Review of statistical mechanics

- Fundamental postulate:

  - Consider an isolated system of N noninteracting identical particles, in volume V,

    Hamiltonian $H = \sum_{i=1}^{N} h(i)$

    single-particle states: $H|\phi_\nu\rangle = \epsilon_\nu|\phi_\nu\rangle$

    Total number of states: $N = \sum_\nu N_\nu$

    total energy: $E = \sum_\nu N_\nu \epsilon_\nu$

  - Microstate: wavefunction $\psi(1, \cdots, N)$

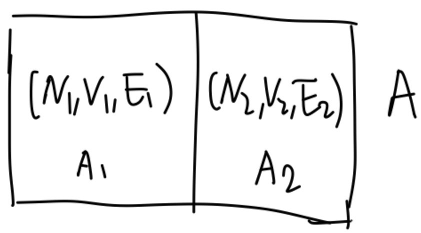
  - Number of microstates corresponding to a macrostate: Ω

$$\Omega(N, V, E).$$

Fundamental postulate:

Given a macrostate, an isolated system in equilibrium, is equally ~~likely~~ to be in any of the microstates that are consistent with the given macrostate!!

- Statistical Mechanics $\leftrightarrow$ Thermodynamics.

(1) 

$E = E_1 + E_2$, E constant. N_1, N_2, V_1, V_2 constant

$\Omega_1(E_1)\,\Omega_2(E_2) = \Omega_1(E_1)\,\Omega_2(E - E_1) = \Omega(E, E_1)$

There is energy exchange until equilibrium.
$\uparrow$ E_1^0, E_2^0.

- Assert that: a system always settles into a macrostate with the most possible microstates.!

$$\Rightarrow 0 = \left.\frac{\partial \Omega}{\partial E_1}\right|_{E_1 = E_1^0} = \left.\frac{\partial \Omega_1}{\partial E_1}\right|_{E_1 = E_1^0} \cdot \Omega_2 + \Omega_1 \cdot \left.\frac{\partial \Omega_2}{\partial E_2}\right|_{E_2 = E_2^0} \cdot (-1)$$

$$\Rightarrow \left.\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\right|_{E_1^0} = \left.\frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\right|_{E_2^0}$$

Then the condition of equilibrium for given N_1, V_1, N_2, V_2 is:

$$\underbrace{\left.\frac{\partial \ln \Omega(E_1)}{\partial E_1}\right|_{N_1,V_1}}_{\beta_1} = \underbrace{\left.\frac{\partial \ln \Omega(E_2)}{\partial E_2}\right|_{N_2,V_2}}_{\beta_2}.$$

In thermodynamics, the condition is $T_1 = T_2$.

where $\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V}$, S is the entropy

In fact: $S = k \ln \Omega$, $\beta = \frac{1}{kT}$, k: Boltzmann constant

$$d(\ln \Omega) = \left.\frac{\partial \ln \Omega}{\partial E}\right|_{N,V} dE + \left.\frac{\partial \ln \Omega}{\partial V}\right|_{N,E} dV + \left.\frac{\partial \ln \Omega}{\partial N}\right|_{V,E} dN$$

$$dS = \frac{1}{T}\, dE + \left.\frac{\partial S}{\partial V}\right|_{N,E} dV + \left.\frac{\partial S}{\partial N}\right|_{V,E} dN$$

$$dE = T dS - T\frac{\partial S}{\partial V} dV - T\frac{\partial S}{\partial N} dN$$

First law of thermodynamics:

μ: chemical potential

$$dE = T dS - P dV + \mu dN.$$

P pressure

$$\Rightarrow \quad P = T\frac{\partial S}{\partial V}, \quad \mu = -T\frac{\partial S}{\partial N}.$$

- Ensembles
  - Microcanonical ensemble.

    isolated system with fixed energy.

    ("almost" fixed: uncertainty principle: $\Delta E \Delta t \sim \hbar$)

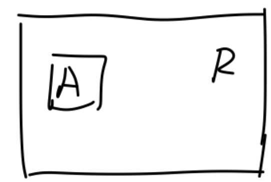
$$P_n = \begin{cases} c, & E \le E_n \le E + \delta E \\ 0, & \text{otherwise.} \end{cases}$$

P_n is the probability of finding $|\psi_n\rangle$

  - Canonical ensemble:

    fixed temperature T

    How to fix a temperature? With heat reservoir!



The probability of finding $|\psi_n\rangle$ is proportional to $\Omega_R(E_{tot}-E_n)$. E_{tot} is total energy.

$E_{tot} \gg E_n$

$$P_n = C\,\Omega_R(E_{tot}-E_n) = C\,e^{\ln \Omega_R(E_{tot}-E_n)}$$

$$\ln \Omega_R(E_{tot}-E_n) \approx \ln \Omega_R(E_{tot}) - \left.\frac{\partial \ln \Omega_R}{\partial E}\right|_{E_{tot}} \cdot E_n + O(E_n^2)$$

$$\approx \ln \Omega_R(E_{tot}) - \left.\frac{\partial \ln \Omega_R}{\partial E}\right|_{E_{tot}-E_n=E_R} \cdot E_n$$

$$= \ln \Omega_R(E_{tot}) - \beta E_n$$

$$\Rightarrow P_n \propto e^{-\beta E_n}$$

Then with $\sum_n P_n = 1$, $P_n = \frac{e^{-\beta E_n}}{Z}$, $Z = \sum_n e^{-\beta E_n}$

Helmholtz free energy. $F = E - TS$

$F = -kT \log Z$ (Proof is too long)

· Grand canonical ensemble

fixed temperature, particle number can change

$E_{tot} = E_A + E_R$, $N_{tot} = N_A + N_R$, E_0, N_0 fixed.

E_A, N_A not fixed

Let $|\psi_{rs}\rangle$ be the r-th eigenstate of N_s particles. with energy $E_{r,s}$

$$P_{rs} = C\,\Omega_R(E_{tot} - E_{r,s}, N_{tot} - N_s) \quad E_{r,s} \ll E_{tot}, \quad N_s \ll N_{tot}$$

$$\ln \Omega_R(E_{tot} - E_{r,s}, N_{tot} - N_s) = \ln \Omega_R(E_{tot}, N_{tot}) - \beta E_{r,s} + \beta \mu N_s$$

$$= \ln \Omega_R(E_{tot}, N_{tot}) - \beta E_{r,s} + \beta \mu N_s$$

then $P_{rs} = \frac{1}{Z_G} e^{-\beta(E_{r,s} - \mu N_s)}$

$$Z_G = \sum_{r,s} e^{-\beta(E_{r,s} - \mu N_s)} \quad \text{Grand partition function}$$

$$= \sum_{r,s} \langle r,s| e^{-\beta(H - \mu N)} |r,s\rangle = \mathrm{Tr}\left(e^{-\beta(H - \mu N)}\right).$$

The statistical operator:

$$\hat{\rho}_G = \frac{1}{Z_G} e^{-\beta(H-\mu N)} \quad , \quad Z_G = \mathrm{Tr}\left(e^{-\beta(H-\mu N)}\right)$$

$$\langle A \rangle = \frac{\mathrm{Tr}\left(e^{-\beta(H-\mu N)} A\right)}{\mathrm{Tr}\left(e^{-\beta(H-\mu N)}\right)} = \mathrm{Tr}(\hat{\rho}_G A)$$

Quantum distribution function:

Consider single-particle system, non-interacting:

single-particle state: $\phi_1, \phi_2, \cdots$

energy: $\epsilon_1, \epsilon_2, \cdots$ $\qquad |n_1 n_2 \cdots\rangle$

number of particles: $n_1, n_2, \cdots$

$$E = \sum_i n_i \epsilon_i, \quad N = \sum_i n_i$$

$$Z_G = \sum_{n_1, n_2, \cdots} e^{-\beta\left(\sum_i n_i \epsilon_i - \mu \sum_i n_i\right)} = \sum_{n_1, n_2, \cdots} e^{-\beta \sum_i (\epsilon_i - \mu) n_i} = \left(\sum_{n_1} e^{-\beta(\epsilon_1-\mu)n_1}\right) \times \left(\sum_{n_2} e^{-\beta(\epsilon_2-\mu)n_2}\right) \cdots$$

For bosons. $n_i = 0, 1, \cdots \infty$,

then $Z_G = \prod_{i=1}^{\infty} \frac{1}{1-e^{-\beta(\epsilon_i-\mu)}}$, $\ln Z_G = -\sum_{i=1}^{\infty} \ln\left(1-e^{-\beta(\epsilon_i-\mu)}\right)$

$$\langle N \rangle = \beta^{-1} \frac{\partial}{\partial \mu}(\ln Z_G) = \sum_i \frac{e^{-\beta(\epsilon_i-\mu)}}{1-e^{-\beta(\epsilon_i-\mu)}} = \sum_i \frac{1}{e^{\beta(\epsilon_i-\mu)}-1}$$

$$n_i^{BE} = \frac{1}{e^{\beta(\epsilon_i-\mu)}-1} \quad \text{Boson-Einstein statistics}$$

For Fermions

$$Z_G^F = \prod_{i=1}^{\infty} \left(1+e^{-\beta(\epsilon_i-\mu)}\right) \Rightarrow \ln Z_G^F = \sum_i \ln\left(1+e^{-\beta(\epsilon_i-\mu)}\right)$$

$$\langle N \rangle = \beta^{-1} \frac{\partial}{\partial \mu}(\ln Z_G^F) = \sum_i \frac{1}{e^{\beta(\epsilon_i-\mu)}+1} = \sum_i f_i^{FD} \quad \text{Fermi-Dirac}$$

$$f_i^{FD} = \frac{1}{e^{\beta(\epsilon_i-\mu)}+1} \quad \text{fermions.} \quad \text{Fermi-Dirac statistics}$$

$$\langle n_{k\sigma} \rangle = \langle c_{k\sigma}^{\dagger} c_{k\sigma} \rangle = \begin{cases} n_{k\sigma}^{BE} = \dfrac{1}{e^{\beta(\epsilon_{k\sigma}-\mu)}-1}, & \text{bosons} \\ f_{k\sigma} = \dfrac{1}{e^{\beta(\epsilon_{k\sigma}-\mu)}+1} & \text{fermions} \end{cases}$$

for Hamiltonian $H = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^{\dagger} c_{k\sigma}$

For fixed particle number N, the chemical potential μ is determined by

$$N = \sum_i \frac{1}{e^{\beta(\epsilon_i-\mu)} \mp 1}.$$

+ : fermion

− : boson.