

Ensemble Theory / Phase Space / Liouville / Microcanonical

(1)

- given a macrostate: N, E, V

- at any time t , the system is equally likely to be in any corresponding microstate

- time develops $\rightarrow$ system moves (dynamics)
 $\rightarrow$ switches between microstates

- at any particular time t we can consider a number of copies of the system

- all copies correspond to macrostate, but in different microstates

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ensemble

- expect that average behaviour over members of ensemble is the same as the time average of one particular system

ensemble average = time average

Phase space

- dynamics can be described according to Hamilton's equations of motion $\Rightarrow \mathcal{H}(\vec{p}^N, \vec{q}^N)$

- variables for a system with ~~3N~~ N particles

- positions and momenta: $\vec{q}^N, \vec{p}^N$

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$6N$ dimensional space $\rightarrow$ phase space

- in phase space the state of the system

is given by a single point (microstate!)

(2)

- given an N -particle system, we do not know which state it is in $\Rightarrow$ we use concept of ensemble (system is in a particular microstate with some probability)
- each state point moves according to Hamilton's equations of motion
 - expect that each point moves on a unique trajectory
 - trajectories can not cross, split into two, or unite into one
 - expect that the probability distribution moves like an "incompressible fluid"

Liouville equation

- governs the flow of points in phase space
- consider classical system w/ $3N$ degrees of freedom
- state specified by $\vec{p}^N, \vec{q}^N$

$$\vec{p}^N = (\vec{p}_1, \dots, \vec{p}_N) \quad \vec{q}^N = (\vec{q}_1, \dots, \vec{q}_N)$$

- if state vector is known at some time t
 - $\rightarrow$ then it is also known at any later time t'
 - $\rightarrow$ and it is also known at any earlier time t''

from Hamilton's equations of motion which are reversible

$$\dot{\vec{q}} = \frac{\partial H}{\partial \vec{p}^N}$$

$$\dot{\vec{p}} = - \frac{\partial H}{\partial \vec{q}^N}$$

- time reversal invariance: if $t \rightarrow -t$ system traces back ^③ the same trajectory as where it came from

$$t \rightarrow -t \quad \begin{aligned} -\dot{\vec{q}} &= \frac{\partial H}{\partial \vec{p}_N} & \dot{\vec{q}} &= -\frac{\partial H}{\partial \vec{p}_N} \\ -\dot{\vec{p}} &= -\frac{\partial H}{\partial \vec{q}_N} & \dot{\vec{p}} &= \frac{\partial H}{\partial \vec{q}_N} \end{aligned} \Rightarrow$$

- this is why trajectories can not intersect, split, or join
 - if two trajectory points are identical at time t then they must be identical for any later or earlier times

- we assume that Hamiltonian does not depend explicitly on time $\Rightarrow H^N(\vec{p}^N, \vec{q}^N) = E$ (constant)

- since for a real system we can not uniquely determine microstate $\rightarrow$ introduce probability density $g(\vec{p}^N, \vec{q}^N; t) d\vec{p}^N d\vec{q}^N$

- definition: $g(\vec{p}^N, \vec{q}^N; t) d\vec{p}^N d\vec{q}^N$ is the probability that the state of the system lies in a volume element $d\vec{p}^N d\vec{q}^N$ near point $\vec{p}^N, \vec{q}^N$

- we can do this since we have argued that the number of points in phase space is constant, so the overall probability of finding the system anywhere in phase space does not change $\Rightarrow$ so we can normalize

$$\int g(\vec{p}^N, \vec{q}^N; t) d\vec{p}^N d\vec{q}^N = 1$$

- if we want the probability of finding the system in some volume R in phase space at time t :

$$P(R) = \int_R g(\vec{p}^N, \vec{q}^N; t) d\vec{p}^N d\vec{q}^N$$

- small uncertainty $\Rightarrow$ sharply peaked distribution

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- consider a volume in phase space V_0 , and the surface S_0 surrounding that volume

$$\frac{d}{dt} P(V_0) = \frac{\partial}{\partial t} \int_{V_0} g(\vec{p}^N, \vec{q}^N; t) d\vec{p}^N d\vec{q}^N$$

$$= - \oint_{S_0} g(\vec{p}^N, \vec{q}^N; t) \vec{V}^N \cdot d\vec{S}^N$$

$$\vec{V}^N = (\dot{\vec{p}}^N, \dot{\vec{q}}^N)$$

- using Gauss's theorem

$$\frac{\partial}{\partial t} \int_{V_0} g(\vec{p}^N, \vec{q}^N; t) d\vec{p}^N d\vec{q}^N = - \int_{V_0} \vec{\nabla}_{\vec{p}^N, \vec{q}^N} \cdot (g(\vec{p}^N, \vec{q}^N; t) \vec{V}) d\vec{p}^N d\vec{q}^N$$

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$\Rightarrow$ where $\vec{\nabla}_{\vec{p}^N, \vec{q}^N} = \left(\frac{\partial}{\partial p_1}, \dots, \frac{\partial}{\partial p_N}, \frac{\partial}{\partial q_1}, \dots, \frac{\partial}{\partial q_N} \right)$

$$\rightarrow \frac{\partial g(\vec{p}^N, \vec{q}^N; t)}{\partial t} + \vec{\nabla}_{\vec{p}^N, \vec{q}^N} \cdot [g(\vec{p}^N, \vec{q}^N; t) \vec{V}] = 0$$

$$\vec{\nabla}_{\vec{p}^N, \vec{q}^N} \cdot [g(\vec{p}^N, \vec{q}^N; t) \vec{V}]$$

$$= \sum_{i=1}^N \left[\frac{\partial g(\vec{p}^N, \vec{q}^N; t)}{\partial p_i} \dot{p}_i + \frac{\partial g(\vec{p}^N, \vec{q}^N; t)}{\partial q_i} \dot{q}_i \right]$$

- volume element in phase space changes in time according to

$$d\vec{p}_t^N d\vec{q}_t^N = J^N(t, t_0) d\vec{p}_{t_0}^N d\vec{q}_{t_0}^N$$

$J^N(t, t_0)$ - Jacobian determinant

$$J^N(t, t_0) = \det \begin{vmatrix} \frac{\partial \vec{p}_t^N}{\partial \vec{p}_{t_0}^N} & \frac{\partial \vec{p}_t^N}{\partial \vec{q}_{t_0}^N} \\ \frac{\partial \vec{q}_t^N}{\partial \vec{p}_{t_0}^N} & \frac{\partial \vec{q}_t^N}{\partial \vec{q}_{t_0}^N} \end{vmatrix}$$

Jacobian satisfies $J^N(t, t_1) J^N(t_1, t_0)$ (5)
 (since determinant obeys the rule $\det[AB] = \det A \det B$)

- expand:

$$\vec{p}_t^N = \vec{p}_{t_0}^N + \Delta t \dot{\vec{p}}_{t_0}^N + O(\Delta t^2)$$

$$\vec{q}_t^N = \vec{q}_{t_0}^N + \Delta t \dot{\vec{q}}_{t_0}^N + O(\Delta t^2)$$

$$J^N(t, t_0) = \begin{vmatrix} 1 + \Delta t \frac{\partial \dot{\vec{p}}_{t_0}^N}{\partial \vec{p}_{t_0}^N} & \Delta t \frac{\partial \dot{\vec{p}}_{t_0}^N}{\partial \vec{q}_{t_0}^N} \\ \Delta t \frac{\partial \dot{\vec{q}}_{t_0}^N}{\partial \vec{p}_{t_0}^N} & 1 + \Delta t \frac{\partial \dot{\vec{q}}_{t_0}^N}{\partial \vec{q}_{t_0}^N} \end{vmatrix}$$

$$= 1 + \Delta t \left(\underbrace{\frac{\partial \dot{\vec{p}}_{t_0}^N}{\partial \vec{p}_{t_0}^N} + \frac{\partial \dot{\vec{q}}_{t_0}^N}{\partial \vec{q}_{t_0}^N}}_{=0 \text{ (Hamilton's equations of motion)}} \right) + O(\Delta t^2)$$

time derivative of Jacobian: $\frac{d J^N(t, t_0)}{dt} = 0$

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$$d\vec{p}_t^N d\vec{q}_t^N = d\vec{p}_{t_0}^N d\vec{q}_{t_0}^N$$

and

$$\vec{\nabla}_{\vec{p}, \vec{q}} \cdot \vec{V} = 0 \quad (\text{follows from Hamilton's EOM})$$

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$$\frac{d}{dt} S(\vec{p}^N, \vec{q}^N, t) + \vec{V} \cdot \vec{\nabla}_{\vec{p}, \vec{q}} S(\vec{p}^N, \vec{q}^N, t)$$

$$\frac{d}{dt} S(\vec{p}^N, \vec{q}^N, t) = 0$$

probability density remains constant around a neighborhood of a point moving with the fluid

we can rewrite:

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$$\frac{\partial S(\vec{p}^N, \vec{q}^N; t)}{\partial t} + \vec{V} \cdot \vec{\nabla}_{\vec{p}^N, \vec{q}^N} S(\vec{p}^N, \vec{q}^N; t) = 0$$

$\frac{\partial}{\partial t}$

$$= \frac{\partial S(\vec{p}^N, \vec{q}^N; t)}{\partial t} + \sum_i \left[\frac{\partial \vec{p}_i}{\partial t} \frac{\partial S(\vec{p}^N, \vec{q}^N; t)}{\partial \vec{p}_i} + \frac{\partial \vec{q}_i}{\partial t} \frac{\partial S(\vec{p}^N, \vec{q}^N; t)}{\partial \vec{q}_i} \right]$$

$$= \frac{\partial S(\vec{p}^N, \vec{q}^N; t)}{\partial t} + \sum_i \left[-\frac{\partial H}{\partial \vec{q}_i} \frac{\partial S(\vec{p}^N, \vec{q}^N; t)}{\partial \vec{p}_i} + \frac{\partial H}{\partial \vec{p}_i} \frac{\partial S(\vec{p}^N, \vec{q}^N; t)}{\partial \vec{q}_i} \right] = 0$$

$$= \frac{\partial S}{\partial t} + [S, H] \rightarrow [,] \text{ Poisson-bracket}$$

other notation

$$\frac{\partial S}{\partial t} = [H, S] \rightarrow i \frac{\partial S}{\partial t} = \mathcal{L} S$$

$\mathcal{L}$ - Liouville operator

Liouville's theorem:

$$\frac{\partial S}{\partial t} = [H, S] \quad \text{or} \quad i \frac{\partial S}{\partial t} = \mathcal{L} S$$

$$\Downarrow$$

solution: $S(\vec{p}^N, \vec{q}^N; t) = e^{i \mathcal{L} t} S(\vec{p}^N, \vec{q}^N; 0)$

$$\text{stationary states: } \mathcal{L} S = 0 \stackrel{!}{=} [H, S]$$

time reversal invariance is satisfied by Liouville

theorem

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irreversible processes are not described

- decays to equilibrium state is not described

- but! if we accept Newtonian dynamics

$\rightarrow$ all we have is Liouvillian evolution

⑦
- an interesting result from the Liouville formalism
is that it is possible to develop a classical version
of the "Heisenberg" vs. "Schrödinger" picture

- consider a time-dependent average

$$\langle O(t) \rangle = \int d\vec{p}^N d\vec{q}^N O(\vec{p}^N, \vec{q}^N) g(\vec{p}^N, \vec{q}^N; t)$$

- $O(\vec{p}^N, \vec{q}^N)$ is some function expressing a
physical quantity

↓

↓

we can write

$$\langle O(t) \rangle = \int d\vec{p}^N d\vec{q}^N O(\vec{p}^N, \vec{q}^N) e^{-i\mathcal{H}t} g(\vec{p}^N, \vec{q}^N; 0)$$

- $e^{-i\mathcal{H}t}$ can be developed in a Taylor series

$$\rightarrow 1 - i\mathcal{H}t + i\frac{\mathcal{H}^2 t^2}{2} + \dots$$

- there will be terms with an even number of
derivatives, others will have an odd
number of derivatives

- consider:

$$\begin{aligned} & \int d\vec{p}^N d\vec{q}^N O(\vec{p}^N, \vec{q}^N) (-i\mathcal{H}) g(\vec{p}^N, \vec{q}^N; 0) \\ &= \int d\vec{p}^N d\vec{q}^N O(\vec{p}^N, \vec{q}^N) \left[\sum_i \left(\frac{\partial \mathcal{H}}{\partial \vec{q}_i} \frac{\partial}{\partial \vec{p}_i} - \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \frac{\partial}{\partial \vec{q}_i} \right) \right] \end{aligned}$$

integrating by parts this can be converted to

$$\begin{aligned} & - \int d\vec{p}^N d\vec{q}^N g(\vec{p}^N, \vec{q}^N) \left[\sum_i \left(\frac{\partial \mathcal{H}}{\partial \vec{q}_i} \frac{\partial O}{\partial \vec{p}_i} \right. \right. \\ & \quad \left. \left. - \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \frac{\partial O}{\partial \vec{q}_i} \right) \right] \end{aligned}$$

- terms with odd powers of t will switch sign,
- terms with even powers of t will not

$$\Downarrow$$

$$\langle O(t) \rangle = \int d\vec{p}^N d\vec{q}^N \left[e^{i\mathcal{L}t} O(\vec{p}^N, \vec{q}^N) \right] \delta(\vec{p}^N, \vec{q}^N; 0)$$

Equilibrium

$$\frac{\partial S}{\partial t} = \{S, H\} = 0$$

satisfied if $\delta(\vec{q}^N, \vec{p}^N) = \text{constant}$ for some region
and zero elsewhere

$$\text{ensemble average: } \langle \delta \rangle = \frac{1}{\omega} \int_{\omega} \delta(q, p) d\omega$$

$\Downarrow$
in this case any microstate is equally likely,
provided that the condition of being
in the chosen region is satisfied
"equal a priori probabilities"

microcanonical ensemble: volume defined by

$$E - \frac{\Delta}{2} \leq H(\vec{q}^N, \vec{p}^N) \leq E + \frac{\Delta}{2}$$

Microcanonical Ensemble

- macrostate (N, V, E) or $E - \frac{1}{2}\Delta$ to $E + \frac{1}{2}\Delta \Rightarrow$ hypershell

volume of phase space within hypershell

$$\omega = \int' d\vec{p}^N d\vec{q}^N$$

$$\delta(\vec{p}^N, \vec{q}^N) = \begin{cases} \text{const} & \text{if } E - \frac{\Delta}{2} \leq H(\vec{q}^N, \vec{p}^N) \leq E + \frac{\Delta}{2} \\ 0 & \text{otherwise} \end{cases}$$

ensemble average vs. time average

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ensemble average:

$$\langle S \rangle_{\text{ens}}(t) = \int d\vec{p}^N d\vec{q}^N S(\vec{p}^N, \vec{q}^N; t) f(\vec{p}^N, \vec{q}^N)$$

- since $\frac{dS}{dt} = 0$ at equilibrium $\Rightarrow \langle S \rangle_{\text{ens}}(t)$ is independent of time

time average:

$$\langle f \rangle_{\text{time}} = \frac{1}{T} \int_0^T f(\vec{p}^N, \vec{q}^N(t)) dt$$

can we switch order of averages?

- time average of ensemble average has to equal the ensemble average, since $\frac{dS}{dt} = 0$

$$\frac{1}{T} \int_0^T \langle S \rangle_{\text{ens}} dt = \langle S \rangle_{\text{ens}}$$

- what about the ensemble average of a time average?

~~$$\int d\vec{p}^N d\vec{q}^N S(\vec{p}^N, \vec{q}^N; t)$$~~

- start with time average of ensemble average

$$\frac{1}{T} \int_0^T \int d\vec{p}^N d\vec{q}^N S(\vec{p}^N, \vec{q}^N; t) f(\vec{p}^N, \vec{q}^N)$$

- use Liouville

$$\begin{aligned} &= \frac{1}{T} \int_0^T \int d\vec{p}^N d\vec{q}^N \left[e^{-i\mathcal{H}t} S(\vec{p}^N, \vec{q}^N; 0) \right] f(\vec{p}^N, \vec{q}^N) \\ &= \frac{1}{T} \int_0^T \int d\vec{p}^N d\vec{q}^N S(\vec{p}^N, \vec{q}^N; 0) \left[e^{i\mathcal{H}t} f(\vec{p}^N, \vec{q}^N) \right] \\ &= \int d\vec{p}^N d\vec{q}^N S(\vec{p}^N, \vec{q}^N; 0) \left[\frac{1}{T} \int_0^T dt e^{i\mathcal{H}t} f(\vec{p}^N, \vec{q}^N) \right] \end{aligned}$$

- the time average $\frac{1}{T} \int_0^T dt e^{i\mathcal{H}t} f(\vec{p}^N, \vec{q}^N)$ depends on initial positions $\vec{p}^N, \vec{q}^N$, in general

- however if it does not depend on $\vec{p}^N, \vec{q}^N$

$\Rightarrow$ we have ~~$\int d\vec{p}^N d\vec{q}^N S(\vec{p}^N, \vec{q}^N; 0)$~~ then $\mathcal{H}$

$$\int d\vec{p}^N d\vec{q}^N \delta(\vec{p}^N, \vec{q}^N; 0) \frac{1}{T} \int_0^T dt e^{i\omega t} f(\vec{q}, \vec{p}) = \frac{1}{T} \int_0^T dt e^{i\omega t} f(\vec{q}, \vec{p}) = \langle f \rangle_{\text{time}} \quad (10)$$

$$\Downarrow$$

$$\langle f \rangle_{\text{av}} = \langle f \rangle_{\text{time}}$$

- under what conditions do we expect this to hold?
- if $T \rightarrow \infty$ system will visit all points of phase space allowed by macrostate constraints
- assumption: equilibrium systems, when measured experimentally, are measured such that $T \rightarrow \infty$
- $\Rightarrow$ ergodicity: assumption that given enough time the system will visit all possible microstates consistent with particular macrostate
- exceptions:
 - coupled harmonic oscillators
 - ~~do~~ - normal modes are decoupled
 - glasses - "infinitely slowly moving liquids"

What can prevent ergodicity?

consider equations of motion:

$$\frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{q}_i} \quad \frac{d\vec{q}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i}$$

$$\Downarrow$$

$$dt = -\frac{d\vec{p}_{1x}}{dH/d\vec{q}_{1x}} = \frac{d\vec{q}_{1x}}{dH/d\vec{p}_{1x}} = \frac{d\vec{p}_{2x}}{dH/d\vec{q}_{2x}} = \dots$$

$6N-1$ equations which give $6N-1$ constants of motion C_i (examples: energy, momentum, ...)

$\rightarrow$ in principle all of them could constrain phase space $\rightarrow$ ergodic theory seeks to determine which constants constrain phase space

- connection of mechanics of microcanonical ensemble and thermodynamics

- ω - allowed region in phase space

ω_0 - volume of one microstate in phase space

$\Downarrow$

number of microstates: $\Gamma = \frac{\omega}{\omega_0}$

$$S = k \ln \Gamma = k \ln(\omega/\omega_0)$$

- determine ω_0 from ~~quantum~~ quantum mechanical considerations

- units of ω_0 - action ($pq \rightarrow \frac{\text{mass distance}^2}{\text{time}}$
 $\rightarrow \text{energy} \times \text{time}$)

- unit of action: h or $\hbar$

Examples

- classical ideal gas

- accessible volume: $\omega = \int d\vec{q}^N d\vec{p}^N$

- two restrictions: 1) positions $\vec{q}$ lie in volume V

$$2) \quad E - \frac{\Delta}{2} \leq H(\vec{p}^N, \vec{q}^N) \leq E + \frac{\Delta}{2}$$

$$\omega = V^N \int_{E - \frac{\Delta}{2} \leq H(\vec{p}^N, \vec{q}^N) \leq E + \frac{\Delta}{2}} d\vec{p}^N = V^N \int_{E - \frac{\Delta}{2} \leq \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \leq E + \frac{\Delta}{2}} d\vec{p}^N$$

- momentum integral: volume of hypershell (spherical)

between radii $\sqrt{2m(E - \frac{\Delta}{2})}$, $\sqrt{2m(E + \frac{\Delta}{2})}$

quote result: $\Delta \left(\frac{m}{2E}\right)^{1/2} \left\{ \frac{2\pi^{3N/2}}{[(3N/2)-1]!} (2mE)^{\frac{(3N-1)}{2}} \right\}$

$$\omega \approx \frac{\Delta}{E} V^N \frac{(2\pi m E)^{3N/2}}{[(3N/2)-1]!} \Rightarrow \omega_0 = h^{3N}$$

- recall: when we counted microstates we used a quantum mechanical system, giving the number of microstates

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$$\Omega = \frac{3N}{2} \frac{V}{E} \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!}$$

(particle in a box) $\Rightarrow$ hence h is present in expression
to obtain ω , only classical arguments were used, so
 h cannot enter

$\Rightarrow$ generally: $\omega_0 = h^{\tilde{N}}$ $\tilde{N}$ - number of degrees of freedom

- consider single particle: $N=3$

$$\mathcal{E}(p) = \frac{1}{h^3} \int d\vec{q} d\vec{p} = \frac{V}{h^3} \frac{4\pi}{3} p^3$$

$$g(p) dp = \frac{d\mathcal{E}(p)}{dp} dp \sim \frac{V}{h^3} 4\pi p^2 dp$$

alternatively one can write in terms of energy

$$\mathcal{E}(E) \sim \frac{V}{h^3} \frac{4\pi}{3} (2mE)^{3/2}$$

$$g(E) dE = \frac{d\mathcal{E}(E)}{dE} dE = \frac{V 2\pi (2m)^{3/2}}{h^3} E^{1/2} dE$$

- simple harmonic oscillator

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

$$\text{solution: } q = A \cos(\omega t + \phi)$$

$$p = -m A \sin(\omega t + \phi)$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$E = \frac{m\omega^2 A^2}{2}$$

- to find trajectory eliminate t

$$\Rightarrow \frac{1}{\omega} \left[\cos\left(\frac{q}{A}\right) - \phi \right] = \left[\sin\left(-\frac{p}{mA}\right) - \phi \right] \frac{1}{\omega}$$

$$\Rightarrow \cos\left(\frac{q}{A}\right) = \sin\left(-\frac{p}{mA}\right)$$

to find trajectory notice that

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$$\cos(\omega t + \phi) = \frac{q}{A}$$

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

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

$$\text{max } E = \frac{m\omega^2 A^2}{2}$$

$$\frac{q^2}{m\omega^2} + \frac{p^2}{2mE} = 1$$

trajectory is elliptical with area $\frac{2\pi E}{\omega}$

- consider oscillator whose energy is restricted to be between $E - \frac{\Delta}{2}$ and $E + \frac{\Delta}{2}$

$$\oint dp dq = \frac{2\pi \Delta}{\omega}$$

- according to quantum mechanics, energies of a harmonic oscillator are $E_n = \hbar\omega(n + \frac{1}{2})$

each E_n corresponds to closed trajectories

area of phase space between two such trajectories

$$\frac{2\pi}{\omega} (E_{n+1} - E_n) = h$$

- number of allowed energy values in interval Δ

$$N = \frac{\Delta}{\hbar\omega}$$

$$\omega_0 = \frac{(2\pi\Delta/\omega)}{(\frac{\Delta}{\hbar\omega})} = h$$

phase space volume $\nwarrow$ number of states in interval

- for N harmonic oscillators: h^N

rough quantum argument

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dimensions of phase space $\rightarrow$ position $\times$ momentum
uncertainty principle $\Rightarrow \Delta q \Delta p \sim \hbar$

Quantum Probability Density

- phase space can not be defined $\rightarrow [q, p] = i\hbar$
position and momentum do not commute
- however, we can define a probability density operator

$\hat{\rho}(t) \rightarrow$ contains all information about the state of the system $\rightarrow$ positive definite, Hermitian

$\langle O(t) \rangle = \text{Tr } \hat{O} \hat{\rho}(t)$ - expectation value as a function of time

$$\text{Tr } \hat{\rho}(t) = 1 \quad (\text{normalized on})$$

- evaluate expectation value using basis $|m_i\rangle$

$$\langle O(t) \rangle = \sum_{i,j} \langle m_i | \hat{O} | m_j \rangle \langle m_j | \hat{\rho}(t) | m_i \rangle$$

- evaluate expectation value using basis of $\hat{O}$

$$\hat{O} |o_i\rangle = O_i |o_i\rangle$$

$$\langle O(t) \rangle = \sum_i \langle o_i | \hat{O} | o_i \rangle \langle o_i | \hat{\rho}(t) | o_i \rangle$$

$$= \sum_{i,j} O_i \delta_{ij} \langle o_j | \hat{\rho}(t) | o_i \rangle$$

$$= \sum_i O_i \langle o_i | \hat{\rho}(t) | o_i \rangle$$

- probability that system is in state i at time t

$$P_i(t) = \langle o_i | \hat{\rho}(t) | o_i \rangle$$

express $\hat{S}(t)$ in the eigenbasis of the

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Hamiltonian

$$\hat{S}(t) = \sum_{i,j} \cancel{e^{-i\frac{Ht}{\hbar}}} |v_i\rangle \langle v_j| e^{-i\frac{Ht}{\hbar}} \hat{S} e^{i\frac{Ht}{\hbar}} |v_j\rangle \langle v_j|$$

$$= \sum_{i,j} |v_i\rangle e^{-i\frac{t}{\hbar}(E_i - E_j)} S_{ij} \langle v_j|$$

$$S_{ij} = \langle v_i | \hat{S} | v_j \rangle$$

stationary $\hat{S}_s$ is one for which $\frac{\partial \hat{S}_s}{\partial t} = 0$

is only possible if $S_{ij} = 0$ for $i \neq j$

(this statement is only valid for non-degenerate systems)

it follows that $\hat{S}_s = f(\hat{H})$, it is a function of the Hamiltonian — in this case both $\hat{H}$ and $\hat{S}$ are diagonal in energy representation

- to generalize to degenerate systems, one must consider other invariants of motion, which commute with each other and the Hamiltonian

- in this case $\hat{S}_s = f(\hat{H}, \hat{I}_1, \dots, \hat{I}_n)$

$\hat{I}_1, \dots, \hat{I}_n$ operators corresponding to invariants