as a probability distribution:

$$\int \rho(\vec{p}, \vec{q}, t) d\Gamma = 1$$

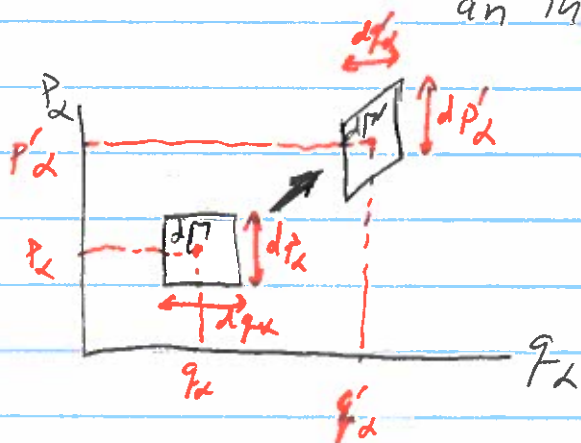
Ensemble average of a function $\theta(\vec{p}, \vec{q})$ is given by

$$\langle \theta \rangle = \int d\Gamma \rho(\vec{p}, \vec{q}, t) \theta(\vec{p}, \vec{q})$$

If $\rho(\vec{p}, \vec{q}, t) = \delta^{3N}(\vec{p} - \vec{p}_0(t)) \delta^{3N}(\vec{q} - \vec{q}_0(t))$ for some exact microstate specified by $\vec{p}_0(t)$ and $\vec{q}_0(t)$, then the system is said to be in a pure state.

Otherwise, the system is in a mixed state.

The time evolution of the phase space density is governed by Liouville's theorem. — $\rho(\Gamma, t)$ behaves like an incompressible fluid.



$$q'_\alpha = q_\alpha + \dot{q}_\alpha dt + \mathcal{O}(dt^2)$$

$$p'_\alpha = p_\alpha + \dot{p}_\alpha dt + \mathcal{O}(dt^2)$$

Due to particle motion, regions of phase space evolve in time. After small time δt :

$$dq'_\alpha = dq_\alpha + \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} dq_\alpha \delta t + \mathcal{O}(\delta t^2)$$

$$dp'_\alpha = dp_\alpha + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} dp_\alpha \delta t + \mathcal{O}(\delta t^2)$$

$$dq'_\alpha \wedge dp'_\alpha \approx dq_\alpha \wedge dp_\alpha \left(1 + \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right) \delta t \right)$$

From Hamilton's eqs,

$$\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} = \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha}$$

$$\frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = -\frac{\partial}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} = -\frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha}$$

$$\Rightarrow dq'_\alpha \wedge dp'_\alpha = dq_\alpha \wedge dp_\alpha$$

$$\Rightarrow d\Gamma' = d\Gamma$$

Hence, all of the pure state is in $d\Gamma'$ or transported to $d\Gamma'$, occupying the same volume in phase space.

$$\rightarrow \rho(p', q', t + \delta t) = \rho(p, q, t)$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{dp_\alpha}{dt} + \frac{\partial \rho}{\partial q_\alpha} \frac{dq_\alpha}{dt} \right) = 0$$

↑ Describes evolution of density along the fluid flow.

We can write this using Hamilton's equations as:

$$\frac{\partial \rho}{\partial t} = \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} \right) = -\{ \rho, H \} = \{ H, \rho \}$$

↑ Poisson bracket.

-Liouville Equation

Consequences of Liouville's Theorem!

1a Time-reversal: $(\vec{p}, \vec{q}, t) \rightarrow (-\vec{p}, \vec{q}, -t)$

$$\{p, H\} \rightarrow -\{p, H\}$$

$$\Rightarrow \rho(\vec{p}, \vec{q}, t) = \rho(-\vec{p}, \vec{q}, -t)$$

Phase space density reverses evolution under time reversal.

2a Time-evolution of ensemble average:

$$\frac{d\langle \theta \rangle}{dt} = \int d\Gamma \frac{\partial \rho(\vec{p}, \vec{q}, t)}{\partial t} \theta(\vec{p}, \vec{q})$$

$$= \sum_{\alpha=1}^{3N} \int d\Gamma \theta(\vec{p}, \vec{q}) \left(\frac{\partial \rho}{\partial p_{\alpha}} \frac{\partial H}{\partial q_{\alpha}} - \frac{\partial \rho}{\partial q_{\alpha}} \frac{\partial H}{\partial p_{\alpha}} \right)$$

$$\stackrel{\text{by part b}}{=} - \sum_{\alpha=1}^{3N} \int d\Gamma \rho(\vec{p}, \vec{q}, t) \left(\frac{\partial \theta}{\partial p_{\alpha}} \frac{\partial H}{\partial q_{\alpha}} - \frac{\partial \theta}{\partial q_{\alpha}} \frac{\partial H}{\partial p_{\alpha}} \right)$$

$$= - \int d\Gamma \{H, \theta\}$$

$$= \langle \{\theta, H\} \rangle$$

3. In equilibrium $\frac{\partial \rho_{eq}}{\partial t} = 0$.

$$\rightarrow \boxed{\{\rho_{eq}, H\} = 0}$$

One solution is $\rho_{eq}(\vec{p}, \vec{q}) = \rho_{eq}(H(\vec{p}, \vec{q}))$ functional of Hamiltonian H .

$$\{\rho(H), H\} = \rho'(H) \{H, H\} = 0.$$

$\Rightarrow \rho$ is constant on surfaces of constant energy H in phase space. — Basic assumption of stat mech.

Microcanonical ensemble: total energy E fixed in an isolated ensemble.

- All members of the ensemble lie on $H(\vec{p}, \vec{q}) = E$
 $\rho = \delta(H - E)$

Equilibrium — uniform density of pts. in ensemble on this surface.

Canonical ensemble: $\rho \propto e^{-\beta H}$

* Similarly, if there are conserved quantities besides the energy, the phase space density is uniform on surfaces of constant conserved quantities, in equilibrium.