

Statistical description of non-equilibrium systems

Challenge: We want to describe (very) large system consisting of many microscopic degrees of freedom

Never really possible in practice to know microscopic state of the system exactly for all degrees of freedom

On the other hand equilibrium systems are characterized by a very limited number of variables
e.g. extensive properties on macroscopic level
 E, N, V

with which we associate an ensemble of microscopic states

e.g. micro-canonical ensemble
 \cong sum of all microscopic states with the same E, N, V

Question: What amount of information is needed to describe non-equilibrium systems?

We will look at classical systems and quantum systems at the microscopic level to first establish & compare how under the most general circumstances dynamics is described

Will then investigate how we can "discard" microscopic information to develop effective descriptions for non-equilibrium systems

Read on Chapter 3 of Pothos

& Chapter 2 of Baym's lecture notes

+ additional material which will be uploaded to web-page

2. Statistical description of non-equilibrium systems

2.1 Statistical description of classical system

Consider a macroscopic system
of $N \gg 1$ degrees of freedom
eg N identical particles

Microscopically the ~~state~~ state of the
system is completely characterized
by $6N$ phase space variables

$$q_{1, \dots, 6N} \text{ and } p_{1, \dots, 6N}$$

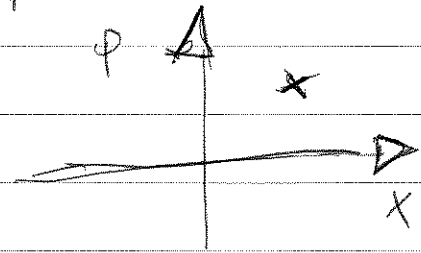
~~Consider~~

If the state of the system is
known exactly, this corresponds
to a point in the $6N$ dimensional
phase space

Example ($N=1$) harmonic oscillator

~~$H(x,p)$~~ $H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$

phase-space variables x, p



Now as particles of \square often not possible to measure all positions & momenta of $N \gg 1$ particles exactly

\rightarrow instead of a fixed value of

$\{q_i\}, \{p_i\}$ we will have

a statistical distribution ~~of~~ of the phase-space variables

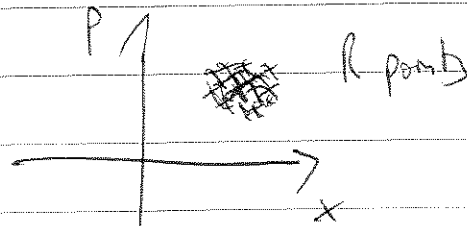
Note that the same is true ~~even if~~ instead of considering a very large system, we consider many ~~copies~~ R of fixed size system with same average properties

Gibbs ensemble: Extremely large number of identical systems, having ~~them~~ m different macroscopic states but in the same macroscopic state

Considering again HO

Example 1)

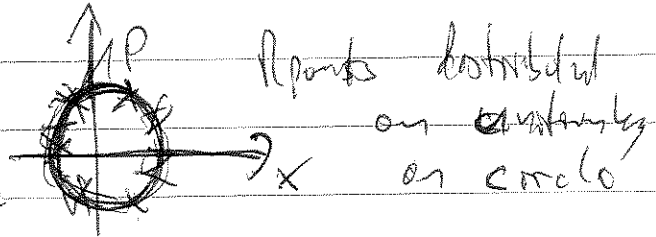
$\langle x \rangle$ and $\langle p \rangle$
known



Example 2) Microcanonical ensemble

E known exactly
but x, p unknown

$$E = H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$



N points distributed
on $E = \text{const}$,
on circle

Now in the limit $N \rightarrow \infty$

points are dense in $6N$ dimensional
phase-space

\rightarrow describe by statistical distribution

Phase-space distribution

Note books use

$$f(\{q_i\}, \{p_i\}, t)$$

$\underbrace{\hspace{2em}}$ coordinates
 $\underbrace{\hspace{2em}}$ momenta
 $\underbrace{\hspace{2em}}$ time

Since f can be thought of as
describing ~~the probability to find~~ probability to find
system in particular microscopic state

$$f(\{q_i\}, \{p_i\}, t) \geq 0 \quad (\text{positive semi-definite})$$

$$\int f(\{q_i\}, \{p_i\}, t) d^{6N}V = 1 \quad (\text{normalized})$$

Phase-space
measure

most natural choice of normalization

$$d^{6N} = \prod_{i=1}^{3N} dq_i dp_i$$

How to compare classical and quantum systems, more convenient to use

identical particles ~~for~~ $d^{6N} = \frac{1}{N!} \prod_{i=1}^{3N} \frac{dq_i dp_i}{(2\pi\hbar)^3}$

distinguishable particles $d^{6N} = \prod_{i=1}^{3N} \frac{dq_i dp_i}{(2\pi\hbar)^3}$

Dimensionless distribution f

Now how does one calculate observables

generally ~~$O = O(q, p, t)$~~

$$O_{ce} = O_{ce}(q, p, t)$$

explicit two dependences (typically not present)

⇒ Evaluate for each member of ensemble and average

$$\langle O_{ce}(t) \rangle = \frac{\int O_{ce}(q, p, t) \rho(q, p, t) d^{6N}}{\int \rho(q, p, t) d^{6N}}$$

Statistical average over different microscopical realizations

Note that there will be fluctuations

Variance: $\sigma_{O_{ce}}^2 = \langle O_{ce}(t)^2 \rangle - \langle O_{ce}(t) \rangle^2$

Evolution of phase-space density

Microscopic perspective

- classical dynamics is deterministic
- evolution of each member of statistical ensemble is described by classical EOM which describes a trajectory in phase space

Hamilton's EOM

$$\dot{q}_i = \frac{d}{dt} q_i = \{q_i, H\}$$

$$\dot{p}_i = \frac{d}{dt} p_i = \{p_i, H\}$$

Canonical variables q_i, p_i

Poisson Bracket

$$\{f, g\} = \sum_{i=1}^{3N} \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right)$$

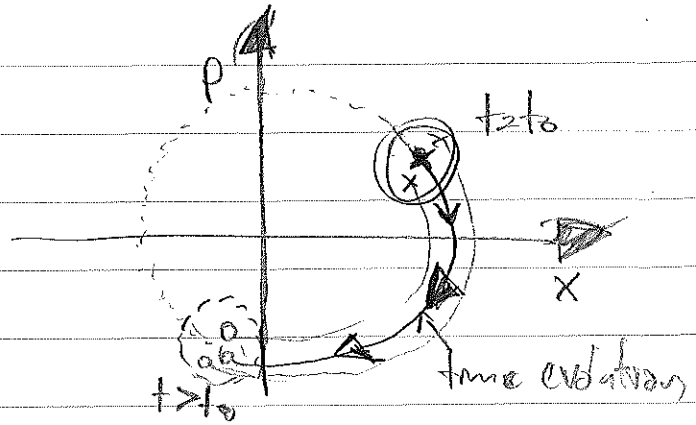
\Rightarrow

$$\begin{cases} \dot{q}_i = \frac{\partial H}{\partial p_i} \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} \end{cases}$$

Note book use different conventions for sign of Poisson bracket

Harmonic Oscillator

Evolution in time corresponds
to motion along orbit
in phase-space



General formulation

$$f(\{q_i\}, \{p_i\}, t) = \int d^{3N} q_i^0 d^{3N} p_i^0 \underbrace{f(\{q_i^0\}, \{p_i^0\}, t_0)}_{\text{initial condition}}$$

$$\times \prod_{i=1}^{3N} \delta(q_i - q_i^{cl}(\{q_i^0\}, \{p_i^0\}, t_0)) \\ \delta(p_i - p_i^{cl}(\{q_i^0\}, \{p_i^0\}, t_0))$$

solution to classical EOM

$\{q_i^{cl}\}, \{p_i^{cl}\}$ satisfy

Hamilton's EOM

$$\frac{\partial}{\partial t} f(\{q_i\}, \{p_i\}, t) = \int d^{3N} q_i^0 d^{3N} p_i^0 f(\{q_i^0\}, \{p_i^0\}, t_0)$$

$$\frac{\partial}{\partial t} \prod_{i=1}^{3N} \delta(q_i - q_i^{cl}(t | \{q_i^0\}, \{p_i^0\}, t_0)) \delta(p_i - p_i^{cl}(t | \{q_i^0\}, \{p_i^0\}, t_0))$$

time dependence only through classical evolution of q_i^{cl} and p_i^{cl}

$$\frac{\partial}{\partial t} \delta(q_i - q_i^{cl}(t, \dots)) \delta(p_i - p_i^{cl}(t, \dots))$$

$$= \dot{q}_i^{cl} \frac{\partial}{\partial q_i^{cl}} + \dot{p}_i^{cl} \frac{\partial}{\partial p_i^{cl}}$$

Hamilton's EOM //

$$= \left. \frac{\partial H}{\partial p_i^{cl}} \right|_{q_i^{cl}, p_i^{cl}} \frac{\partial}{\partial q_i^{cl}} = \left. \frac{\partial H}{\partial q_i^{cl}} \right|_{q_i^{cl}, p_i^{cl}} \frac{\partial}{\partial p_i^{cl}}$$

integral only has support for $p_i = p_i^{cl}$ $q_i = q_i^{cl}$

$$\frac{\partial}{\partial q_i^{cl}} \delta(q_i - q_i^{cl}(t, \dots)) = - \frac{\partial}{\partial q_i} \delta(\dots)$$

$$= - \left. \frac{\partial H}{\partial p_i} \right|_{q_i, p_i} \frac{\partial}{\partial q_i} + \left. \frac{\partial H}{\partial q_i} \right|_{q_i, p_i} \frac{\partial}{\partial p_i}$$

will generate such terms for all i

So upon pulling them out of integral

$$\frac{\partial}{\partial t} f(\{q_i\}, \{p_i\}, t) = \sum_{i=1}^{2N} \left(\frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} \right) f(\{q_i\}, \{p_i\}, t)$$

$$\Rightarrow \frac{\partial}{\partial t} f = \{H, f\} \quad \text{Liouville equation}$$

Equivalently we can rewrite this in the form

$$\frac{\partial f}{\partial t} = -i \mathcal{L} f$$

where \mathcal{L} is Liouville operator

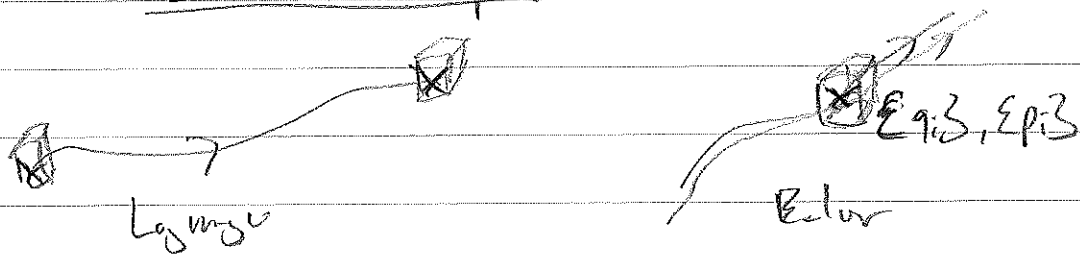
$$\mathcal{L} = i \{H, \cdot\}$$

So formally the solution is given by

$$f(\{q_i\}, \{p_i\}, t) = \exp(-i \mathcal{L} (t-t_0)) f(\{q_i\}, \{p_i\}, t_0)$$

Note that in our derivation of Liouville equation we have adopted Lagrangian viewpoint following individual trajectories of phase space points

Instead one can also look at a fixed point $\{q_i, p_i\}$ in phase-space and look how many trajectories pass through this point as a function of time
 → Eulerian viewpoint



Since we know how far a given point the system evolves by Hamilton's EOM we can look at

$$\frac{d}{dt} f(\{q_i, p_i, t\}) = \frac{\partial f}{\partial t} + \sum_{i=1}^{3N} \frac{\partial f}{\partial q_i} \dot{q}_i + \sum_{i=1}^{3N} \frac{\partial f}{\partial p_i} \dot{p}_i$$

using $\dot{q}_i = \frac{\partial H}{\partial p_i}$ and $\dot{p}_i = -\frac{\partial H}{\partial q_i}$

$$\frac{d}{dt} f = \frac{\partial f}{\partial t} + \{f, H\} = 0$$

$$\boxed{\frac{d}{dt} f = 0}$$

alternative form of Liouville equation expressing conservation of phase-space density (probability is conserved)

Now from Euler viewpoint Liouville Eqn
 takes the form of continuity equation

$$\frac{d\Gamma}{dt} + \sum_{i=1}^{3N} \left[\frac{\partial \Gamma}{\partial q_i} \dot{q}_i + \frac{\partial \Gamma}{\partial p_i} \dot{p}_i \right] = 0$$

$$\underbrace{\frac{\partial \Gamma}{\partial q_i} \dot{q}_i + \frac{\partial \Gamma}{\partial p_i} \dot{p}_i}_{\nabla_{q,p} \cdot \dot{\mathbf{z}}_i} = 0$$

Now under Hamiltonian evolution $\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right)^{EOM} = \left(\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right) = 0$

$$\Rightarrow \frac{d\Gamma}{dt} + \nabla_{q,p} \cdot (\Gamma \dot{\mathbf{z}}) = 0$$

Similarly using the same trick, one can
 show that also the phase-space volume element
 is conserved

$$\frac{d}{dt} (d^{6N} V) = 0$$

Hence using

$$\int f(\dots) d^{6N} V$$

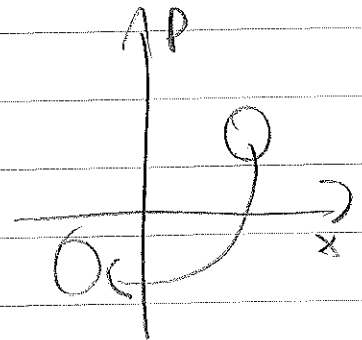
$$\frac{d}{dt} \left(\int f d^{6N} V \right) = 0$$

we find alternative formulation of Liouville's theorem

Phase space volume occupied by
set of microstates is preserved
under Hamiltonian evolution

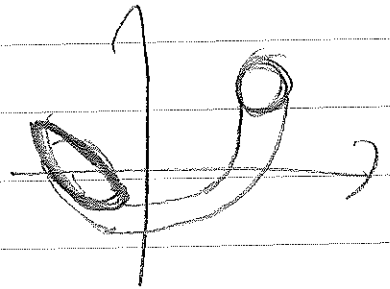
Example 1) Harmonic oscillator

→ transition of volume



Example 2) Anharmonic oscillator

→ transition of deformation
of volume



Evolution of macroscopic observables

We had

$$\langle O(t) \rangle = \frac{\int d^{6N}v \ O(q,p,t) \ f(q,p,t)}{\int d^{6N}v \ f(q,p,t)}$$

will focus on observables $O(q,p)$

i.e. no explicit time dependence

eg kinetic energy $E_{kin} = \sum_i \frac{p_i^2}{2m}$

using Liouville's theorem and Liouville's Eqn

$$\langle O(t) \rangle = \int d^{6N}v \ O(q,p) e^{-i\mathcal{L}(t-t_0)} f_0(q,p)$$

Now what is more useful is to directly look at POMs of observables

$$\begin{aligned} \frac{d}{dt} O(q,p) &= \sum_{i=1}^N \frac{\partial O}{\partial q_i} \dot{q}_i + \frac{\partial O}{\partial p_i} \dot{p}_i \\ &= \{O, H\} = i\mathcal{L}O \end{aligned}$$

Of course the same things valid at the level of expectation values

$$\frac{d}{dt} \langle O(t) \rangle = \langle \{O, H\} \rangle$$

Explicitly $\frac{d}{dt} \langle O(t) \rangle = \frac{d}{dt} \int d^{6N}v \ O f$
 $= \int d^{6N}v \ \left(\frac{d}{dt} O \right) f + O \left(\frac{d}{dt} f \right) = \left\langle \frac{d}{dt} O \right\rangle$

2.2 Statistical description of quantum systems

While a microscopic realization of a classical system is described by phase-space variables $\{q, p\}$, $\{Q, P\}$ in \mathcal{M} the microscopic realization is described by a

wave-function $|\psi\rangle$ (pure state)

density matrix $\hat{\rho}$ (mixed state)

Generally for a pure state $|\psi\rangle$, the wave-function is characterized by a complete set of commuting operators (CSCO) whose eigenstates $\{|\phi_n\rangle\}$ form an orthonormal basis of the Hilbert space \mathcal{H}

General form of a pure state is an arbitrary superposition

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle \quad (\text{normalized } \sum_n |c_n|^2 = 1)$$

and the expectation value of an observable \hat{O} is given by

$$\langle \hat{O} \rangle = \langle \psi | \hat{O} | \psi \rangle = \sum_{n,m} \langle \phi_n | \hat{O} | \phi_m \rangle c_n^* c_m$$

Note that a single measurement will not necessarily reveal this \rightarrow need to repeat

Now in reality it is hardly possible to know exact quantum state of a system (\rightarrow requires measurement of ρ)

So instead we will be dealing with statistical mixtures, where for some states

$\{|\psi_i\rangle\}$ the system
is in the state $|\psi_i\rangle$
with probability $p_i \geq 0$

$$\sum_i p_i = 1$$

this is appropriately expressed by density operator

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle \langle \psi_i|$$

probability projection of state $|\psi_i\rangle$

which describes statistical superposition of quantum states

\rightarrow analogous to phase-space distributions in classical case

Expectation values of
Observables are averages over different states

$$\begin{aligned}\langle \hat{O} \rangle &= \sum_i p_i \langle \psi_i | \hat{O} | \psi_i \rangle \\ &= \sum_{i,m} p_i \langle \psi_i | \phi_m \rangle \langle \phi_m | \hat{O} | \phi_m \rangle \langle \phi_m | \psi_i \rangle \\ &= \sum_{i,m} p_i \langle \phi_m | \hat{O} | \phi_m \rangle \langle \phi_m | \psi_i \rangle \langle \psi_i | \phi_m \rangle \\ &= \text{tr} [\hat{O} \hat{\rho}]\end{aligned}$$

We also note the following properties

$$\hat{\rho} \text{ is Hermitian} \quad \hat{\rho}^\dagger = \hat{\rho} \quad \square$$

$$\text{tr} [\hat{\rho}] = 1 \quad (\text{expectation value of identity is } 1)$$

$$\begin{aligned}\text{tr} [\hat{\rho}] &= \sum_i p_i \sum_m \langle \phi_m | \psi_i \rangle \langle \psi_i | \phi_m \rangle \\ &= \sum_i p_i \sum_m |\langle \phi_m | \psi_i \rangle|^2 = \sum_i p_i = 1 \quad \square\end{aligned}$$

$$\hat{\rho} \text{ is positive: } \langle \phi | \hat{\rho} | \phi \rangle \geq 0 \\ \text{Semi-definite}$$

$$\langle \phi_m | \hat{\rho} | \phi_m \rangle = \sum_i p_i |c_{mi}|^2 \geq 0 \quad \square$$

Evolution of quantum systems

Consider first pure state in Schrödinger picture

$$i\hbar \frac{d}{dt} |\psi_i(t)\rangle = \hat{H} |\psi_i(t)\rangle$$

using $\hat{H} = \hat{H}^\dagger$

$$-i\hbar \frac{d}{dt} \langle \psi_i(t) | = \langle \psi_i(t) | \hat{H}$$

Since statistical probabilities p_i
are time independent

$$i\hbar \frac{d}{dt} \hat{\rho} = \sum_i p_i i\hbar \frac{d}{dt} |\psi_i(t)\rangle \langle \psi_i(t)|$$

$$= \sum_i p_i \left(\hat{H} |\psi_i(t)\rangle \langle \psi_i(t)| - |\psi_i(t)\rangle \langle \psi_i(t)| \hat{H} \right)$$

$$= [\hat{H}, \hat{\rho}]$$

Liouville-von Neumann equation:

$$\frac{d}{dt} \hat{\rho} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] = -i\mathcal{L} \hat{\rho}$$

can define quantum Liouville operator

$$\mathcal{L} = \frac{1}{\hbar} [\hat{H}, \cdot]$$

Comparing with classical dynamics

$$\mathcal{L} = i \{H, \cdot\}$$

classical

$$\mathcal{L} = \frac{1}{\hbar} [H, \cdot]$$

quantum

we find

$$i\hbar \{ \cdot, \cdot \} \rightarrow [\cdot, \cdot]$$

which is the canonical quantization condition

Evolution operator for time evolution

Schrödinger picture:

Define $U(t, t_0)$ such that for any state

$$U(t, t_0) |\psi_i(t_0)\rangle = |\psi_i(t)\rangle$$

$$\begin{aligned} \text{then } i\hbar \frac{d}{dt} U(t, t_0) |\psi_i(t_0)\rangle &= i\hbar \frac{d}{dt} |\psi_i(t)\rangle \\ &= \hat{H} |\psi_i(t)\rangle \\ &= \hat{H} U(t, t_0) |\psi_i(t_0)\rangle \end{aligned}$$

$$\text{Hence } \boxed{i\hbar \frac{d}{dt} U(t, t_0) = \hat{H} U(t, t_0)}$$

Solution formally given by

$$U(t_0, t_0) = 1$$

$$U(t, t_0) = \mathcal{T} \exp\left(\frac{-i}{\hbar} \int_{t_0}^t dt' \hat{H}\right)$$

time ordering

for t independent Hamiltonian

$$U(t, t_0) = \exp\left(\frac{-i}{\hbar} \hat{H}(t-t_0)\right)$$

Note that time ordering formally defined by expanding exponential and $\mathcal{T} \exp\left(-\frac{i}{\hbar} \int \hat{H}\right) = \mathcal{T} \left(1 - \frac{i}{\hbar} \int \hat{H} \dots\right)$ and applying time ordering to every term

Similarly

$$\hat{\rho}(t) = U(t, t_0) \hat{\rho}(t_0) U^\dagger(t, t_0)$$

where

$$U(t, t_0) = \overline{\text{T}} \exp\left(\frac{-i}{\hbar} \int_{t_0}^t H\right)$$

anti time
ordered

Evolution operator is unitary

$$U^\dagger(t, t_0) U(t, t_0) = 1$$

Evolution of observables:

Schrödinger picture:

$$\langle \hat{O}(t) \rangle = \text{Tr} [\hat{\rho}(t) \hat{O}_S]$$

$$= \text{Tr} [U(t, t_0) \hat{\rho}(t_0) U^\dagger(t, t_0) \hat{O}_S]$$

where for simplicity we considered
observables without explicit time dependence

Due to cyclicity of trace
can also be interpreted as

$$\langle \hat{O}(t) \rangle = \text{Tr} \left[\underbrace{\hat{\rho}(t_0)}_{\text{time independent density}} \underbrace{U^\dagger(t, t_0) \hat{O} U(t, t_0)}_{\text{time dependent observable}} \right]$$

Horowitz picture:

$$\hat{\rho}_H(t) = \hat{\rho}_H(t_0) = \hat{\rho}_S(t_0)$$

$$\hat{O}_H(t) = U^\dagger(t, t_0) \hat{O}_H(t_0) U(t, t_0)$$

or in terms of Schrödinger operator

$$\hat{O}_H(t) = U^\dagger(t, t_0) \hat{O}_S U(t, t_0)$$

Differentiating w.r.t to time t
we obtain

$$i\hbar \frac{d}{dt} \hat{O}_H(t) = \left[-U^\dagger(t, t_0) \hat{H} \right] \hat{O}_H(t_0) U(t, t_0) \\ + U^\dagger(t, t_0) \hat{O}_H(t_0) \hat{H} U(t, t_0)$$

which for two indep Hamiltonians, say $[\hat{A}, \hat{B}] = 0$ $\forall t_0$

$$\frac{d}{dt} \hat{O}_H(t) = \frac{1}{i\hbar} [\hat{O}_H, \hat{H}]$$

Heisenberg equation

irrespective of position we get for expectation values

$$\frac{d}{dt} \langle \hat{O}(t) \rangle = \frac{1}{i\hbar} \langle [\hat{O}, \hat{H}] \rangle$$