2. ELEMENTS OF ENSEMBLE THEORY

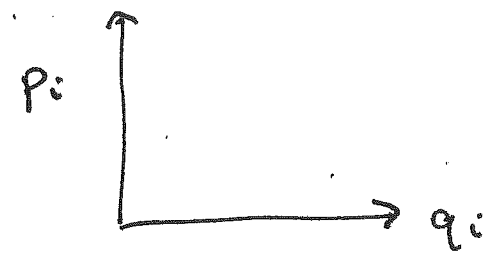
Idea of replacing the time average by the average over many identical macrostates, distributed randomly amongst the microstates

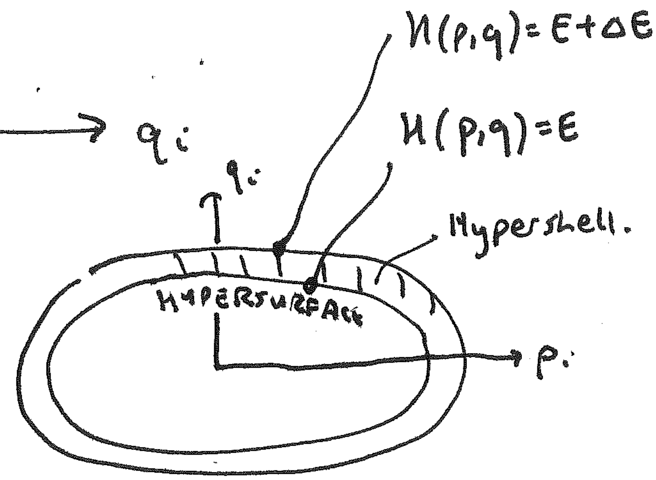
$$\overline{A} = \underset{T\to\infty}{Lt} \frac{1}{T}\int_0^T A(t)\,dt \qquad \text{Time average}$$

$$\langle A\rangle = \sum p_i \langle i|A|i\rangle \qquad \text{Ensemble Average.}$$

We will examine this through classical mechanics

PHASE SPACE





$$\left.\begin{array}{l} (q_1 \cdots q_{3N}, p_1 \cdots p_{3N}) \\[1em] \dot{q}_i = \dfrac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{array}\right\}$$

Density of states in phase space $= \rho(q_i, p_i)$

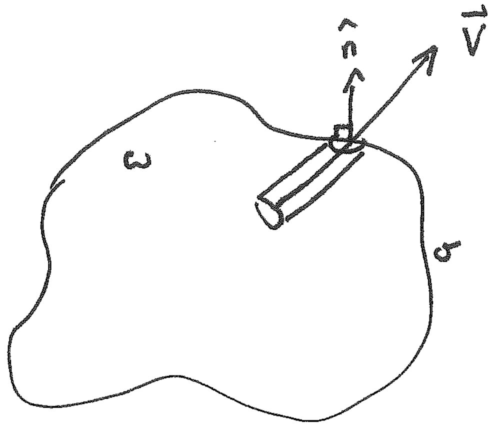
$d\omega = d^{3N}q \, d^{3N}p$ = volume integral in phase space.

$$\langle f \rangle = \frac{\int f(q,p)\,\rho(q,p)\,d\omega}{\int \rho(q,p)\,d\omega}$$

In a stationary ensemble $\frac{d\rho}{dt}$ at fixed q,p is fixed

$$\left.\frac{\partial \rho}{\partial t}\right|_{q,p} = \text{constant}$$

& $\langle f \rangle$ is independent of time.



2.1 Liouville's Theorem

Phase space is incompressible

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0$$

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial t} \int \rho \, d\omega = \int \frac{\partial \rho}{\partial t} \, d\omega$$ change in number of states inside ω

6N dimension divergence

$$\text{Flow out} = \int \rho (\vec{v} \cdot \hat{n}) \, d\sigma = \int \nabla \cdot (\rho v) \, d\omega$$ By Divergence Thm

$$= -\frac{\partial n}{\partial t} = -\int \frac{\partial \rho}{\partial t} \, d\omega$$

$$\Rightarrow \quad \boxed{\nabla \cdot (\rho \vec{v}) + \frac{\partial \rho}{\partial t} = 0}$$ Continuity

Now lets evaluated the continuity equation using Hamiltonian dynamics.

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

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

$$\Rightarrow \boxed{\frac{\partial \rho}{\partial t} + \sum\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) = \frac{d\rho}{dt} = 0}$$

or $$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

$$[\rho, H] = \sum\left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right)$$ = Poisson bracket of ρ with H.

But equilibrium means $\dfrac{\partial \rho}{\partial t} = 0$, so this in turn

implies $[\rho, H] = 0$. One way to satisfy this

is simply ρ = constant. Another is to have

$$\rho(q,p) = \rho[H(q,p)]$$

Since H is a constant of the motion, ρ is too.

There are various kinds of distribution.

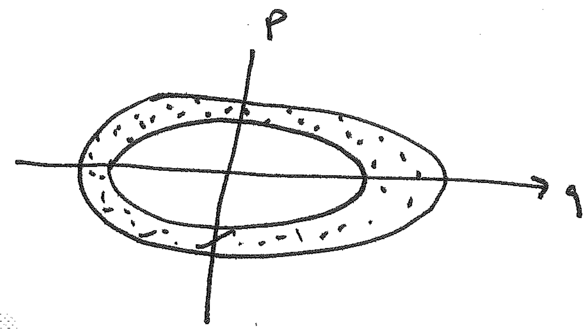
<u>Microcanonical</u> $\rho = \rho_0 \, \delta_\Delta(H(q,p) - E)$

$$\delta_\Delta(x) = \begin{cases} 1 & x \in [-\Delta/2, \Delta/2] \\ 0 & \text{otherwise} \end{cases}$$

<u>Canonical</u> $\rho(q,p) = \exp\left(-\dfrac{H(q,p)}{k_B T}\right)$.

Microcanonical

$$\rho(q,p) = \begin{cases} \text{Const} & E-\Delta/2 \le H \le E+\Delta/2 \\ 0 & \text{otherwise.} \end{cases}$$



$\langle f \rangle$ = ensemble average of f

= time average (ensemble avge) ← time independent.

= ensemble avge (time avge) ← Averaging over t + ensemble indpdt

= time avge of f Subtle — If ergodic.

= f_{exp} if experiment averages over times long enough.

$\Gamma = \omega / \omega_0$ $\qquad$ ω_0 = unit of phase space.

$S = k_B \ln [\omega/\omega_0]$

Now the dimensions of ω_0 are $[\omega_0] = (\text{angular momentum})^{3N}$

From the classical gas we learned that

$$\frac{\omega}{\omega_0} = d^{3N} n = V^{3N} \frac{d^{3N} k}{(2\pi)^{3N}} = V^{3N} \frac{d^{3N} p}{(2\pi\hbar)^{3N}}$$

$$= \frac{V^{3N} d^3 p}{(h)^{3N}} = \frac{\omega}{\omega_0}$$

$\Rightarrow$ $\boxed{\omega_0 = h^{3N}}$.

PLANCK'S CONSTANT SETS THE BASIC UNIT OF PHASE SPACE

p.s. We found $\Gamma = \frac{\partial \Sigma_N}{\partial E} \Delta = \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \left(\frac{\Delta}{E}\right) \left(\frac{V}{h^3}\right)^N$.

e.g. Simple Harmonic Oscillator

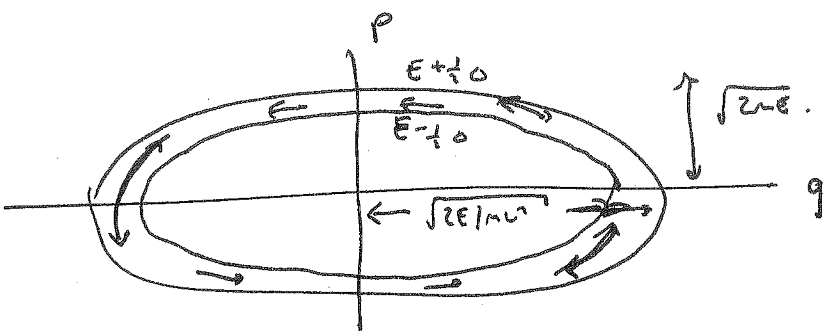
$$H(q,p) = \frac{1}{2}kq^2 + \frac{1}{2m}p^2$$

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

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

$$E = \frac{1}{2}m\omega^2 A^2$$

$$\frac{1}{2}m\omega^2 q^2 + \frac{p^2}{2m} = E \iff \frac{q^2}{(2E/m\omega^2)} + \frac{p^2}{(2mE)} = 1$$



$A = \pi ab$
$= 2\pi\left(\frac{E}{\omega}\right)$

$$\int dq\,dp = 2\pi\left(\frac{E+\frac{1}{2}\Delta}{\omega}\right) - 2\pi\left(\frac{E-\frac{1}{2}\Delta}{\omega}\right) = \frac{2\pi\Delta}{\omega}$$

$E - \frac{1}{2}\Delta \leq H \leq E + \frac{1}{2}\Delta$

QM $\quad E = \hbar\omega\left(n + \frac{1}{2}\right)$

$\Delta E = \hbar\omega \qquad \Delta\omega = 2\pi\frac{\hbar\omega}{\omega} = h$.

N harmonic oscillators $\quad \omega_0 = h^N$.

Quantum States and Phase Space

$(\Delta q \Delta p)_{min} \gtrsim \hbar$

In any phase space of 2N dimensions, the corresponding "volume of uncertainty is then $\sim \hbar^N$

Phase space is split into elementary cells of volume $\sim \hbar^N$.

Detailed calculation shows that $\omega_0 = h^N$.

e.g photons in a cavity

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

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

corresponds to the Raleigh expression.

$$\# = V\left(\frac{4\pi \nu^2}{c^3}\right) d\nu = \frac{d\omega}{h^3} = \frac{d\omega}{\omega_0}.$$

In practice both expressions $\times 2$ to account for two polarizations.