Lecture 8

08.02.2018

Quantum ideal gases, Bose-Einstein distribution

Maxwell-Bolzmann statistics

- Consider a generic ensemble of N free particles that can occupy discrete energy levels $\{\epsilon_{\mathrm{i}}\}$ with the occupation numbers $\{\mathrm{n}_{\mathrm{i}}\}$

$$N = \sum_i n_i \,, \qquad U = \sum_i n_i \epsilon_i$$

- Each energy state ϵ_i has a «degeneracy» g_i(density of states = nr of microstates at that energy level for one particle)

Multiplicity of a macrostate

- Number of configurations with n_1 particles in the energy state ϵ_1, n_2 particles in the energy state $\epsilon_2, \cdots etc$

$$N! \prod_i \frac{1}{n_i!}$$

- Each particle in ϵ_i energy level has g_i available microstates, hence $g_i^{n_i}$ ways of arranging n_i particles in g_i degenerate states.

- The total number of configurations for *distinguishable* particles

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

- The total number of configurations for *indistinguishable* particles (for a given partition $\{n_i\}$)

$$W = \prod_i \frac{g_i^{n_i}}{n_i!}$$

Maxwell-Boltzmann distribution

Equilibrium distribution of particles over energy states

$$\boldsymbol{n_i = \frac{N}{Z_1} g_i \mathrm{e}^{-\beta\epsilon_i}, \;\; Z_1 = \sum_{i=1} g_i\, e^{-\beta\epsilon_i}}$$

- Probability to find a particle in the energy level ϵ_i: $\boldsymbol{p_i = \frac{g_i}{Z_1}\mathrm{e}^{-\beta\epsilon_i}}$

- Average energy

$$\mathrm{U} = \mathrm{N}\langle\epsilon_i\rangle = N\sum_i p_i\epsilon_i = \frac{N}{Z_1}\sum_i \epsilon_i g_i e^{-\beta\epsilon_i} = -\frac{\partial}{\partial\beta}\ln\; Z_1^N$$

- Helmholtz free energy

$$F(T,N) = -kT\ln\; Z_N\,, \qquad Z_N \equiv Z_1^N\;(dist), \qquad Z_N \equiv \frac{Z_1^N}{N!}\;(indist),$$

- Entropy

$$\frac{S}{k} = N\log Z_1 + \frac{U}{kT} = -Nk\sum_i p_i\ln p_i$$

Indistinguishable, **classical** free particles

$$Z_N(T) = \frac{Z_1^N}{N!} = e^{-\beta F_N(T)}, \qquad \Xi(T,\mu) = \sum_{n=0}^{\infty} \frac{1}{n!} Z_1^n e^{\beta n \mu} = e^{-\beta\Omega}$$

- Helmholtz free energy

$$F_N(T) = -NkT\left(\ln\left(\frac{Z_1}{N}\right) + 1\right)$$

- Chemical potential

$$\mu(T,N) = -\left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln\frac{Z_1}{N} \rightarrow Z_1 = N\,\lambda^{-1},\ \lambda = e^{\beta\mu} \text{(fugacity)}$$

- Landau free energy:

$$\Omega = -kT\ln\left(\sum_{n=0}^{\infty}\frac{1}{n!}Z_1^n\lambda^n\right) = -kT\ln\left(e^{Z_1\lambda}\right) = -kT\,\lambda Z_1 = -NkT$$

Classical ideal gas

$$Z_N(T) = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N = e^{-\beta F_N(T)}, \qquad \Xi(T,\mu) = e^{Vz} = e^{-\beta\Omega},$$

$$\Lambda(T) = \frac{h}{\sqrt{2\pi mkT}}, \qquad z = \frac{\lambda}{\Lambda^3}$$

- Helmholtz free energy

$$F_N(T) = -NkT\left(\ln\left(\frac{V}{N\Lambda^3(T)}\right) + 1\right)$$

- Chemical potential

$$\mu(T,N) = -\left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln\frac{V}{N\Lambda^3(T)} \ll 0 \rightarrow N = zV$$

- Landau free energy:

$$\Omega = -kTzV = -NkT$$

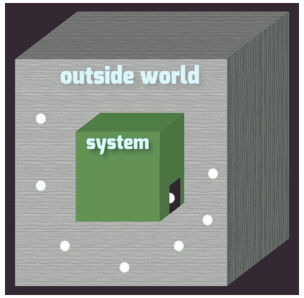
Quantum statistics: Bose-Einstein distribution

Bosons: quantum particles with integer values of spin

- Consider an ensemble of N free bosons that occupy energy levels $\{\epsilon_\mathrm{i}\}$ with the occupation numbers $\{\mathrm{n_i}\}$ such that

$$N = \sum_i n_i$$

Find the equilibrium occupation number n_i of bosons in an energy state ϵ_i



Grand-canonical ensemble for free quantum particle

Probability of the system being in a given microstate is proportional to the probability that the reservoir is in *any state that accomodate that particular microstate*

Probability ratio between two microstates (the system can exchange energy $\Delta U_R = -\Delta E$*, and particles* $\Delta N_R = -\Delta N$*)*

$$\frac{P(s_1)}{P(s_2)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)} = e^{\frac{[S_R(s_1)-S_R(s_2)]}{k}} = e^{\beta\Delta U_R} e^{-\beta\mu\Delta N_R} = e^{-\beta\Delta E}\, e^{\beta\mu\Delta N}$$

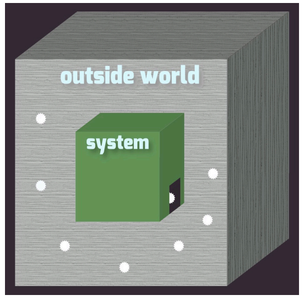
Probability of the system in <u>a specific microstate</u> a fixed T and μ

$$P(s) = \frac{1}{\Xi(T,\mu)} e^{-\beta(E_s-\mu N_s)}$$

Grand-canonical Partition function

$\Xi(T,\mu) = \sum_s e^{-\beta(E_s-\mu N_s)}$ counts all the accessible microstates weighted by the Gibbs factor

What is the microstate *s*?



Grand-canonical ensemble for free quantum particle

Each particle can occupy the energy states ϵ_j, $\boldsymbol{where\ j = 0, 1, 2, \cdots}$ is the state number

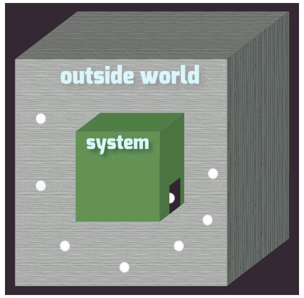
For N identical particles, there are $\boldsymbol{n_j}$ number of particles (occupation number) in the energy state $\boldsymbol{\epsilon_j}$

The energy of a specific microstate with $\boldsymbol{N_s = \sum_j n_j}$ particles is $\boldsymbol{E_s = \sum_j n_j \epsilon_j}$

$\sum_s$ ≡sum over all particles number $\boldsymbol{N_s}$ and over all the partitions of particles $\boldsymbol{N_s}$ in the quantum states with total energy $\boldsymbol{E_s}$

$$\Xi(T,\mu) = \sum_{N_s} \sum_{\substack{\{n_j\} \\ \sum_j n_j = N_s}} e^{-\beta(E_s - \mu N_s)} = \sum_{\{n_j\}} e^{-\beta \sum_j n_j(\epsilon_j - \mu)}$$

$$\Xi(T,\mu) = \left(\sum_{n_1} e^{-\beta n_1(\epsilon_1-\mu)}\right) \cdot \left(\sum_{n_2} e^{-\beta n_2(\epsilon_2-\mu)}\right) \cdot\cdot \left(\sum_{n_3} e^{-\beta n_3(\epsilon_3-\mu)}\right) \cdots$$



Occupation number of a microstate

Probability that the system is in a specific microstate a fixed T and μ

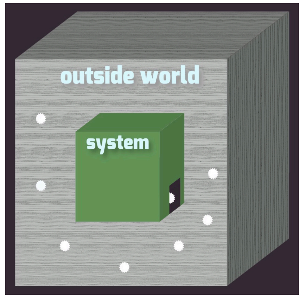
$$P(s) = \frac{1}{\Xi(T,\mu)} e^{-\beta(E_s - \mu N_s)} = \frac{e^{-\beta n_1(\epsilon_1-\mu)} \cdot e^{-\beta n_2(\epsilon_2-\mu)} \cdot e^{-\beta n_3(\epsilon_3-\mu)} \ldots}{\left(\sum_{n_1} e^{-\beta n_1(\epsilon_1-\mu)}\right) \cdot \left(\sum_{n_2} e^{-\beta n_2(\epsilon_2-\mu)}\right) \cdot \left(\sum_{n_3} e^{-\beta n_3(\epsilon_3-\mu)}\right) \ldots}$$

$$\boldsymbol{P(s) = \frac{e^{-\beta n_1(\epsilon_1-\mu)}}{\left(\sum_{n_1} e^{-\beta n_1(\epsilon_1-\mu)}\right)} \cdot \frac{e^{-\beta n_2(\epsilon_2-\mu)}}{\left(\sum_{n_2} e^{-\beta n_2(\epsilon_2-\mu)}\right)} \cdot \frac{e^{-\beta n_3(\epsilon_3-\mu)}}{\left(\sum_{n_3} e^{-\beta n_3(\epsilon_3-\mu)}\right)} \cdots}$$

$$\boldsymbol{P(s) = P(n_1) \cdot P(n_2) \cdot P(n_3) \cdots}$$

Probability for an occupation number n of the given energy state at fixed T and μ

$$\boldsymbol{P(n) = \frac{e^{-\beta n(\epsilon-\mu)}}{\left(\sum_n e^{-\beta n(\epsilon-\mu)}\right)}}$$



Free BOSONS in grand canonical ensemble

The number of bosons in each energy states can be any non-negative integer: $\boldsymbol{n} = \mathbf{0}, \mathbf{1}, \mathbf{2} \cdots$

$$\sum_{n=0}^{\infty} e^{-\beta n(\epsilon-\mu)} = \frac{1}{1-e^{-\beta(\epsilon-\mu)}}, \quad for\ \mu < \epsilon\ \ (for\ every\ \epsilon!)$$

Probability for having $\boldsymbol{n}$ bosons in a given energy state a fixed T and $\boldsymbol{\mu}$

$$P_{\epsilon}(n) = \left(1 - e^{-\beta(\epsilon-\mu)}\right) e^{-\beta n(\epsilon-\mu)}$$

Find the average number of bosons $\langle \boldsymbol{n} \rangle$ (occupation number) in the given energy state ϵ a fixed T and $\boldsymbol{\mu}$

Bose-Einstein distribution

Average number of bosons $\langle n \rangle$ with energy ϵ a fixed T and μ

$$\langle n \rangle(\epsilon) = \sum_{n=0}^{\infty} nP(n) = \left(1 - e^{-\beta(\epsilon-\mu)}\right) \sum_{n=0}^{\infty} n\, e^{-\beta n(\epsilon-\mu)}$$

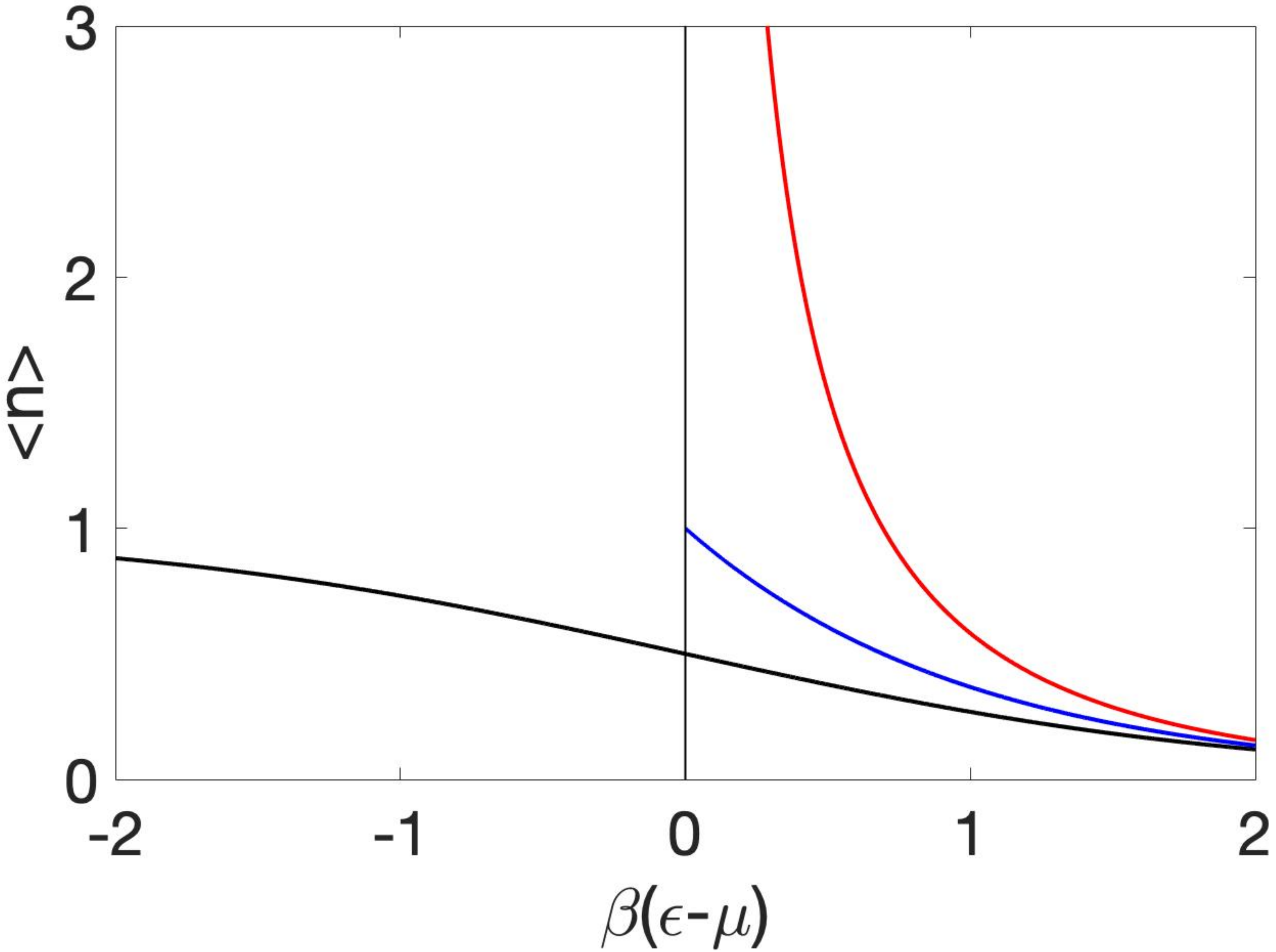
$$= -(1 - e^{-x}) \frac{d}{dx} \sum_{n=0}^{\infty} e^{-nx}, \qquad x = \beta(\epsilon - \mu)$$

$$= -(1 - e^{-x}) \frac{d}{dx} \left(\frac{1}{1 - e^{-x}} \right), \qquad x = \beta(\epsilon - \mu)$$

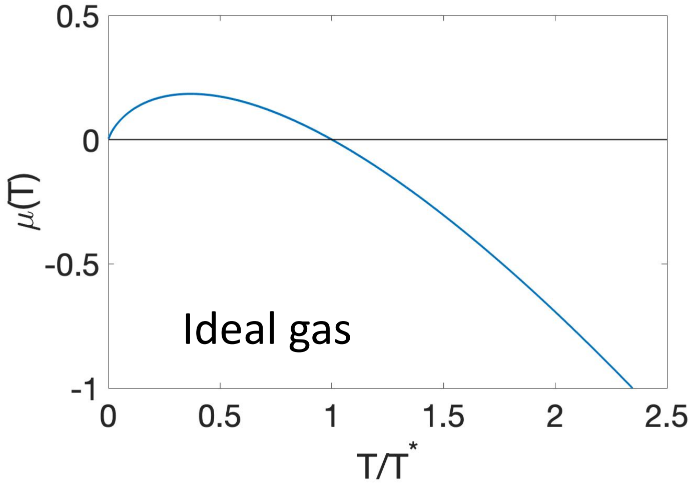
$$\langle n \rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

Bose Einstein distribution

$$\langle n\rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$



Classical limit



Bose-Einstein distribution for the average occupation number of an energy level

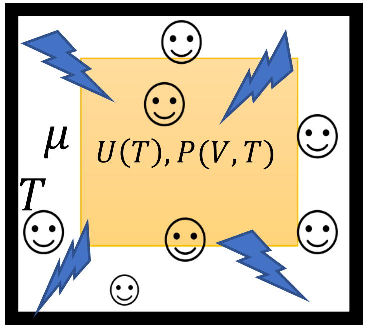
$$\langle n \rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

High T limit ($\lambda = e^{\beta\mu} \ll 1$)

Maxwell-Boltzmann distribution

$$\langle \boldsymbol{n} \rangle(\boldsymbol{\epsilon}) = \frac{\boldsymbol{\lambda}}{\boldsymbol{e^{\beta\epsilon} - \lambda}} \rightarrow_{\lambda\rightarrow 0} \langle \boldsymbol{n} \rangle(\boldsymbol{\epsilon}) \approx \boldsymbol{\lambda e^{-\beta\epsilon}}$$

$$\langle \boldsymbol{n} \rangle(\boldsymbol{\epsilon}) \approx \boldsymbol{N}\frac{\boldsymbol{e^{-\beta\epsilon}}}{\boldsymbol{Z_1}}, \qquad \boldsymbol{Z_1 = N\lambda^{-1}}$$



Grand canonical ensemble --- Classical limit

The energy of a specific microstate s with $N_s = \sum_j n_j$ particles is $E_s = \sum_j n_j \epsilon_j$

$$\Xi(T,\mu) = \prod_j \left(\sum_{n_j} e^{-\beta n_j (\epsilon_j - \mu)} \right) = e^{-\beta\Omega}$$

High T limit ($\lambda = e^{\beta\mu(T)} \ll 1$)

$$\Omega = -kT \sum_j \ln\left[\sum_{n_j} \lambda^{n_j} e^{-\beta n_j \epsilon_j} \right]$$

$$\approx_{\lambda\to 0} -kT \sum_j \ln\left[1 + \lambda e^{-\beta\epsilon_j}\right]$$

$$\approx_{\lambda\to 0} -kT \sum_j \lambda\, e^{-\beta\epsilon_j} = -kT\,\lambda \left(\sum_j e^{-\beta\epsilon_j} \right) = -kT\,\lambda\, Z_1 = -kT \ln \Xi$$

$$\Xi_{\text{classical}} = e^{\lambda Z_1} = \sum_{n=0}^{\infty} \frac{1}{n!} Z_1^n e^{\beta n \mu}$$

Bose-Einstein distribution: counting of microstates

- Each energy levels ϵ_i has a degeneracy g_i

Number of ways of arranging n_i bosons in g_i quantum states with energy level ϵ_i:

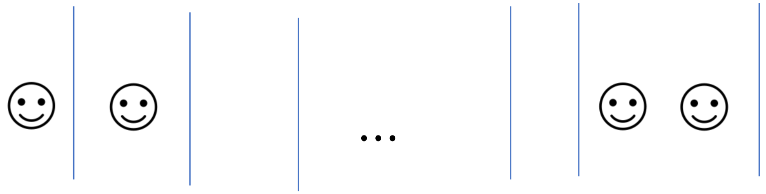
g_i degenerate energy levels $\sim g_i$ identical boxes

n_i particles $\sim n_i$ identical balls

Number of ways of distributing n_i balls between g_i boxed equals the number of combinations with n_i balls and $(g_i - 1)$ −walls between the lined up boxes

$$\mathrm{W_i}(n_i, g_i) = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

The total number of configurations for all energy levels for a given partition $\{n_i\}$*:*

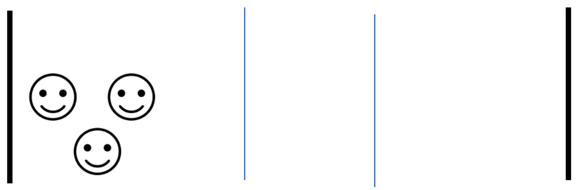


$$\mathrm{W_b}(\{n_i\}) = \prod_i \mathrm{W}_i(n_i, g_i) = \prod_i \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$$

Multiplicity of a macrostate is dominated by the largest $\mathrm{W_b}(\{n_i\})$, corresponding to the equilibrium distribution

Bose-Einstein distribution: counting of microstates

How many configurations there are with 3 bosons and 3 energy states?



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Bose-Einstein statistics (grand-canonical)

- Sponteneous fluctuations induce a change in the population number

$$n_i \rightarrow n_i + 1$$

- Change in entropy:

$$\Delta S = k\left[\ln\frac{(n_i + g_i)!}{(n_i + 1)!} - \ln\frac{(n_i + g_i - 1)!}{n_i!}\right] = k\ln\frac{g_i + n_i}{n_i + 1}$$

- Change in energy:

$$\Delta U = \epsilon_i$$

- Change in number of particles: $\Delta N = 1$

- These spontaneous fluctuations are in thermodynamic equilibrium: $T\Delta S = \Delta U - \mu\Delta N$

Bose-Einstein statistics

$$T\Delta S = \Delta U - \mu \Delta N$$

$$kT \ln \frac{\mathrm{g_i + n_i}}{\mathrm{n_i}} = \epsilon_i - \mu$$

Occupation number of energy level ϵ_i

$$n_i = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} - 1}$$

Filling fraction of energy level ϵ_i

$$f_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

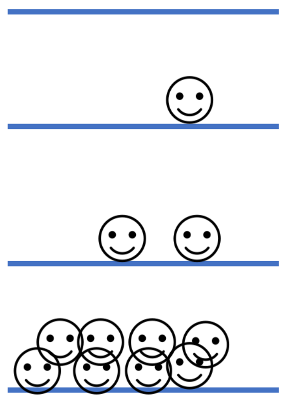
Bose-Einstein statistics

Occupation number of energy level ϵ_i

$$n_i = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} - 1}$$

Number of particles

$$N(T,\mu) = \sum_i n_i = \sum_i \frac{g_i}{e^{\beta(\epsilon_i - \mu)} - 1}$$



Internal energy

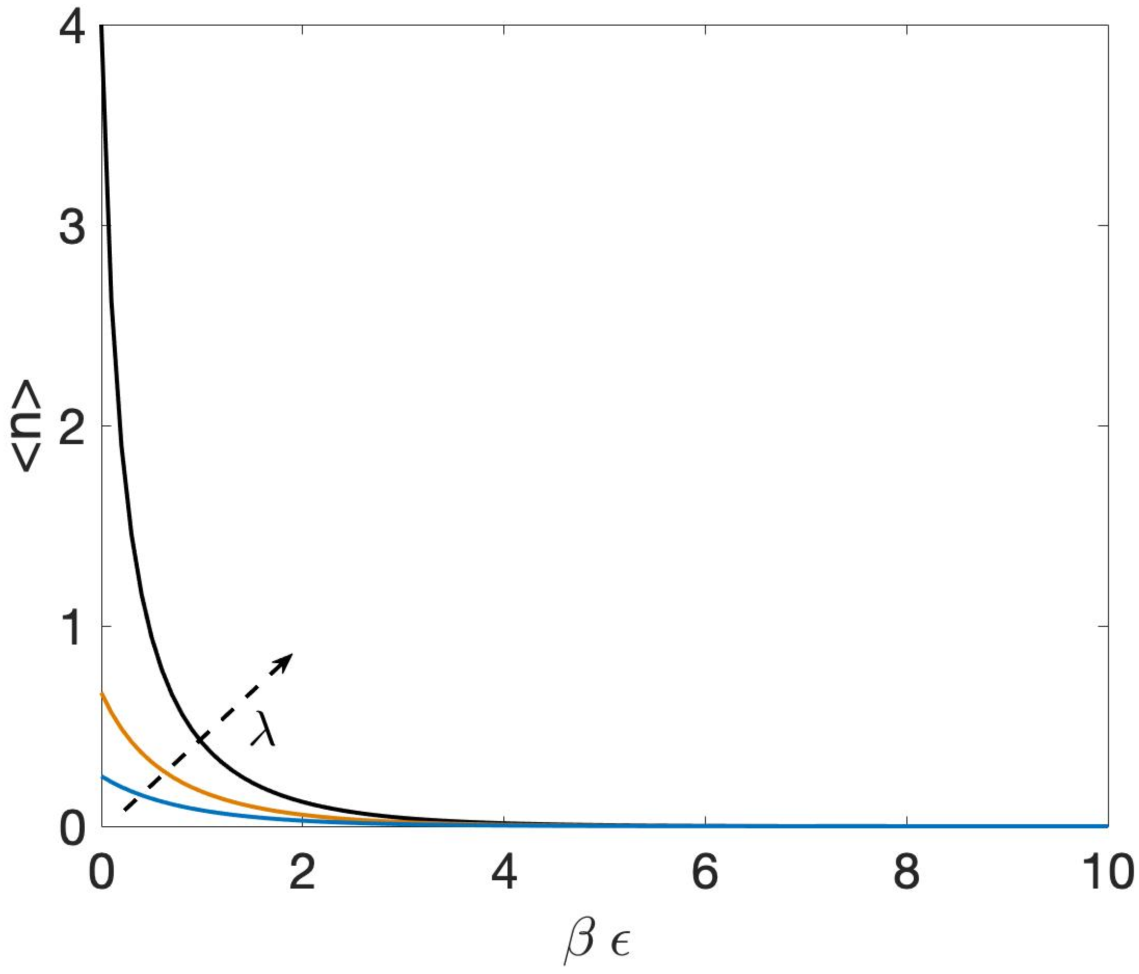
$$U(T,\mu) = \sum_i \epsilon\, n_i = \sum_i \frac{\epsilon\, g_i}{e^{\beta(\epsilon_i - \mu)} - 1}$$

Bose-Einstein statistics

Occupation number of energy level ϵ

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon-\mu)} - 1} = \frac{1}{e^{\beta\epsilon}\lambda^{-1} - 1},$$

$$0 < \lambda = e^{\beta\mu} \leq 1, \qquad \mu \leq 0$$



Bose-Einstein statistics

Occupation number of energy level ϵ

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