Introduction to Statistical Mechanics

Limitations of Thermo

- Cannot get the equation of state
- Cannot derive specific heats
- How do the microscopic & macro connect
- Can one "derive" thermodynamics from microscopic structure ?

Basic Structure

Analogy of a system of 10 dice

1. Specify the state of the system (microstate)
   - which face is uppermost for each of 10 die

2. Statistical Ensemble

   ↳ a large # of copies of original system

   → many similar experiments performed under similar conditions

   → the outcome of each will be different in general

3. **Basic Postulate about a priori probabilities.**

→ each face has equal probability of being uppermost

4. **Probability calculations**

Apply basic postulate to theoretically calculate the probabilities of outcomes of any experiment

Examples

1. Specification of state.

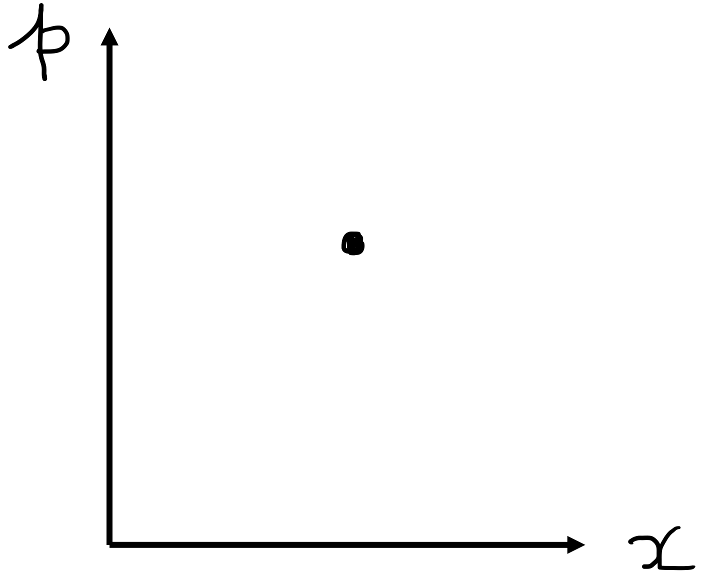
   1. spin system of N spins

      only two states $\uparrow \downarrow$ microstates.

   2. Gas $\sim 10^{23}$ molecules

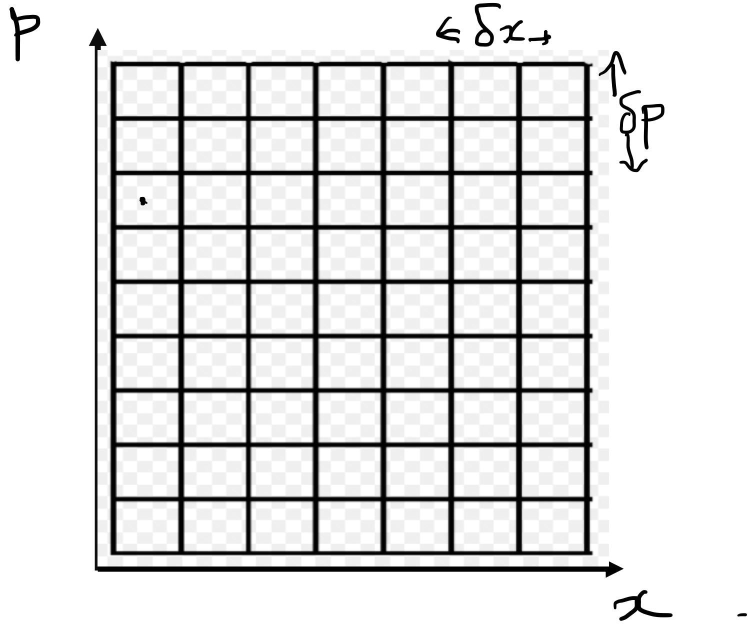
      single molecule (x, p)

      N particles (x_i, p_i) $i = 1 \cdots N$.



$x - p$ space ; phase space

microstate $\longrightarrow$ point in phase space



$$\delta p \, \delta x = h_0$$

state : x between $x \longrightarrow x + \delta x$

p between $p \longrightarrow p + \delta p$.

(x, p) lies in the i^{th} cell of phase space.

f coordinates $\longrightarrow$ degrees of freedom

$x_1, x_2, \dots\dots\dots x_f$

$p_1, p_2, \dots p_f$

N point particles

$f = 3N$.

phase space has $2f$ dimensions

"Microstate" of system

Enumerate the cells of phase space in some convenient order and label with an index r $(r = 1, 2, 3 \dots)$.

State of the system is specified by specifying the cell in which your representative pt. lies in phase space.

Statistical Ensemble

Example : 3 spins — 3 particles with spin $\frac{1}{2}$.

- each spin can point up or down $\uparrow \downarrow$, (magnetic quantum numbers).
- Each particle has a magnetic moment along the z-axis, $\mu \uparrow$, or $-\mu \downarrow$.
- Energy $= -\mu H \uparrow$ $\qquad \uparrow H$

  $= \mu H \downarrow$

Total

State index r	Quantum nos	Magnetic moment	Energy
1.	$+ + +$	3μ	$-3\mu H$
2.	$+ + -$	μ	$-\mu H$
3.	$+ - +$	μ	$-\mu H$
4	$- + +$	$+\mu$	$-\mu H$
5.	$+ - -$	$-\mu$	μH
6.	$- + -$	$-\mu$	μH
7	$- - +$	$-\mu$	μH
8.	$- - -$	-3μ	$3\mu H$

Ex. Suppose we know that total energy $= -\mu H$

$(++-)$ $(+-+)$ $(-++)$

system can be in any of these states.

→ Do not know rel. probability of these states occurring.

Basic Postulate of a priori probabilities

Isolated system $\longrightarrow$ $E = \text{const}$.

many microstates corresponding to this

$\boxed{\text{Isolated system in equilibrium is \underline{equally likely} to be found in any of its microstates}}$