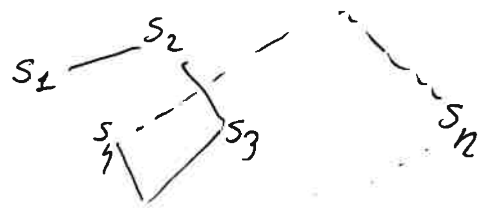
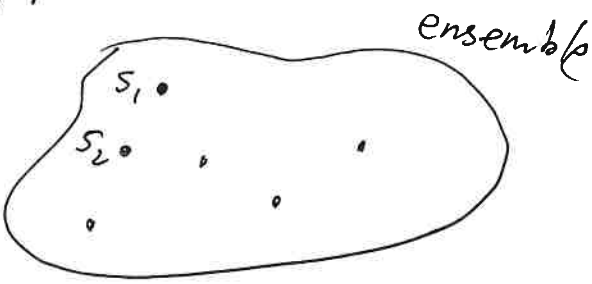
(2) Theory of Ensembles

A macrostate $\{E, V, N\}$ corresponds to a huge set of μ-states of number $\Omega(E, V, N)$.

These states are equally probable.





After long enough time we can assume that the $\boxed{\text{time average} = \text{ensemble average}}$

The Ergodic assumpsion $\langle f(t) \rangle = \langle f \rangle_{\text{ensemble}}$.

This why looking at ensembles is so useful to us

(2.1) Phase space of a classical system

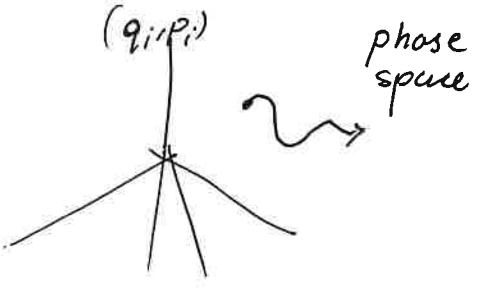
μ-state of a classical system is defined by specifying all positions and momenta of the particles:

$$+\begin{cases} 3N \text{ positions } & q_1, q_2 \cdots q_{3N} \quad (x_i, y_i, z_i) \\ 3N \text{ momenta } & p_1, p_2 \cdots p_{3N} \quad (p_x, p_y, p_z) \end{cases}$$

This set is a point in $\mathbb{R}^{6N} \equiv \boxed{\text{PHASE SPACE}}$

(q_i, p_i)

This point evolves in time

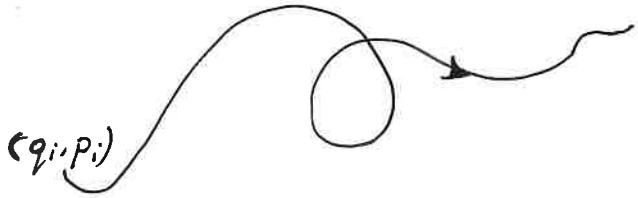


The time evolution is determined by the <u>canonical equations of motion</u> (a.k.a. Hamiton's Eqs.)

$$\left\{ \begin{aligned} \dot{q}_i &= \frac{\partial \mathcal{H}}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial \mathcal{H}}{\partial q_i} \end{aligned} \right\} \quad \begin{array}{l} 6N \text{ equations} \\ i = 1, 2, \ldots 3N \end{array}$$

- The function $\mathcal{H}(q_i, p_i)$ is the <u>Hamiltonian</u>.

  $(\dot{q}_i, \dot{p}_i)$ is the <u>velocity</u> vector in phase space,



example: free particle in gravity

$$\mathcal{H} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz$$

$$\dot{x} = \frac{p_x}{m}; \quad \dot{y} = \frac{p_y}{m}; \quad \dot{z} = \frac{p_z}{m}$$

$$\dot{p}_x = 0; \quad \dot{p}_y = 0; \quad \dot{p}_z = -mg$$

- Usually the trajectory is limited to a finite region in phase space

  $q_i \in V$

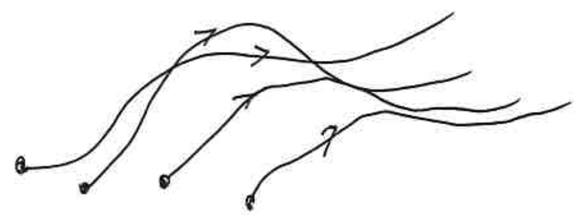
  E limits both p_i, q_i through $\mathcal{H}(p, q)$

- In particular if total energy is conserved

  hypersurface $\boxed{\mathcal{H}(q_i, p_i) = E = \text{const.}}$

  If E is not accurately determined the trajectory is in the hypershell $(E - \frac{\Delta}{2}, E + \frac{\Delta}{2})$.

- The movement of an ensemble of μ-states:



- We can describe the motion by the density function $\rho(q, p, t)$

$$q_i \quad p_i \quad i = 1, \dots 3N$$

$\rho\, d^{3N}p\, d^{3N}q \equiv$ # of systems (points) in $d^{3N}q\, d^{3N}p$

- The density function tells the distribution of μ-states in phase space, as a function of time.

- We can now define the ensemble average of a quantity $f(q,p)$.

$$\langle f \rangle = \frac{\int f(q,p)\,\rho(q,p,t)\, d^{3N}q\, d^{3N}p}{\int \rho(q,p,t)\, d^{3N}q\, d^{3N}p}$$

integration over whole Phase Space

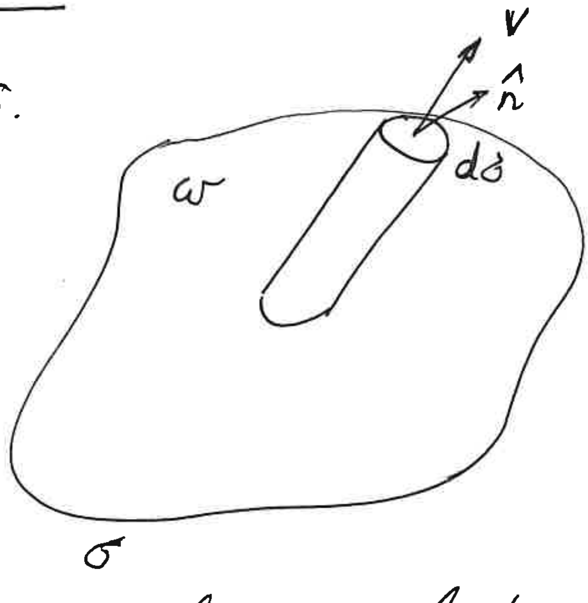
* Note that $\langle f \rangle$ may be a function of time.
* The ensemble is <u>stationary</u> if ρ does not depend on time explicitly $\boxed{\frac{\partial \rho}{\partial t} = 0}$

This implies that $\Rightarrow \frac{\partial \langle f \rangle}{\partial t} = 0$ as well

* Of course, a system at equilibrium is stationary.

Liouville's theorem

Consider a volume $\omega \in$ P.S.
with surface σ



$$\left.\begin{array}{l}\text{rate of}\\ \text{change}\\ \#\text{ systems}\end{array}\right\} = \frac{\partial}{\partial t}\int_\omega \rho \, d\omega$$

where $d\omega = d^{3N}q \, d^{3N}p$

On the other hand, the rate is also equal to the flux through the surface

$$\int_\sigma \rho \, \vec{v} \cdot \hat{n} \, d\sigma \underset{\substack{\text{divergence}\\ \text{theorem}}}{=} \int_\omega \operatorname{div}(\rho \bar{v}) \, d\omega$$

Here, divergence is

$$\operatorname{div}(\rho v) = \sum_{i=1}^{3N} \frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \sum_{i=1}^{3N} \frac{\partial}{\partial p_i}(\rho \dot{p}_i)$$

Since points do not appear/disappear spontaneously

$$\frac{\partial}{\partial t}\int_\omega \rho \, d\omega = -\int \operatorname{div}(\rho \bar{v}) \, d\omega$$

$$\Rightarrow \int_\omega \left[\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \bar{v})\right] d\omega = 0$$

$$\Rightarrow \boxed{\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \bar{v}) = 0}$$

equation of continuity

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \rho\frac{\partial \dot{q}_i}{\partial q_i}\right) + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial p_i}\dot{p}_i + \rho\frac{\partial \dot{p}_i}{\partial p_i}\right) = 0$$

$$\Rightarrow \quad \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) + \rho\sum_{i=1}^{3N}\underbrace{\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right)}_{\equiv 0}$$

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 \mathcal{H}}{\partial p_i\,\partial q_i} \qquad \frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial}{\partial p_i}\left(-\frac{\partial \mathcal{H}}{\partial q_i}\right) = -\frac{\partial^2 \mathcal{H}}{\partial p_i\,\partial q_i}$$

$$\Rightarrow \quad \frac{\partial \rho}{\partial t} + \underbrace{\sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}\right)}_{\text{this is the Poisson bracket } [\rho, \mathcal{H}]}$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\times\dot{q}_i + \frac{\partial \rho}{\partial p_i} * \dot{p}_i\right) = \frac{\partial \rho}{\partial t} + [\rho, \mathcal{H}] = 0$$

Liouville's theorem: The total time derivative of the density vanishes. Or: in a f.o.r. moving with the systems $\rho = \text{const.}$

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* The "fluid" in P.S. is incompressible.
* If $[\rho, \mathcal{H}] = 0$ then also $\frac{\partial \rho}{\partial t} = 0$

Of course if ρ is independent of coordinates $[\rho, \mathcal{H}] = 0$

This corresponds to an ensemble that uniformly distributed over all μ-states at all times.

Then the ensemble average is

$$\langle f \rangle = \frac{1}{\varpi} \int f(q,p)\, d\omega \qquad \text{because } \rho = \rho_0$$

=> any point is equally likely
[postulat of equal prob.]

* Another way to satisfy $\frac{\partial \rho}{\partial t} = 0$ is to have $\rho\left[\mathcal{H}(q,p)\right]$

Then

$$\frac{\partial \rho}{\partial q_i} \underbrace{\frac{\partial \mathcal{H}}{\partial p_i}}_{\frac{\partial q_i}{\partial t}} - \frac{\partial \rho}{\partial p_i} \underbrace{\frac{\partial \mathcal{H}}{\partial q_i}}_{\left(-\frac{\partial p_i}{\partial t}\right)}$$

$$= \frac{\partial \rho}{\partial \mathcal{H}} \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial \mathcal{H}} \frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} = 0$$

For example if $\rho(q,p) \sim e^{-\mathcal{H}(q,p)/T}$ $\quad \frac{\partial \rho}{\partial t} = 0$

(2.3) The microcanonical Ensemble

- Macrostate is defined by (N, V, E).
- Equivalently we can define hypershell $\left[E - \frac{\Delta}{2}, E + \frac{\Delta}{2}\right]$
- Each of the μ-states is equally probable.
- The shell is defined $\quad E - \frac{1}{2}\Delta \leq \mathcal{H}(q,p) \leq E + \frac{1}{2}\Delta$

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* The microcanonical ensemble is a collection of systems with a density function ρ

$$\rho = \begin{cases} \rho(q,p) = \text{const.} & \text{in shell} \\ 0 & \text{outside} \end{cases}$$

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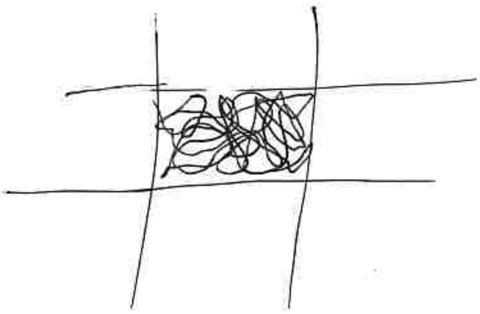
* The ensemble average is stationary $\quad \frac{\partial \langle f \rangle}{\partial t} = 0$

$$\langle f \rangle = \overbrace{\overline{\langle f \rangle}}^{\sim \text{ time average}} \underset{\text{averages are independent}}{=} \langle \bar{f} \rangle \underset{\text{same for all members of ensemble}}{=} \bar{f} = \overbrace{f_{exp}}^{\text{measurement}}$$

Ensemble average of any physical quantity $\langle f \rangle$ is equal to the expected value of measurement f_{exp}

Ergodic theorem (Boltzmann): After long enough time, A μ-state will pass through all states in the relevant phase space



We want to connect between the mechanics of μ-states and the TD of the macrostate

We know that $\Gamma \propto \omega$

Γ: # of states; ω: volume of hypershell

We need to find the fundamental volume ω_0 of 1 μ-state

Then $(\Omega =)\ \Gamma = \dfrac{\omega}{\omega_0} \Rightarrow S = \ln \Gamma = \ln\left(\dfrac{\omega}{\omega_0}\right)$ etc.

The scaling of ω_0 is $(\Delta x \cdot \Delta p)^{3N} \sim h^{3N}$ | postpone

(2.4) Examples

A. Ideal gas: $\sum_i \frac{p_i^2}{2m} = E$

$$\omega = \int_\Gamma d^{3N}q \, d^{3N}p = V^N \int d^3p$$

$$E - \frac{\Delta}{2} \leq \sum \frac{p_i^2}{2m} \leq E + \frac{\Delta}{2}$$

We can compare to counting states

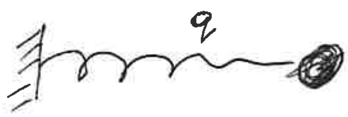
$$\begin{cases} \sum_{r=1}^{3N} n_r^2 = \frac{8mV^{2/3}}{h^2} E = \left(\frac{V^{1/3} 2\sqrt{2mE}}{h} \right)^2 \\ \sum_{r=1}^{3N} p_r^2 = \left(\sqrt{2mE} \right)^2 \end{cases}$$

$$\omega \sim V^N (2mE)^{\frac{3N}{2}}$$

$$\Gamma \sim \left(\frac{V^{1/3} 2\sqrt{2mE}}{h} \right)^{3N} \frac{1}{2^{3N}} = \frac{V^N (2mE)^{3N/2}}{h^{3N}}$$

$$\longrightarrow \boxed{\omega_0 = h^{3N}}$$

B. Harmonic oscillator



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

Hamilton's equations $\begin{cases} \dot{q} = \frac{p}{m} \\ \dot{p} = m\ddot{q} = -Kq \end{cases}$ Newton's law

$$q = A \cos(\omega t + \phi) \qquad \omega = \sqrt{\frac{K}{m}}$$

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

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$$\underbrace{E = \frac{1}{2}\kappa q^2 + \frac{p^2}{2m}} = \frac{1}{2}\kappa A^2\cos^2(\omega t+\phi) + \frac{\omega^2 A^2}{2m}\sin^2(\ )$$

$$= \frac{1}{2}\kappa A^2 = \frac{1}{2}m\omega^2 A^2 = \text{const.}$$

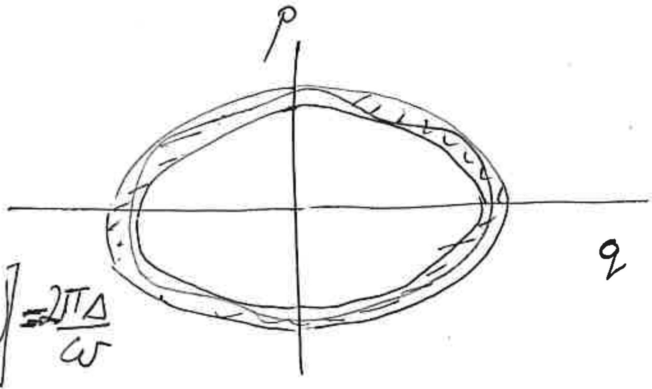
This defines phase-space

$$\left(\times\frac{1}{E} :\right) \quad \underbrace{\frac{p^2}{2mE}}_{b^2} + \frac{q^2}{\underbrace{(2E/m\omega^2)}_{a^2}} = 1 \quad \text{an } \underline{\text{ellipse}}$$

$$\text{Area} = \pi ab = \frac{2\pi E}{\omega}$$

As usual we consider the hypershell $(E-\frac{\Delta}{2}, E+\frac{\Delta}{2})$

With volume



$$W = \int dq\, dp = \frac{2\pi}{\omega}\left[\left(E+\frac{\Delta}{2}\right) - \left(E-\frac{\Delta}{2}\right)\right] = \frac{2\pi\Delta}{\omega}$$

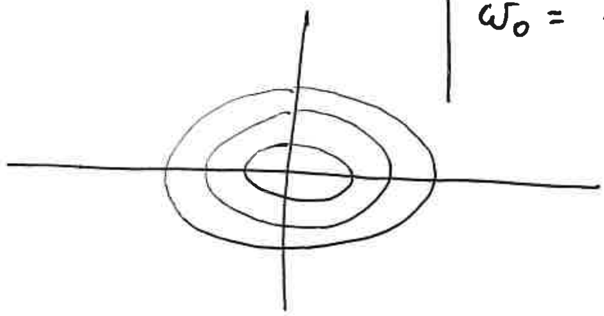
From Q.M we know the energies of the oscillator

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega \quad n = 0, 1, 2\ldots$$

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

So the shell that corresponds to one state has $\Delta E = \hbar\omega$

So that



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

If $E \gg \Delta \gg \hbar\omega$ the number of eigenstates is $\frac{\Delta}{\hbar\omega}$

Similary for N oscillators $\omega_0 = h^N$

(2.5) Quantum States and the Phase Space

Why h is so significant?

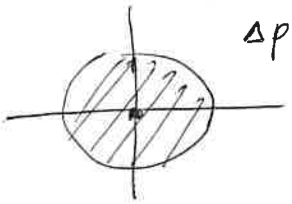
The uncertainty principle:

We cannot specify simultaneously both the position and momentum of a particle.

$$(\Delta q \, \Delta p) \geq \hbar$$

This tells that around every point (q, p) there is a region where the system could be.

$$\Delta p \Delta q \sim \hbar$$



So we can think of P.S. cells where all positions in a cell are non-distinct.

Relativistic particles (photons)

$$p = \hbar k = \hbar \frac{\omega}{c}$$

Then

$$\int d^3q \, d^3p = V \cdot 4\pi p^2 dp = V \, 4\pi \left(\frac{\hbar}{c}\right)^3 \omega^2 d\omega$$

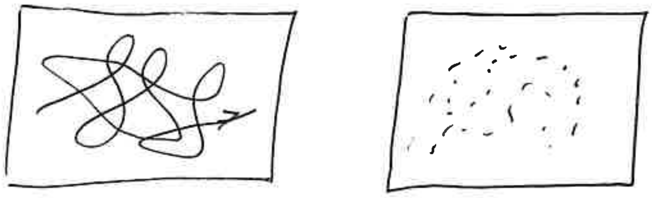
Rayleigh had an expression for # of states

$$V \cdot (4\pi)(2\pi)^3 \frac{\omega^2 d\omega}{c^3}$$

from which we see that $\omega_0 = h^3$

Summary Ch. 2

* Ensembles in Phase Space:



$$d\omega = d^{3N}q \, d^{3N}p$$

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

* Density function $\rho(q,p,t)$
  obey Liouville's theorem $\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$

* Stationary system $\frac{\partial \rho}{\partial t} = 0$ equilibrium

* Microcanonical Ensemble
  Macro state (E, V, N)
  constant E manifold $\mathcal{H} = E$

* $\Omega = \frac{1}{h^{3N} N!} \int d\omega \, \delta(\mathcal{H} - E)$