Statistical Description based on the STATES of the TOTAL system

The Liouville Equation : A Probabilistic View

$\Gamma \equiv \{q_i, p_i\}$ momenta, coordinates : phase space point

$d\Gamma \equiv$ volume element in phase space

$$d\Gamma = \prod_i dq_i \prod_i dp_i$$

$\rho(\Gamma, t)\, d\Gamma$: Probability that the system is in volume element $d\Gamma$ around Γ at time t.

$\rho(\Gamma, t=0)$: initial condition

probability is conserved $\int d\Gamma \, \rho(\Gamma, t) = 1$

trajectories are continuous and differentiable

continuity eq. for ρ:

$$\frac{\partial}{\partial t} \rho(\Gamma, t) + \mathrm{div}\left(\rho(\Gamma, t) \, \dot{\vec{v}}\right) = 0$$

↳ velocity in phase space

$$\vec{v} = \{\dot{q}_i, \dot{p}_i\} = \left\{ \frac{\partial H}{\partial p_i}, -\frac{\partial H}{\partial q_i} \right\}$$

$$\operatorname{div} \vec{v} = \sum_i \left(\frac{\partial}{\partial q_i} \dot{q}_i + \frac{\partial}{\partial p_i} \dot{p}_i \right) =$$

$$= \sum_i \left(\frac{\partial}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = 0$$

"incompressible fluid" $\longrightarrow$ Liouville equation

$$0 = \frac{\partial}{\partial t} \rho + \operatorname{div}(\rho \vec{v}) = \frac{\partial}{\partial t} \rho + \rho \underbrace{\operatorname{div} \vec{v}}_{0} + \vec{v} \cdot \operatorname{grad} \rho$$

$$= \left(\frac{\partial}{\partial t} + \vec{v} \cdot \operatorname{grad} \right) \rho$$

convective derivative

ρ is just transported via convection

$$\rho(\Gamma + dt\,\vec{v},\ t + dt) = \rho(\Gamma, t)$$

$$\parallel$$

$$\rho(\Gamma, t) + \left(\vec{v} \cdot \operatorname{grad} \rho\right) dt + \frac{\partial \rho}{\partial t}\, dt$$

$$\Rightarrow \boxed{\frac{\partial \rho}{\partial t} + \vec{v} \cdot \operatorname{grad} \rho = 0}$$

$\rho(\Gamma)$ for thermal equilibrium = ?

$$\rho(\Gamma, t) = \rho\left(H(\Gamma)\right) \Rightarrow \frac{\partial \rho}{\partial t} = 0$$

$$\mathrm{grad}\,\rho = \left\{ \frac{\partial \rho}{\partial q_i}, \frac{\partial \rho}{\partial p_i} \right\} = \left\{ \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial q_i}, \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p_i} \right\} =$$

$$= \left\{ -\frac{\partial \rho}{\partial H}\dot{p}_i, \frac{\partial \rho}{\partial H}\dot{q}_i \right\} = \frac{\partial \rho}{\partial H}\left\{ -\dot{p}_i, \dot{q}_i \right\}$$

$$\dot{\vec{v}} \cdot \mathrm{grad}\,\rho = \frac{\partial \rho}{\partial H} \sum_i \left(-\dot{p}_i \dot{q}_i + \dot{q}_i \dot{p}_i \right) = 0$$

<u>Any</u> $\rho = \rho(H(\Gamma))$ is STATIONARY

Stationarity is a necessary condition for equilibrium.

Try the SIMPLEST assumption $\Rightarrow$

$\underline{\rho(\Gamma) = \text{const.}}$ (IS stationary)

BUT only for those points that are accessible

($\rightarrow$ conservation laws, constraints)

- energy conservation $H(\Gamma) = E \rightsquigarrow \rho(\Gamma) \propto \delta(H(\Gamma) - E)$
- momentum " (but does not occur for hard walls)
- angular " (same story)
- size and shape of container

$$\int d\Gamma \ldots = \int_V d^3\vec{r}_1 \int_V d^3\vec{r}_2 \ldots \int_V d^3\vec{r}_N \int d^3\vec{p}_1 \ldots \int d^3\vec{p}_N \ldots$$

microcanonical distribution function:

$$\rho(\Gamma) = \frac{\delta(H(\Gamma)-E)}{\underbrace{\int d\Gamma\, \delta(H(\Gamma)-E)}} \Rightarrow \int d\Gamma\, \rho(\Gamma) = 1$$

$\rightarrow$ area of hypersurface of constant energy

average of an observable $A = A(\Gamma)$

$$\boxed{\langle A \rangle = \int d\Gamma\, \rho(\Gamma)\, A(\Gamma)}$$

(so-called ENSEMBLE average)

has to be distinguished from the <u>TIME</u>

average

$$\bar{A} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, A(\Gamma(t))$$

trajectory in phase space

(this is the physical situation!)

$$\bar{A} \overset{?}{=} \langle A \rangle$$ If yes, then the system is called ergodic

(for <u>all</u> A)

For an ergodic system: The trajectory comes arbitrarily close to any phase space point (sooner or later), <u>and</u> all subvolumes of the phase space are, on average, visited with the same frequency.

Fortunately, seems to hold for most physical systems!

COUNTING STATES

$\int d\Gamma$ = # of states of a system

(integer)

this is achieved via quantum mechanics! (QM)

result of QM: phase space volume $d\Gamma$

$$\boxed{\text{corresponds to } \# \text{ of states} = \frac{d\Gamma}{(2\pi\hbar)^{3N}}}$$

3N : N particles, 3D spaces

— Planck's constant (action)

One simple example:

→ one particle in 1D, periodic box of size L, mass m

QM: Schrödinger eq.

$$i\hbar \frac{\partial}{\partial t} \underbrace{\psi(x,t)}_{\text{complex!}} = \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \right]}_{\text{Hamilton operator}} \psi(x,t)$$

↳ potential

$\hat{p} := \frac{\hbar}{i}\frac{\partial}{\partial x}$ operator for the momentum

$$\frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$|\Psi(x,t)|^2 \, dx$: q.m. probability to find the particle in dx

$$\int dx \, |\Psi|^2 = 1 \qquad \omega \longrightarrow E = \hbar\omega$$

<u>Ansatz:</u> $$\Psi(x,t) = \exp\left(-i \overbrace{\frac{E}{\hbar}}^{\omega} t\right) \phi(x)$$

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = E \, \Psi(x,t)$$ "energy eigenstate"

$$E \, \phi(x) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) \phi(x)$$

stationary Schrödinger equation

$$E\,\phi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi$$; <u>Ansatz</u>:

$$\phi = \frac{1}{\sqrt{L}}\exp\Big(i\frac{2\pi}{L}\underbrace{n}_{\text{integer}}x\Big) \qquad \phi(x+L) = \phi(x)$$

normalization

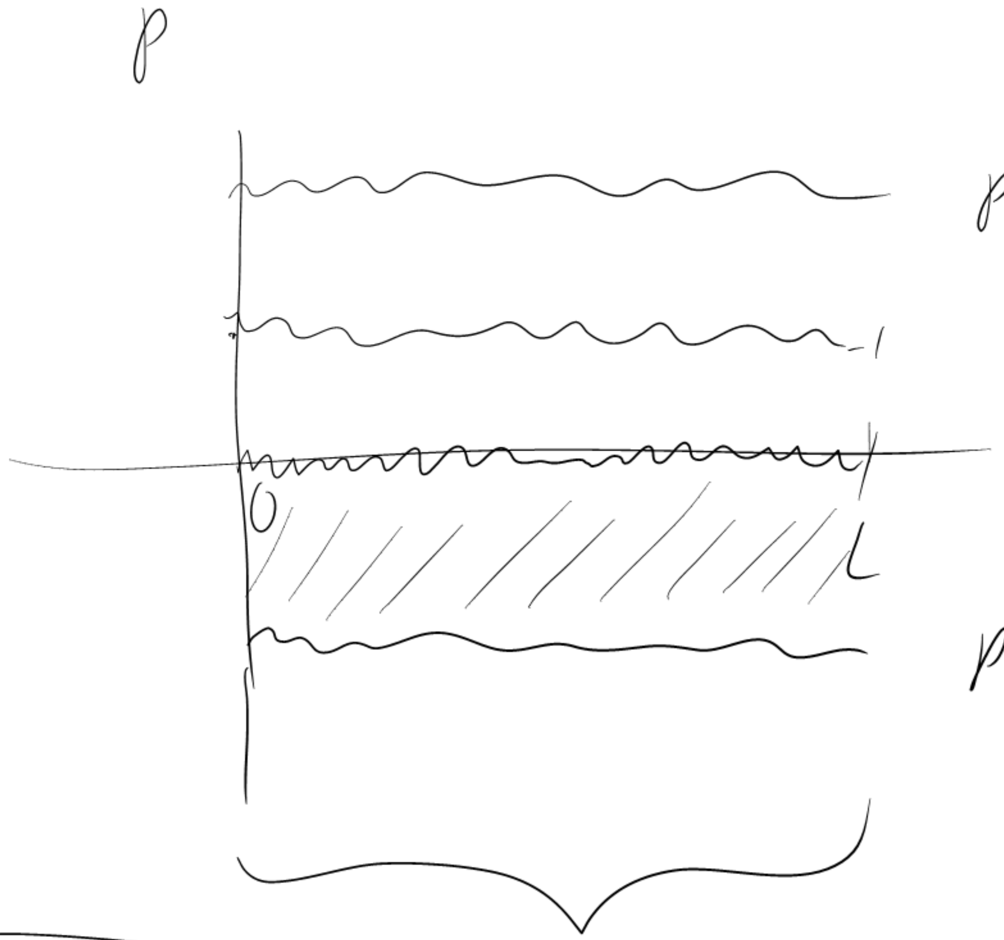
$$\int_0^L dx\,|\phi|^2 = 1$$

$$\frac{\partial^2}{\partial x^2}\phi = -\left(\frac{2\pi n}{L}\right)^2\phi \Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi = +\left(\frac{2\pi\hbar}{L}\right)^2\frac{n^2}{2m}\phi$$

$$\boxed{E = \frac{1}{2mL^2}(2\pi\hbar)^2 n^2}$$

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\phi = \phi\,\frac{\hbar}{i}\, i\,\frac{2\pi n}{L} \Rightarrow \boxed{p = \frac{2\pi\hbar}{L}\, n}$$

n any integer



$n = +2$ $\qquad p = (2\pi\hbar/L)\cdot 2$

$n = +1$ $\qquad p = 2\pi\hbar/L$

$n = 0$

$n = -1$ $\qquad p = -2\pi\hbar/L$

$$\Delta p = \frac{2\pi\hbar}{L}$$

$$\Delta x = L$$

$$\boxed{\Delta p \cdot \Delta x = 2\pi\hbar}$$

$\boxed{2\pi\hbar \text{ per quantum state}}$