ideal systems

Phonons, Photons, black body radiation,
Fermions, Bosons, electrons in metals.

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \qquad E = E_1 + E_2 + \dots$$

$$Z = \sum_E e^{-\beta E} = \sum_{E_1 E_2} e^{-\beta(E_1 + E_2)} = Z_1 Z_2$$

moment or cumulant generating functions

"Equipartition theorem"

$$Z_1 \qquad \frac{Kx^2}{2} + \frac{p^2}{2m} \qquad \text{single degree of freedom}$$

$$p(E) \sim e^{-\beta E}$$

$$E_1 = \frac{\int dx \, \frac{Kx^2}{2} e^{-\beta \frac{Kx^2}{2}}}{\int_{-\infty}^{+\infty} dx \, e^{-\beta \frac{Kx^2}{2}}}$$

$$E_1 = \frac{\partial}{\partial(-\beta)} \log \int_{-\infty}^{+\infty} e^{-\beta \frac{Kx^2}{2}} dx = \frac{\partial}{\partial(-\beta)} \log \frac{(2\pi)^{1/2}}{(\beta K)^{1/2}}$$

$$= \frac{1}{2\beta} = \frac{k_B T}{2}$$

$$3N \qquad E = N E_1 = \frac{3}{2} N k_B T$$

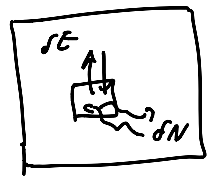
$$\Omega(N, V, E) \rightarrow Z = \int \Omega(E) e^{-\beta E} dE$$

$$E \rightarrow E - T \cdot S \rightarrow E - TS - \mu \cdot N$$

$$E(N, V, S) \rightarrow A(N, V, T) \rightarrow (\mu, V, T)$$

$$p(E_j) \sim e^{-\beta E_j}$$

$$p(E_j, N_j) \sim e^{-\beta(E_j - \mu N_j)}$$



$T = \text{const}$
$\mu = \text{const}$

$$E - TS - \mu N \equiv A - \mu N$$

$$E = TS + PV + \mu N$$ Euler's equation

$$-PV = E - TS - \mu N \qquad \Xi = \sum_j e^{-\beta(E_j - \mu N_j)}$$

$S = k_B \log \Omega$ Micro-canonical, NVE

$A = -k_B T \log Z$ Canonical, NVT

$PV = k_B T \log \Xi$ Grand-canonical, μVT

$$\langle E \rangle = \frac{\sum E_j e^{-\beta(E_j - \mu N_j)}}{\sum e^{-\beta(E_j - \mu N_j)}} = \frac{\frac{\partial}{\partial(-\beta)} \Xi}{\Xi} = \frac{\partial \log \Xi}{\partial(-\beta)}$$

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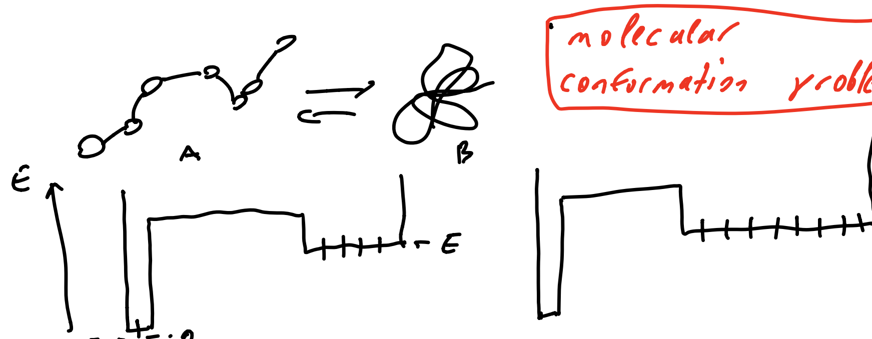
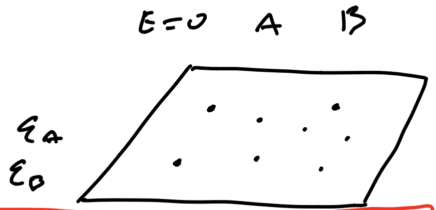
molecular conformation problem



$$P(B) = \frac{5e^{-\beta E}}{1 + 5e^{-\beta E}} \qquad P(B) = \frac{10e^{-\beta E}}{1 + 10e^{-\beta E}}$$

$$P(B) = e^{-\beta(E - T\log 5)} \qquad \frac{P(B)}{P(A)} = e^{-\beta(F_B - F_A)}$$



$$\Xi_1^{\,N} = \Xi$$

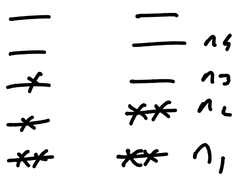
$$\Xi = \sum_\nu e^{-\beta(E_\nu - \mu N_\nu)} =$$

$$= 1 + e^{-\beta(\varepsilon_A - \mu_A)} + 5e^{-2\beta(\varepsilon_B - \mu_B)}$$

molecule adsorption problem

$$P(A) = \frac{e^{-\beta(\varepsilon_A - \mu_A)}}{1 + e^{-\beta(\varepsilon_A - \mu_A)} + 5e^{-2\beta(\varepsilon_B - \mu_B)}}$$

$$\psi(x_1, x_2 \ldots x_r) = \hat{A}\, \varphi(x_1)\varphi(x_2)\ldots\varphi(x_N)$$



$$\text{microstate} = \{n_1, n_2 \ldots n_N\}$$

occupation numbers

$$E = \sum_i n_i \varepsilon_i \qquad N = \sum_i n_i$$

$$\Xi(\beta, \mu) = \sum_\nu e^{-\beta(E_\nu - \mu N_\nu)}$$

$$\Xi(\beta, \mu) = \sum_i e^{-\beta(\varepsilon_i - \mu_i) n_i}$$

Bosons

$$\Xi = \prod_{i=1}^{N} \Xi_i = \prod_{i=1}^{N} \underbrace{\sum_{n_i=0}^{\infty} e^{-\beta(\varepsilon_i - \mu_i) n_i}}$$

$$1 + x + x^2 + \ldots x^n = \frac{1}{1-x}$$

$$\Xi_i = \left(1 - e^{-\beta(\varepsilon_i - \mu)}\right)^{-1}$$

$$\Xi = \Xi_i^{\,N} \qquad \frac{\langle n_i \rangle}{N} \qquad \frac{\langle n_i \rangle}{N} \sim e^{-\beta \varepsilon_i}$$

$$\langle n_i \rangle = \frac{\partial}{\partial \beta \mu_i} \log \Xi = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}$$

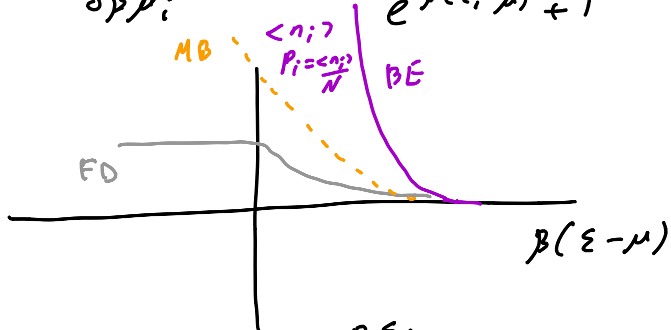
Bose-Einstein statistics

Fermions

$$\Xi = \prod_{i=1}^{N} \Xi_i = \prod_{i=1}^{N} \sum_{n=0}^{1} e^{-\beta(\varepsilon_i-\mu)n_i} = \prod_{i=1}^{N} \left(1+e^{-\beta(\varepsilon_i-\mu)}\right)$$

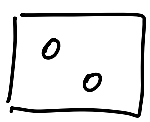
$$\langle n_i \rangle = \frac{\partial}{\partial \beta\mu_i} \log \Xi = \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1}$$

Fermi-dirac statistics



$$\mu \to -\infty \quad \to \quad e^{-\beta\varepsilon_i}$$

$$pV = k_B T \log \Xi$$



$$P_{FD} > P_{MB} > P_{BE}$$

$N = \text{const}$