2 Microscopic → Macroscopic

Book: p4-11. (Ch 1).

Macroscopic view → thermodynamics, very general and powerful set of theories providing bulk information.

Microscopic description → it involves knowing about all of the details of all of the particles in the system (both classically and QM). Work out the amount of information required to do this. e.g. 10^{23} atoms each with position and momentum for each t. Alternatively look at arrangements so thats 10^{23}! Microscopic detail has too much information.

We need to bridge these extremes — statistical physics.

Definitions.

Macrostate - specification of the state of the system based on macroscopic quantities e.g. N, V, $\overset{(E)}{U}$, T, P, $\underline{B}$, $\underline{E}$ containing minimal information of the state.

Microstate - complete specification of the state of the system (consistent with theory)

Macrostates have various subdivisions, sometimes called ensembles.

Constant particle number, constant ~~temperature~~ energy, constant volume $(N, \overset{U}{\cancel{T}}, V)$

- microcanonical ensemble.

Constant particle number, temperature, volume (N, T, V)

- canonical ensemble.

Constant temperature, volume, chemical potential (μ, T, V)
- grand canonical ensemble.

A macrostate will have $\sim N!$ microstates. We label the number of microstates Ω. In the microcanonical ensemble we ~~ket~~ have (N, U, V) Ω is the number of ways of organising the particles to have this particular set of values of N, U, V.

<u>How to assign microstate probabilities</u>?

Could make a large (infinite) number of experiments so that the number of microstates were all sampled enough to gain information on probability - but this is impractical.

We must <u>hypothesise</u> a priori what these probabilities are.

- the principle of equal probabilities (in the micro cannonical ensemble).

There is no energy cost (constant u) for changing one microstate to another. So the are all equally likely.

<u>Distributions</u> - an intermediate description of a system, e.g.

With N particles lets have states i available (single particle states) and in each on of these states we can have $\{n_i\}$ particles.

If we simplify this example to 2 states, labelled 1 and 2 then if degenerate $\varepsilon(1) = \varepsilon(2)$, do similar if we have more states $\varepsilon(3) = \varepsilon(4)$

ordering by energy : $\underbrace{\varepsilon(1), \varepsilon(2)}_{\varepsilon_1}, \underbrace{\varepsilon(3), \varepsilon(4)}_{\varepsilon_2} \ldots \underbrace{\varepsilon(2\ell-1) \varepsilon(2\ell)}_{\varepsilon_\ell} \ldots$

and $n_{\varepsilon_1} = 2$, $n_{\varepsilon_2} = 2$, ..., $n_{\varepsilon_n} = 2$, ...

Generalise $\sum_{i} n_i = \sum_{i} n_{\varepsilon_i} = N$,

$\uparrow$ particles $\qquad$ $\uparrow$ index over states

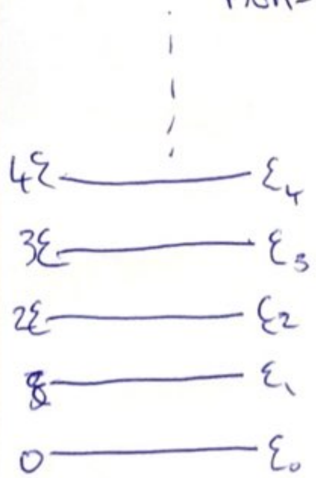
$$\sum_{i} n_i\, \varepsilon(i) = \sum_{i} n_{\varepsilon_i}\, \varepsilon_i = U.$$

$\uparrow$ particles $\qquad$ $\uparrow$ states

Confusion – beware if in textbooks sums are over states or over particles.

Example. Let's take 4 particles, (A, B, C, D) distributed in non-degenerate states with energies

$$\varepsilon_0 = 0, \quad \varepsilon_1 = \varepsilon, \quad \varepsilon_2 = 2\varepsilon, \quad \varepsilon_3 = 3\varepsilon \ \ldots$$



Lets pick a macrostate $N = 4$, $U = 4\varepsilon_1$ (V).

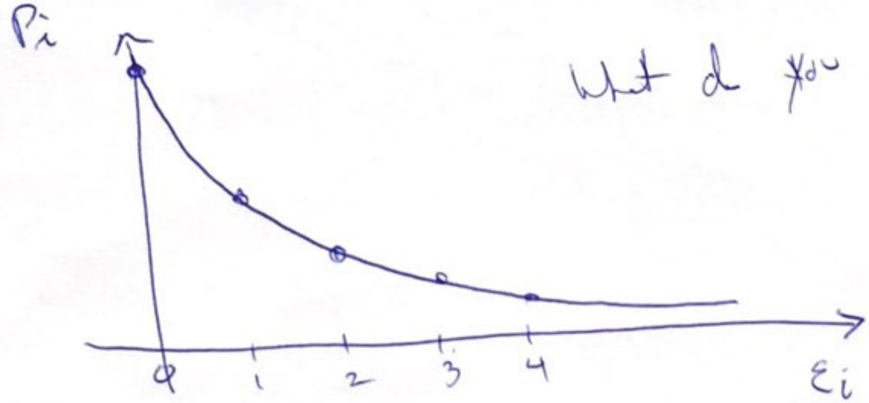
Distributions	ε_0	ε_1	ε_2	ε_3	ε_4	Microstates $\Omega(D)$
D_1	3	0	0	0	1	$4!/(3!\,0!\,0!\,0!\,1!) = 4$
D_2	2	1	0	1	0	$4!/(2!\,1!\,0!\,1!\,0!) = 12$
D_3	1	2	1	0	0	$4!/(1!\,2!\,1!\,0!\,0!) = 12$
D_4	2	0	2	0	0	$4!/(2!\,0!\,2!\,0!\,0!) = 6$
D_5	0	4	0	0	0	$4!/(0!\,4!\,0!\,0!\,0!) = 1$
average n per state.	$\frac{60}{35}$	$\frac{40}{35}$	$\frac{24}{35}$	$\frac{12}{35}$	$\frac{4}{35}$	$\Omega_T = 35.$

12	0
24	12
12	24
12	0
0	4

We know the average population per state; so what is the probability of finding a particle in a state, let's normalise average n per state.

	ε_0	ε_1	ε_2	ε_3	ε_4
Probability	$\frac{60}{140}$	$\frac{40}{140}$	$\frac{24}{140}$	$\frac{12}{140}$	$\frac{4}{140}$
$\sim$	0.43	0.29	0.17	0.09	0.03

We have calculate the occupation of state i wrt. ε_i



What do you think this means?

Boltzmann distribution.