Classical dynamics

Hamilton's equations $$\boxed{\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}}$$

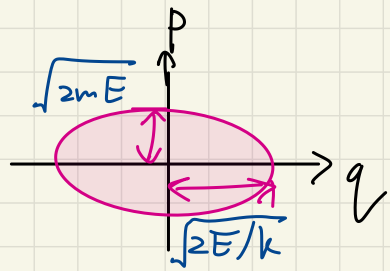
Example Harmonic oscillator $H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2$ $\quad \omega \sqrt{\frac{k}{m}}$

$$\left.\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} = \frac{p}{m} \\ \dot{p} &= -\frac{\partial H}{\partial q} = -m\omega^2 q \end{aligned}\right\} \begin{aligned} \ddot{q} &= \frac{\dot{p}}{m} = -\omega^2 q \\ \ddot{p} &= -m\omega^2 \dot{q} = -\omega^2 p \end{aligned}$$

$$\Rightarrow \quad q(t) = q(0)\cos\omega t + p(0)\sin\omega t$$
$$p(t) = p(0)\cos\omega t - q(0)\sin\omega t$$

$$E = \frac{1}{2} m\omega^2 q_{max}^2 \Rightarrow q_{max} = \sqrt{\frac{2E}{m\omega^2}} = \sqrt{\frac{2E}{k}}$$

$$E = \frac{p_{max}^2}{2m} \Rightarrow p_{max} = \sqrt{2mE}$$



Phase space density

PDF over coordinate (q, p) in phase space is often denoted by $\rho(\vec{q}, \vec{p})$

rho

$$\rho(\vec{q}, \vec{p}) \geq 0 \quad \forall \vec{q}, \forall \vec{p}$$

$$\int d^{3N}q \, d^{3N}p \, \rho(\vec{q}, \vec{p}) = 1$$

A microstate of a classical system at time t is specified by the instantaneous positions and momenta of all the particles in the system.

$$\text{Phase-space coordinates: } \{q_j, p_j\}_{j=1,\dots,3N}$$

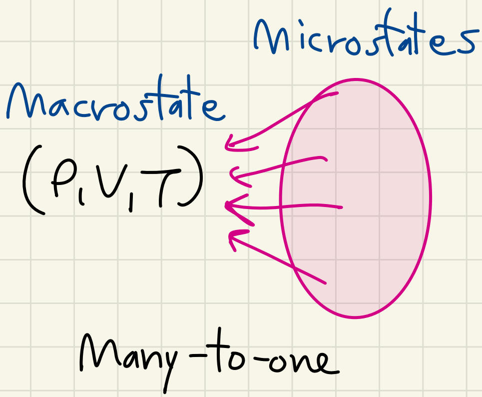
$$\text{Infinitesimal volume element } d\Gamma = d^{3N}q\, d^{3N}p = \prod_{j=1}^{3N} dq_j\, dp_j$$

Given a dynamics (the Hamiltonian $H(\vec{q},\vec{p})$), its solution given some initial condition traces out a trajectory in the phase space.

$$\text{Trajectory: } \vec{\mu} = \begin{pmatrix} \vec{q}(t) \\ \vec{p}(t) \end{pmatrix} \qquad \text{Velocity: } \vec{v} = \begin{pmatrix} \dot{\vec{q}}(t) \\ \dot{\vec{p}}(t) \end{pmatrix}$$

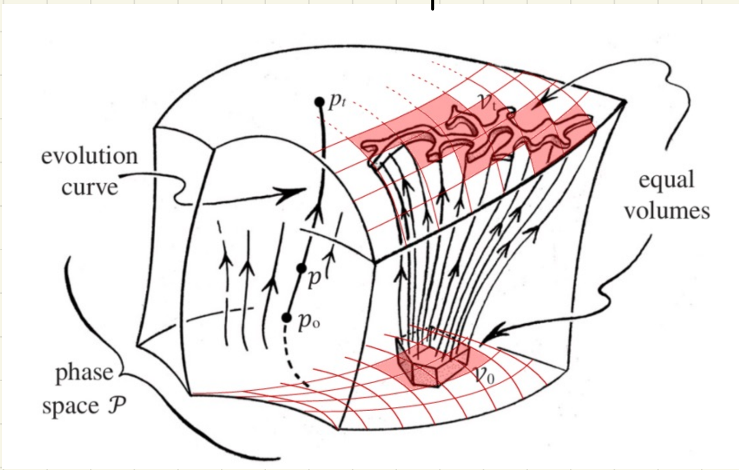
When there is a conserved quantity, for example the energy E, every admissible trajectory must lies within a hypersurface of constant energy.

A macrostate is specified by thermodynamical state variables such as the volume V, the pressure P, or the temperature T, for example.



Continuity equation No source or sink, like incompressible fluid

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \underbrace{\overset{\text{Flux}}{\vec{J}}}_{\rho \vec{v}} = 0$$



arxiv: 2209.04632

$$\vec{v} = \begin{pmatrix} \dot{q}_1 \\ \vdots \\ \dot{q}_{3N} \\ \dot{p}_1 \\ \vdots \\ \dot{p}_{3N} \end{pmatrix}$$

$$\vec{\nabla} \cdot (\rho \vec{v}) = \partial_j (\rho v_j) = (\partial_j \rho) v_j + \rho\, \partial_j v_j$$

$$= (\vec{\nabla} \rho) \cdot \vec{v} + \rho\, \vec{\nabla} \cdot \vec{v}$$

$$= \underbrace{\sum_{j=1}^{3N} \left(\frac{\partial \rho}{\partial q_j} \frac{dq_j}{dt} + \frac{\partial \rho}{\partial p_j} \frac{dp_j}{dt} \right)}_{} + \rho \cancelto{0}{\sum_{j=1}^{3N} \left(\frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right)}$$

$$\frac{\partial \rho}{\partial q_j} \frac{\partial H}{\partial p_j} - \frac{\partial \rho}{\partial p_j} \frac{\partial H}{\partial q_j}$$

$$\frac{\partial \dot{q}_j}{\partial q_j} = \frac{\partial^2 H}{\partial q_j \partial p_j} = \frac{\partial^2 H}{\partial p_j \partial q_j} = -\frac{\partial \dot{p}_j}{\partial p_j}$$

$$\|$$

(Poisson bracket) $\{\rho, H\}$

$$\{f, g\} := \frac{\partial f}{\partial q} \frac{\partial g}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial g}{\partial q}$$

$$\therefore \boxed{\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0}$$

(Analogous to $\dot{\hat{\rho}} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}]$ in quantum)

Liouville's Thm

$$\frac{d\rho[\vec{q}(t), \vec{p}(t), t]}{dt} = 0$$

The probability density in the neighborhood of a moving phase-space point is constant along the trajectory. (Doesn't mean that the shape of the distribution $\rho(\vec{q}, \vec{p})$ is not changing in time! as the simplified notation $d\rho/dt = 0$ might suggest.)

Proof ■ Recall how the chain rule works when applying to a function of spatial coordinates which also varies w.r.t. time
("convective derivative")

$$\frac{d}{dt} f(x(t), y(t), z(t)) = (\vec{\nabla} f) \cdot \frac{\partial \vec{r}}{\partial t} + \frac{\partial f}{\partial t}$$

$$\frac{d\rho}{dt} = \sum_{j=1}^{3N} \left(\frac{\partial \rho}{\partial q_j} \frac{\partial q_j}{\partial t} + \frac{\partial \rho}{\partial p_j} \frac{\partial p_j}{\partial t} \right) + \frac{\partial \rho}{\partial t} \qquad \text{(Chain rule)}$$

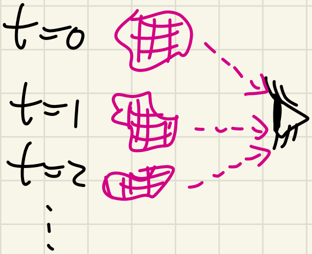
But we have just shown that this sum is nothing but $\{\rho, H\}$.
Moreover, the continuity equation implies that $\partial\rho/\partial t = -\{\rho, H\}$.
Therefore, $d\rho/dt = 0$.

$\square$

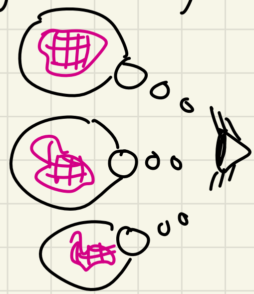
Consequences of Liouville theorem in statistical mechanics

$$d\Gamma = d^{3N}q\, d^{3N}p = \prod_{j=1}^{3N} dq_j\, dp_j$$

Ensemble average $\langle \mathcal{O} \rangle = \int d\Gamma\, \mathcal{O}(\vec{\mu})\, \rho(\vec{\mu}, t)$



? or ensemble average



(Ergodic hypothesis)

Equilibrium $\Rightarrow$ $\frac{\partial \rho_{eq}}{\partial t} = 0 \Rightarrow \{\rho, H\} = 0 \Rightarrow$ ρ is a function of H

<u>Ex</u> ρ uniform on a constant-energy hypersurface (Boltzmann's postulate = microcanonical)

$\rho = e^{-k_B H/T} = e^{-\beta H}$ (Canonical)