I MICROCANONICAL ENSEMBLE

§1. FOUNDATIONS OF STATISTICAL PHYSICS

Goal : Description of phenomena in
macroscopic world

- electrons in metals and insulators
- superconductivity and superfluidity
- magnetism
- different phases of water (ice, liquid, vapor)
- other phase transitions
- gases
- liquids
- amorphic systems, alloys
- polymers, membranes
- biological systems (DNA, aminoacids, ...)
- ....

I Common feature :

huge number of components / particles

$$\sim 10^{18} - 10^{24} \ \frac{1}{cm^3}$$

①

Amount of matter in SI unit system is
given in __mol__   [20/05/2019]
              (from molecule)

A mol of matter contains __exactly__

$$6,02214076 \cdot 10^{23}$$

structural elements (need to be pointed out)

Avogadro number   exact value by definition

$$N_A = 6,02214076 \cdot 10^{23} \quad mol^{-1}$$

[A day of mol is celebrated on oct. 23
            10/23 $6^{\underline{00}}$ am ÷ $6^{\underline{00}}$ pm]

N_A — is approximately a number of ^{12}C
        carbon isotop atoms in $0,012$ kg
        of carbon (old definition of mol).

www.gum.gov.pl

Examples

(i) 18 g of water (18 ml) — 1 mol H_2O

(ii) 22,4 l of the air — 1 mol of O_2 and N_2
                                                together

(iii) 7,8 mld people on the Earth
  (ex. 7,8 bilion) $7,8 \cdot 10^{9}$ — $1,3 \cdot 10^{-14}$ mol of
                                                                    people

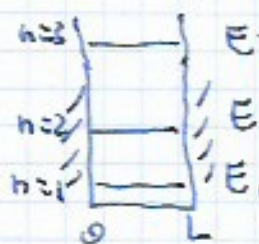(iv) visible Universe $3 \cdot 10^{23}$ stars — 1 mol of stars

2

II. Common feature:

Quantum systems $\Rightarrow$ discrete energy levels

Example

•) infinite quantum well

$$\hat{H} = \frac{\hat{P}^2}{2m}$$

$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$

$n = 1, 2, 3, \ldots$

$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(n \frac{\pi}{L} x\right)$

•) harmonic oscillator

$$\hat{H} = \underbrace{\frac{\hat{P}^2}{2m}}_{E_{kin}} + \underbrace{\frac{k}{2} x^2}_{E_{pot}}$$
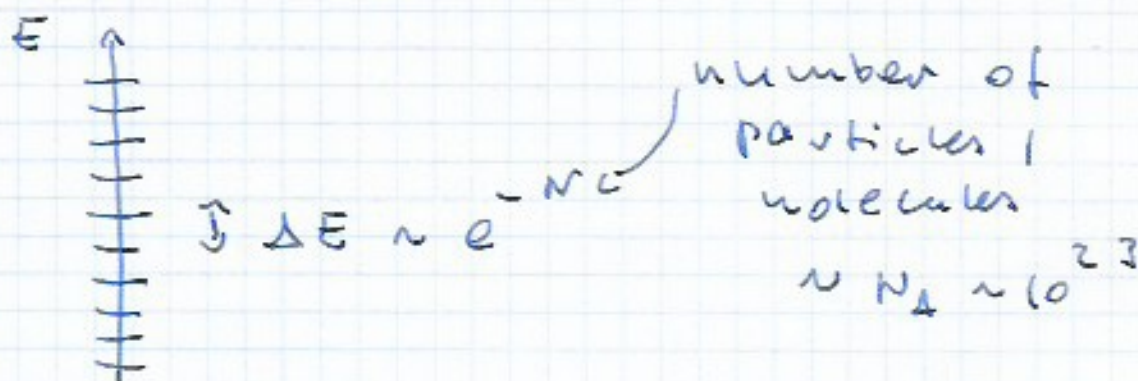
$\omega^2 = \frac{k}{2}$

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

$n = 0, 1, 2, \ldots$

$\psi_n(x) = N_n \, \mathcal{H}_n(x) \, e^{-\frac{m^2\omega^2}{\hbar^2} \frac{x^2}{2}}$

$\square$

In macroscopic systems distances between discrete levels are exponentially small

$$\hat{J} \quad \Delta E \sim e^{-Nc}$$

number of particles / molecules

$\sim N_A \sim 10^{23}$

Hence, an arbitrary small (weak) perturbation (any interaction with environment) yields transitions from E to $E \pm \Delta E$ almost continually in time.

See also: Ten theorems about quantum mechanical measurements, N.G. van Kampen, Physica A 153, 97–113 (1988)

③

Microscopic description of many body-system
(mechanical)

Quantum mechanics

$$\Psi = \Psi(t, \underbrace{\bar{r}_1, \ldots \bar{r}_N})$$

complex
- wave function

$\sim 10^{23}$ variables

Unitary
evolution

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \qquad - \text{ Schrödinger eq.}$$

$$|\Psi(t, \bar{r}_1, \ldots \bar{r}_N)|^2 d_{3N} r = \text{ probability to find } N$$
$$\text{particles at } \bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N$$
$$\text{at time } t.$$

this probability changes in time. The knowledge
of the wave function seems to be impractical.

Classical mechanics

phase
space

position $\bar{\ell}_i$

$$(\bar{\ell}, \bar{p}) = (\underbrace{\bar{\ell}_1, \ldots \bar{\ell}_N, \bar{p}_1 \ldots \bar{p}_N})$$

6N degrees of freedom
$\sim 10^{23}$

momentum

$$\bar{p}_i = m \frac{d\bar{\ell}_i}{dt}$$

Newton's equation

$$\frac{d\bar{p}_i}{dt} = \bar{F}_i + \sum_{j \neq i} \bar{F}_{ij}$$

$$i = 1, \ldots, N$$
$$10^{23}$$

Even if we know $(\bar{\ell}_i(t), \bar{p}_i(t)) \; \forall t$
this seems to be impractical.

④

Important observation

Though $\Psi = \Psi(t)$, $(\vec{q}(t), \vec{p}(t))$ are changing in time due to chaotic motion of particles and an interaction with the environment some <u>macroscopic properties</u> of the system <u>do not change</u>

thermodynamic equilibrium

$$T, \; P, \; V, \; n = \frac{N}{V} = const.$$

temperature   pressure   volume   density

More precisely

Small fluctuations in time around the average

equilibrium
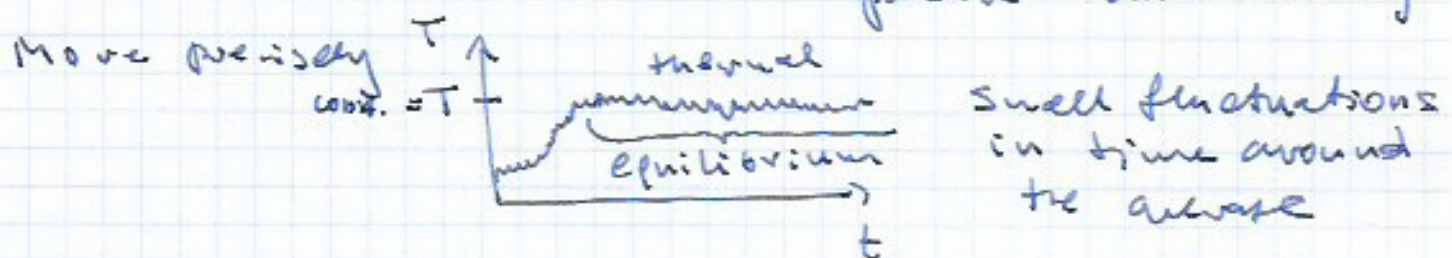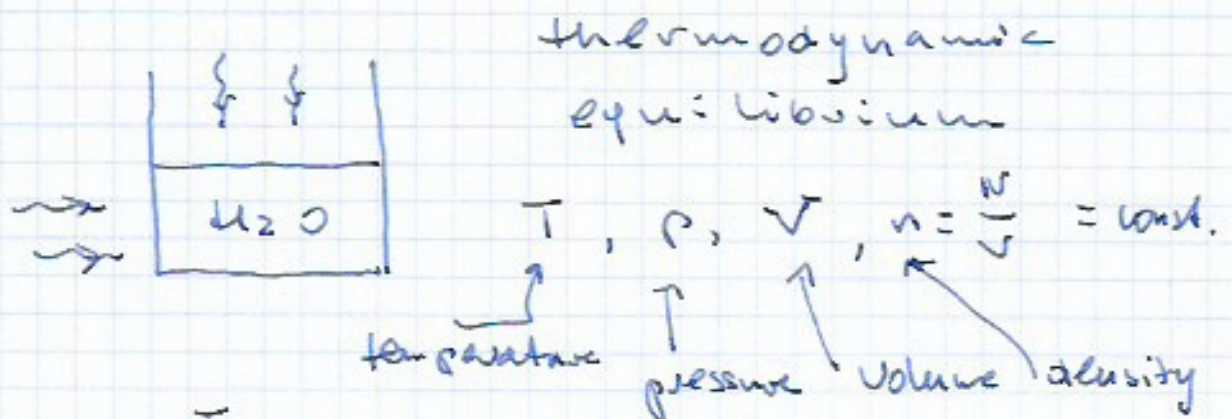
<u>Thermodynamics</u> (hydrodynamics) deals with a macroscopic description of many-body systems providing relationships between macroscopic quantities determined in experiments

(P, V) — (pressure, volume)
$(\vec{B}, \vec{M})$ — (magnetic induction, magnetization)
$(\vec{E}, \vec{P})$ — (electric field intensity, polarization)
(γ, L) — (surface tension, width)
:

> Statistical physics wants to derive
> thermodynamic relations from
> microscopic equations of motion.

Two important concepts

(i) <u>Microstate</u> (mechanical state) — a state of a system at time t given by $\Psi(t, \vec{r}_1 ... \vec{r}_N)$ or $(\vec{q}(t), \vec{p}(t))$ or any other quantities describing the system as much accurately as possible.

(ii) <u>Macrostate</u> (thermodynamical state) — a state of a system described by few relevant macroscopic (thermodynamic) variables:

either

$(U, V, N, ...)$ — <u>extensive variables</u>

internal energy, volume, number of particles

(proportional to number of particles)

or

$(T, P, \mu, ...)$ — <u>intensive variables</u>

temperature, pressure, chemical potential

(independent from a number of particles)

or their combinations.

⑥

Example: two-level system

binary alloy, spins 1/2, atoms on optical lattices,
coins

Consider N spins 1/2

Microstate: one of 2^N combinations of
spin arrangements

$$\{ \uparrow_1 \downarrow_2 \downarrow_3 \downarrow_4 \uparrow_5 \uparrow_6 \downarrow_7 \downarrow_8 \uparrow_9 \uparrow_{10} \downarrow_{11} \cdots \cdots \uparrow_{N-1} \downarrow_N \}$$

Macrostate: macroscopic variable $M = N_\uparrow - N_\downarrow$,
a state with a fixed M

E.g. $\underline{N = 3}$, $2^3 = 8$ - microstates

$$\{\uparrow\uparrow\uparrow\} \qquad\qquad M = 3$$

$$\{\downarrow\uparrow\uparrow\}, \{\uparrow\downarrow\downarrow\}, \{\uparrow\downarrow\uparrow\} \qquad M = 1$$

$$\{\uparrow\downarrow\downarrow\}, \{\downarrow\downarrow\uparrow\}, \{\downarrow\uparrow\downarrow\} \qquad M = -1$$

$$\{\downarrow\downarrow\downarrow\} \qquad\qquad M = -3$$

four possible macrostates

Two macrostates $M = \pm 1$ are realized by
three microstates, correspondingly.

More during tutorials. □

⑦

§2. BASIC POSTULATE OF STATISTICAL PHYSICS

We have seen that for a given macrostate can be realized by many different microstates.

Which one does the nature choose?

Ludwig Boltzmann — hypothesis of molecular chaos:

> For a closed / isolated system in thermal equilibrium all possible microstates realizing any given macrostate are equally probable.

Two views!

element of ignorance

1) If we cannot decide in which equivalent microstate the system exists then because of our ignorance we have to average over all possible microstates with the same probabilities.

self-averaging hypothesis

2) Measurement means to observe a system for some time. In this time a system can change microstates many times ($\sim 10^{32}$). The observed quantity is an average over those microstates.

$$\{\uparrow\uparrow\downarrow\} \quad \{\uparrow\downarrow\uparrow\} \quad \{\uparrow\uparrow\downarrow\} \quad \{\downarrow\uparrow\uparrow\} \quad \{\uparrow\downarrow\uparrow\}$$

$$\longrightarrow time$$

$$P_{\uparrow\uparrow\downarrow} \qquad P_{\uparrow\downarrow\uparrow} \qquad P_{\uparrow\uparrow\downarrow} \qquad P_{\downarrow\uparrow\uparrow} \qquad P_{\uparrow\downarrow\uparrow}$$
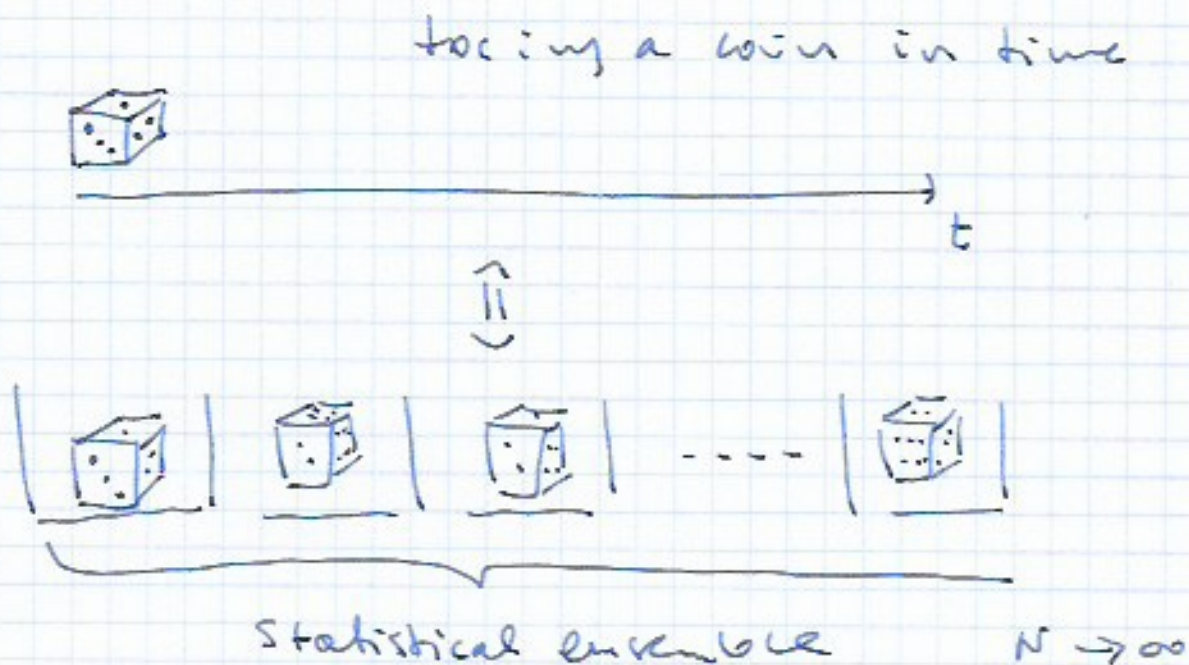
we need to know these probability distributions ⑧

According to ergodic hypothesis of Boltzmann
we can consider an ensemble of systems
with many (infinitely many) elements with
given probabilities.

tocing a coin in time

$$t$$

$$\hat{\Uparrow}$$

Statistical ensemble $N \to \infty$

Instead of averaging in time a process of
observation we average over many
samples from a statistical ensemble of
this system (no more time is involved)

Statistical physics ⟷ thermostatics

Description and understanding
of a macroscopic system is
statistical in its origin.

How to find corresponding probabilities?

From Boltzmann hypothesis all microstates realizing a given macrostate are equally probable a priori.

This statement is sufficient to find all statistical properties of the system.

How it works?

Ω — number of all microstates (partition function)

y_i — a variable characterizing a given macrostate

Ω_i — number of microstates with the same y_i

From the postulates of equal probabilities a priori we get

$$i = 1, ..., n$$

$$P_i = P(y = y_i) = \frac{\Omega_i}{\Omega} .$$

↑ random variable

Consistency proof

$$P_i = \sum_{\substack{\text{all} \\ \text{microstates} \\ \text{with } y = y_i}} \frac{1}{\Omega} = \frac{\Omega_i}{\Omega} \qquad \square$$
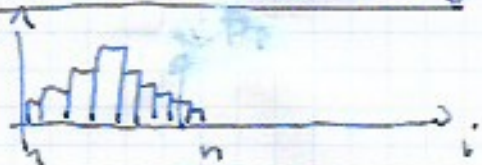
Average $\qquad \langle y \rangle = \sum_{i=1}^{n} y_i P_i = \frac{1}{\Omega} \sum_{i=1}^{n} y_i \Omega_i$

n-th moment $\qquad \mu_n = \langle y^n \rangle = \sum_{i=1}^{n} y_i^n P_i = \frac{1}{\Omega} \sum_{i=1}^{n} y_i^n \Omega_i$

Variance $\qquad \sigma_y^2 = \langle (y - \langle y \rangle)^2 \rangle = \langle y^2 \rangle - \langle y \rangle^2 =$
$$= \mu_2 - \mu_1^2$$

probability distribution of random variable y

$$P(y) = \frac{\Omega_i}{\Omega} = \frac{\Omega(y = y_i)}{\Omega}$$

⑩

In case of continuous random variable y

$$p(y) = \frac{\Omega(y)}{\Omega}$$

$$\mu_n = \langle y^n \rangle = \int_{-\infty}^{\infty} dy \; y^n \; p(y) = \frac{1}{\Omega} \int_{-\infty}^{\infty} dy \; y^n \; \Omega(y)$$

e.g. average $\langle y \rangle = \frac{1}{\Omega} \int_{-\infty}^{\infty} y \; \Omega(y) \; dy$

normalization

$$1 = \langle 1 \rangle = \frac{1}{\Omega} \underbrace{\int_{-\infty}^{\infty} dy \; \Omega(y)}_{\Omega} = \frac{\Omega}{\Omega} = 1$$

warning : in statistical physics with many degrees of freedom the integral measure has to be modified properly

$$d_{3N} q \; d_{3N} p \longrightarrow \frac{d^{3N} q \; d^{3N} p}{h^{3N} \; N!}$$

$\uparrow$
Planck
constant.

see later on.