Ensemble average vs time average

$F(p,q)$: some dynamical variable
→ no explicit time dependence

Ensemble average $\quad \langle F \rangle(t) = \frac{1}{n} \sum_{k=1}^{n} F^{k}(t)$

$F^{k}(t)$ – value of this quantity for the k-th member of ensemble

When microstates are labelled by continuous parameters – e.g., (p_a, q_a) for molecules of gas

$$\sum_{k} \longrightarrow \int d^{Nd}p \, d^{Nd}q$$

However, technically the number of points in any volume of phase space is infinite.

To get a reasonable definition need another assumption.

⇒ * Divide up phase space into cells – each with a volume h_0^{Nd}
* h_0 is a (dimensional) quantity introduced by hand
* Declare: all points in this cell correspon
to the same state[illegible]

$$\sum_{K} \longrightarrow \int \frac{d^{Nd}p\, d^{Nd}q}{h_0^{Nd}}$$

In classical theory, h_0 is some artefact used to <u>count states</u>

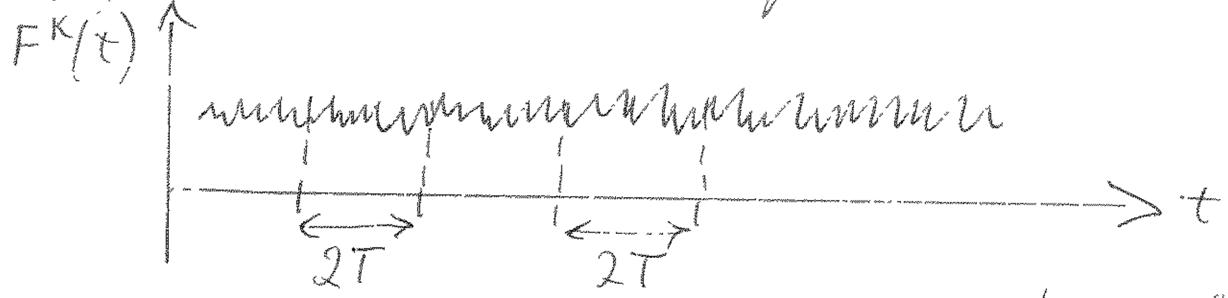
We will see that in quantum mechanics h_0 becomes <u>Planck constant</u>

Equilibrium $\langle F(t) \rangle$ is time independent

Consider now the behavior of a single member of the ensemble:

$F(p, q)$ clearly evolves in time

Even in equilibrium an individual $F^K(t)$ will have time dependence



Break up the time into <u>large</u> intervals of $2T$ each. The <u>time average</u> is then defined as

Time average: $$\underbrace{\{F^K(t)\}}_{} \equiv \frac{1}{2T} \int_{t-\Theta}^{t+\Theta} dt'\, F^K(t')$$

Note, $$\frac{1}{\eta} \sum_{K} \{F^K(t)\} = \frac{1}{\eta} \sum_{K} \frac{1}{2T} \int_{t-\Theta}^{t+\Theta} dt'\, F^K(t') =$$

$$= \frac{1}{2T} \int_{t-\Theta}^{t+\Theta} dt' \left[\frac{1}{\eta} \sum_{K} F^K(t')\right] = \{\langle F^K(t) \rangle\}$$

Stationary Situations

In these situations a typical $F(P,q)$ has the property:

* The behavior of $F_K(t)$ $[F_K(P,q,t)]$ is similar for any sufficiently large time interval "2T".

Ergodic Hypothesis

For "typical" systems the function $F_K(t)$ for each system in the ensemble will pass through all the values accessible to it in the course of a sufficiently long time.

* If this holds — for some given member of ensemble, and for large enough T, snapshots in time intervals

$$\left.\begin{matrix}(t_0 - T,\ t_0 + T)\\ (t_0 + T,\ t_0 + 2T)\end{matrix}\right) \rightarrow \text{should look very similar}$$

* Similarly, each such time interval 2T should be representative of a member of the ensemble

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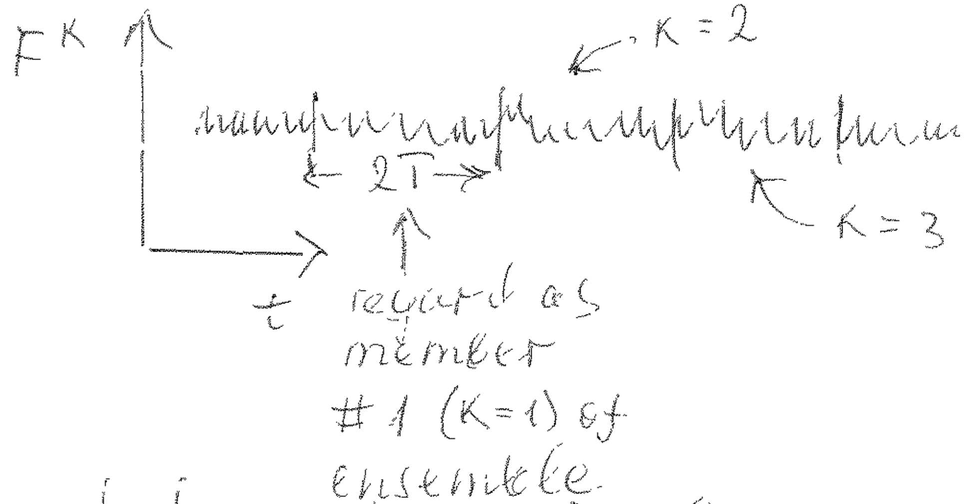


Provided we choose T large enough, time average same for all members of ensemble.

(1) $\{F^K(t)\} = \{F\}$ independent of K

Similarly, ensemble average is the same for all time intervals

(2) $\langle F(t)\rangle = \langle F\rangle$ independent of time

Ensemble average of (1)

$$\langle \{F^K(t)\}\rangle = \{F\}$$

Time average of (2)

$$\{\langle F(t)\rangle\} = \langle F\rangle$$

$$\Rightarrow \boxed{\{F\} = \langle F\rangle}$$ → Time average = = ensemble average

Comments:

* There are many systems which are not ergodic
→ these are integrable

* while one expects most interacting systems to be ergodic → hard to prove! → only 4 examples known

The Basic postulate → apriori probability

How we determine probabilities?
In Stat Mech the basic postulate is

> All states (microstates) which can lead to a specified macrostate are equally probable

Example: 3 spins in an external H

$$\text{energy: } \varepsilon = \begin{cases} +\mu H & \Uparrow \\ -\mu H & \Downarrow \end{cases}$$

Suppose total energy is $E = +\mu H$.
This is the only specification of the macrostates. Possible microstates & probability:

spin 1	spin 2	spin 3	probability
+	+	−	1/3
+	−	+	1/3
−	+	+	1/3

Important: probability of an individual spin is not the same for **up** and **down** state:

$$\left.\begin{array}{l} \text{In fact, prob. to be } + \text{ is } 2/3 \\ \text{prob. to be } - \text{ is } 1/3 \end{array}\right\} \text{ for single spin!}$$

27b)

Constraints on Probabilities

Microcanonical ensemble - all states of the same E are equally probable.

If system is composed of many subsystems: does this mean that each subsystem is equally likely to be in each of its possible states?

See Example with spins of 3 particles (p. 27a)

$$\left.\begin{array}{l}\text{Generally,}\\ \text{Probability for}\\ \text{occurance in}\\ \text{some state}\end{array}\right\} = \frac{1}{N}\left(\begin{array}{l}\text{nu. of members}\\ \text{of ensemble}\\ \text{in this state}\end{array}\right)$$

when apart from E, some other parameter is specified, $\{y_k\}$

$$\Rightarrow \quad \Omega(E, y_k) = \left\{\begin{array}{l}\text{subset of all states}\\ \text{of energy } E\\ \text{condition } y_k\end{array}\right.$$

$$P(y_k) = \frac{\Omega(E, y_k)}{\Omega(E)}$$

Systems with Continuous States

For systems with states specified by a set of continuous variable, e.g., particles in a large box — we need to modify the statement

Naively, in equilibrium

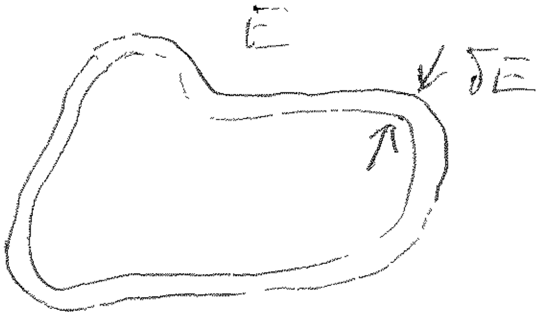
$$\rho(p, q) = c\,\delta[H(p, q) - E]$$

To make better sense of this we modify this by

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

$\Omega(E)$ = nu. of states with energy in the window $(E - \delta E, E + \delta E)$ =

$$= \int_{\delta E} d^{Nd}p \, d^{Nd}q$$



26)

Microcanonical Ensemble (NR gas)

Appropriate for <u>isolated</u> systems

$$\rho(\vec{X}) = \begin{cases} C\,\delta[H(\vec{X}) - E] & \text{for } \forall \vec{X} \\ 0 & \text{otherwise} \end{cases}$$

C - normalization factor

$E - \delta E \leq H(\vec{X}) \leq E + \delta E \Rightarrow$ probability is the same

Example:

N distinguishable particles in d-space dimensions (e.g. ions in crystal)

Basic unit in phase space volume: $\sqrt{h}$

$$\sum_{\substack{\text{points in} \\ \text{phase space}}} \longrightarrow \frac{1}{(h^{1/2})^{2Nd}} \int d^{2Nd} X$$

$\Rightarrow$ **Normalization of Ω:**

$\tilde{\Omega}$ - volume not normalized

$\Omega = \dfrac{\tilde{\Omega}}{(h^{1/2})^{Nd}}$ - normalized volume

why? $\longrightarrow \Omega = \dfrac{1}{A} \int d^{2Nd} X = \dfrac{[pq]^{Nd}}{A} = \dfrac{\left[\frac{kg\cdot m}{s}\right]^{2Nd}}{A}$

$\Rightarrow \left\{ \begin{array}{l} A = \left[\frac{kg\cdot m^2}{s}\right]^{Nd} \\ [h] = \left[\frac{kg\cdot m^2}{s}\right] \end{array} \right\}$ [action] $\equiv$ [energy][time]

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$\Rightarrow A = h^{Nd}$ or $(\sqrt{h})^{2Nd}$

Because of equal probabilities

$\Downarrow$

$\Omega \sim$ nu. of states

$$\Rightarrow \text{Set} \quad \Omega(E) = \frac{1}{h^{Nd}} \int_{E \le H(X) \le E+\delta E} d^{2Nd}X$$

to make Ω -dimensionless $\Rightarrow \times [\text{action}]^{-3N}$

$\Rightarrow$ counts nu. of particles in energy shell

Note: factor $1/h^{Nd}$ in front of $\int$, because $\Omega(E)$ must be dimensioless for entropy.

Define entropy:

$$S = k_B \ln \Omega(E)$$

when identical particles:

$$\left.\begin{matrix} \text{particle } 1 \text{ at } \vec{x}_1 \\ \text{— '' — } 2 \text{ at } \vec{x}_2 \end{matrix}\right\} \equiv \left\{\begin{matrix} \text{particle } 2 \text{ at } \vec{x}_1 \\ \text{— '' — } 1 \text{ at } \vec{x}_2 \end{matrix}\right.$$

$$\Rightarrow \Omega_{\text{identical}} = \frac{1}{N!} \Omega_{\text{distinguishable}}$$

δE = Tolerance (not needed in classical treatment)

2b)

E - surface: $\Gamma(E)$ = no. of points with E

lume of
phase space : $\Omega(E)$ = no. of points in shell

For discrete spectrum, $\Omega(E)$ is not
a smooth function

However, in thermo limit, when

$$\frac{E}{N} < \delta E << E$$

δE should be irrelevant

(In fact $\frac{\delta E}{E} = \mathcal{O}\left(\frac{1}{\sqrt{N}}\right)$

29)

Volume and area of n-dimensional sphere (hypersphere)

R - radius; Volume:

$$V_n(R) = \int_{x_1^2+\dots+x_n^2 \le R^2} \cdots \int dx_1 \cdots dx_n = C_n R^n \quad (1)$$

→ just from a dimensional analysis

Corresponding area: $S_{n-1}(R)$ (locus points $x_1^2+\dots+x_n^2 = R^2$)

We can add shells:

$$\begin{cases} V_n(R) = \int_0^R S_{n-1}(r)\, dr & (2) \\ S_{n-1}(R) = \dfrac{dV_n(R)}{dR} = n C_n R^{n-1} & (3) \end{cases}$$

Need to compute $C_n \Rightarrow$ so, equate (1) = (2) and use (3)

$$\int_{x_1^2+\dots+x_n^2 \le R^2} \cdots \int dx_1 \cdots dx_n = n C_n \int_0^R r^{n-1} dr \quad (4)$$

→ solve in rectangular or hyperspheric coordinates

In n-dimensions: $dx_1 \dots dx_n = r^{n-1} dr \underbrace{d\Omega_{n-1}}_{\text{all angular factors}}$ (5)

For example: for $n=2 \Rightarrow d\Omega_1 = d\theta$
$d=2 \Rightarrow d\Omega_2 = \sin\theta\, d\theta\, d\varphi$ } n-1 angular variables in n-dim.

$\Rightarrow$ all ang. variables sit in constants (if integrate over spherically-symmetric function):