Lecture 10

15.02.2018

Recap/Summary

Module II: Non-interacting particles, multiplicity function, partition function

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on. 6. feb.	Classical free particles, Maxwell-Boltzmann distribution
fr. 8. feb.	Quantum ideal gases, Bose-Einstein distribution
on. 13. feb.	Fermi-Dirac distribution
fr. 15. feb.	Summary and questions

Compendium—Chapter 2
Pathria’s book- Chapter 6 (6.1-6.4)

Free particles

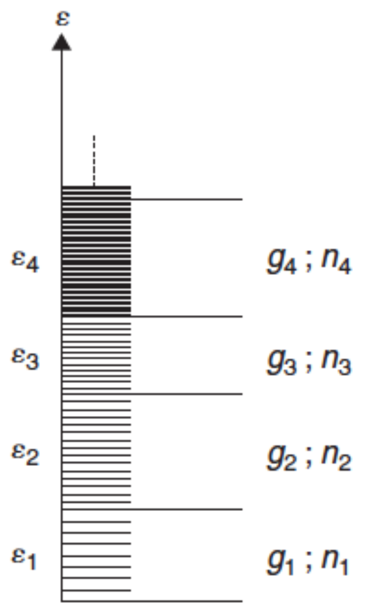
- Mutual interactions between particles is negligible:

  - ➢ ideal spin systems (*paramagnetism*) -- **distinguishable particles**

  - ➢ ideal classical gases
  - ➢ ideal quantum gases

  } ➢ **indistinguishable particles**

Maxwell-Boltzmann: free particles



- Equilibrium distribution of particles in an energy state

$$n_i = \frac{N}{Z_1} e^{-\beta\epsilon_i} = e^{-\beta(\epsilon_i - \mu)}, \quad Z_1 = \sum_i e^{-\beta\epsilon_i}, \quad N = Z_1 e^{\beta\mu}$$

- Probability of a specific microstate at fixed T and μ in the equilibrium

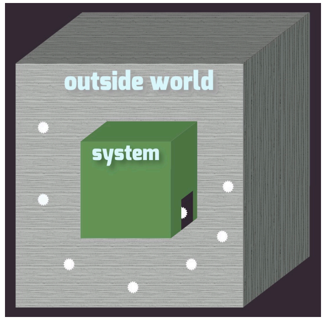
$$P(s) = \frac{1}{\Xi(T,\mu)} \frac{1}{N_s!} e^{-\beta(E_s - \mu N_s)}, \qquad N_s = \sum_i n_i, \qquad E_s = \sum_i \epsilon_i n_i$$

- Grand-canonical partition function (sum over global particle numbers and sum over all the energy states for each individual particle)

$$\Xi(T,\mu) = \sum_{N_s} \frac{1}{N_s!} \sum_{E_s} e^{-\beta(E_s - \mu N_s)} = \sum_{N_s} \frac{1}{N_s!} \prod_{k=1}^{N_s} \sum_{\epsilon_k} e^{-\beta(\epsilon_k - \mu)}$$

$$\Xi(T,\mu) = \sum_{N_s} \frac{1}{N_s!} \left(\lambda \sum_i e^{-\beta\epsilon_i}\right)^{N_s} = e^{\lambda Z_1}, \qquad \lambda = e^{\beta\mu}, \qquad Z_1 = \sum_i e^{-\beta\epsilon_i}$$

Maxwell-Boltzmann: free particles



- Probability of having N_s particles in a macroscopic state at T and μ

$$P(N_s) = \frac{1}{\Xi(T,\mu)} \frac{1}{N_s!} \sum_{\boldsymbol{E_s}} e^{-\beta(E_s - \mu N_s)} = \frac{1}{N_s!} (Z_1 \lambda)^{N_s} e^{-Z_1 \lambda}$$

$$P(N_s, N\rangle) = \frac{1}{N_s!} N^{N_s} e^{-N}, \qquad \langle N_s \rangle = N(T,\mu) = Z_1(T)\lambda(T,\mu)$$

Total number of particles in a macrostate is a fluctuating (random)quantity drawn from a *Poisson distribution with* $\langle N_s \rangle = N$ *as the average number*

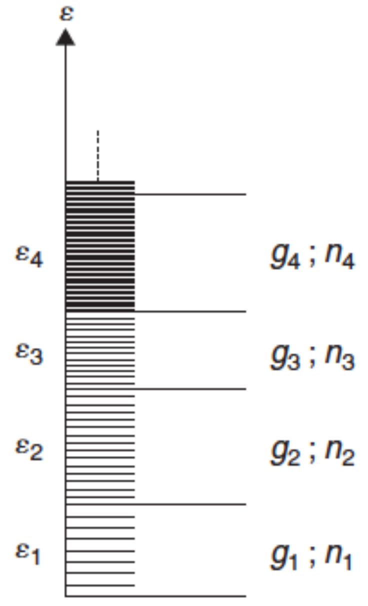
- $\langle \Delta N_s^2 \rangle = \langle N_s^2 \rangle - \langle N_s \rangle^2 = \langle N_s \rangle$
- ***Relative number fluctuations*** $\frac{\langle \Delta N_s^2 \rangle}{\langle N_s \rangle^2} = \frac{1}{N} = \frac{1}{Z_1 \lambda} \ll 1$

Maxwell-Boltzmann: free particles

- Probability for an occupation number n in ϵ_i energy state

$$P_i(n) = \frac{\frac{1}{n!}\left(\lambda e^{-\beta\epsilon_i}\right)^n}{\left(\sum_n \frac{1}{n!}(\lambda e^{-\beta\epsilon_i})^n\right)} = \frac{1}{n!}\frac{\left(\lambda e^{-\beta\epsilon_i}\right)^n}{\exp(\lambda e^{-\beta\epsilon_i})}$$

$$P_i(n, n_i) = \frac{1}{n!} n_i^n e^{-n_i}, \qquad n_i = \langle n \rangle_i = \lambda e^{-\beta\epsilon_i}$$

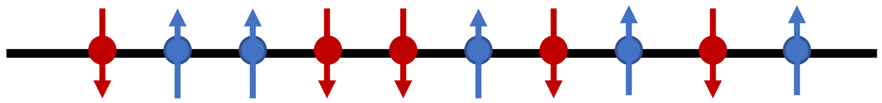


Occupation number of an energy state is also a random number following *Poisson distribution with* $n_i = \lambda e^{-\beta\epsilon_i}$

- $\langle \Delta n^2 \rangle_i = \langle n^2 \rangle_i - \langle n \rangle_i^{\,2} = n_i$

- ***Relative number fluctuations*** $\frac{\langle \Delta n^2 \rangle_i}{n_i^2} = \frac{1}{n_i} = \frac{Z_1 e^{\beta\epsilon_i}}{N} \ll 1$

System of free spins



- Maxwell-Boltzmann distribution (MBD): probability that a spin occupies a microstate//fraction of spins in a (single-particle) microstate

$$\frac{n_s}{N} = \frac{1}{Z_1(T)} e^{-\beta \epsilon_s}, \qquad \epsilon_s = -s\mu B, \qquad s = \pm 1$$

- 1-particle partition function $Z_1(T) = \sum_{s=\pm 1} e^{-\beta \epsilon_s} = 2\cosh(\beta \mu B)$
- N-partition function $Z_N(T) = Z_1^N = 2^N \cosh^N(\beta \mu B)$
  - Average spin energy $\langle \epsilon \rangle = \frac{1}{Z_1} \sum_s \epsilon_s \, e^{-\beta \epsilon_s} = -\mu B \tanh(\beta \mu B)$
  - Average total energy $\mathrm{U} = \mathrm{N}\langle \epsilon \rangle = -N\mu B \tanh(\beta \mu B)$
- *Grand-canonical partition* $\Xi(T, \mu) = \sum_{N_s} (\boldsymbol{\lambda Z_1})^{\boldsymbol{N_s}} = \frac{\mathbf{1}}{\mathbf{1} - \boldsymbol{\lambda Z_1}}$

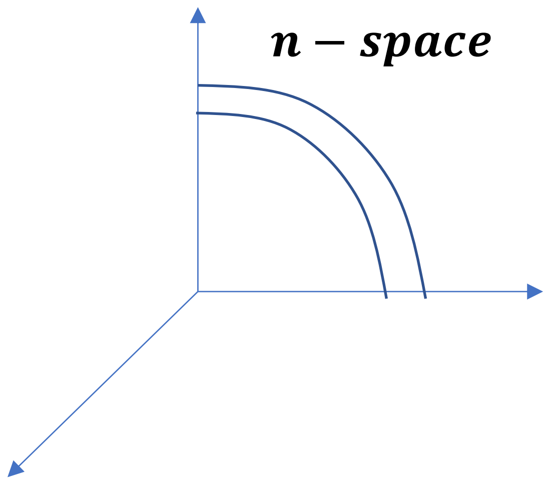
Ideal gas

- **Energy levels for each particle**

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

- **Quantum numbers**

$$\boldsymbol{n} = (n_x, n_y, n_z), n_i = 0, \pm 1, \pm 2, \cdots$$



$$Z_1 = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (n_x^2+n_y^2+n_z^2)} = \left(\int_{-\infty}^{\infty} dn\, e^{-\beta\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2}\right)^3 = \frac{V}{\Lambda(\mathrm{T})^3}$$

$$\text{thermal wavelength } \Lambda(\mathrm{T}) = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$

$$Z_1 = \int_0^{\infty} d\epsilon\, \mathrm{D}(\epsilon) e^{-\beta\epsilon}$$

$$D(\epsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{1/2} = 4\pi n^2 \left|\frac{dn}{d\epsilon}\right|$$

$D(\epsilon)d\epsilon$ number of microstates with energy between ϵ and $\epsilon + d\epsilon$ (for 1 particle)

Thermodynamics of the ideal gas

$$\mathrm{Z_N} = \frac{Z_1^N}{N!} = \frac{V^N}{N!\,\Lambda^{3N}}$$

- Helmholtz free energy

$$F = -kT \ln Z_N = -NkT\left(\ln\left(\frac{Z_1}{N}\right) + 1\right)$$

  - Pressure $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V}$
  - Chemical potential $\mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln\frac{Z_1}{N} = -kT\ln\frac{V}{N\Lambda^3} = kT\ln\frac{P\Lambda^3}{kT}$
  - Internal energy $U = -\frac{\partial}{\partial\beta}\log Z_N = \frac{3}{2}NkT$

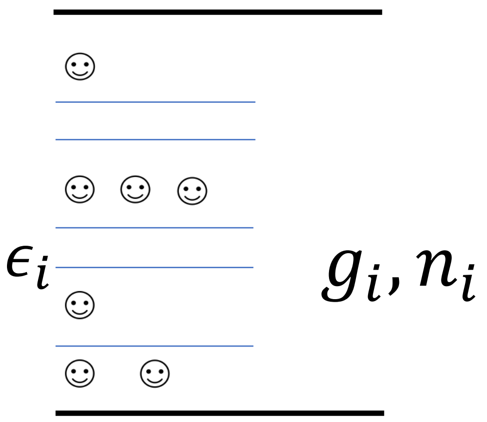
- Grand-canonical partition

$$\Xi(T,\mu) = \sum_{\boldsymbol{N_s}} \frac{\mathbf{1}}{\boldsymbol{N_s}!}(\boldsymbol{\lambda Z_1})^{N_s} = \boldsymbol{e^{\lambda Z_1}} = \boldsymbol{e^{-\beta\Omega}} \rightarrow \boldsymbol{\Omega = -\mathrm{NkT}}, \qquad \mathbf{N} = \boldsymbol{\lambda Z_1}$$

Bose-Einstein statistics:

- Equilibrium (average) occupation number for an energy state

$$\langle \boldsymbol{n_i} \rangle = \frac{\mathbf{1}}{\boldsymbol{e^{\beta(\epsilon_i - \mu)}} - \mathbf{1}} = \frac{\mathbf{1}}{\boldsymbol{e^{\beta\epsilon_i}\lambda^{-1}} - \mathbf{1}}$$

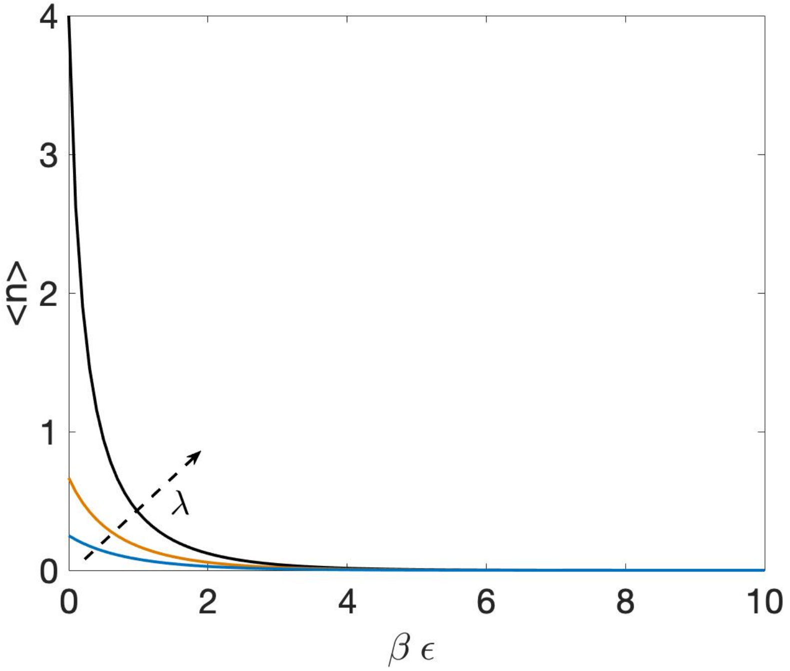


- Probability of a specific microstate at fixed T and μ in the equilibrium

$$\boldsymbol{P(s)} = \frac{\mathbf{1}}{\boldsymbol{\Xi(T,\mu)}} \boldsymbol{e^{-\beta(E_s - \mu N_s)}}, \qquad N_s = \sum_i n_i\,, \qquad E_s = \sum_i \epsilon_i n_i$$

- Grand-canonical partition function

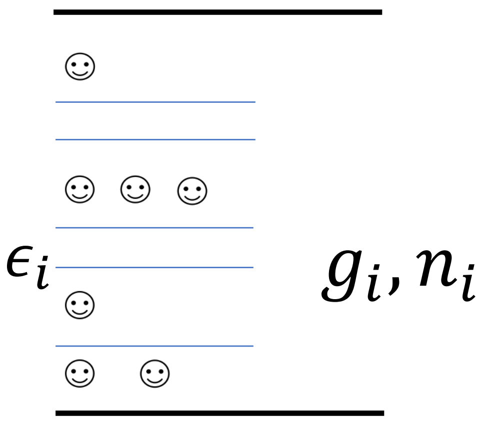
$$\Xi^{(BE)}(T,\mu) = \prod_i \left(\sum_{n_i=0}^{\infty} \left(\lambda e^{-\beta\epsilon_i}\right)^{n_i} \right) = \prod_i \left(\frac{1}{1 - \lambda e^{-\beta\epsilon_i}} \right)$$



Bose-Einstein statistics:

- Probability for having n bosons in a given energy state

$$P_i^{(BE)}(n) = \left(1-\lambda e^{-\beta\epsilon_i}\right)\left(\lambda e^{-\beta\epsilon_i}\right)^n = \frac{1}{\langle n_i\rangle + 1}\left(\frac{\langle n_i\rangle}{\langle n_i\rangle + 1}\right)^n$$



geometric distribution: probability that a particle occupies an energy state is independent of the number of particles already in that states --- tendency of «bunching» together

$$\langle n^2\rangle_i = \sum_{n=0}^{\infty} n^2 \frac{1}{\langle n_i\rangle + 1}\left(\frac{\langle n_i\rangle}{\langle n_i\rangle + 1}\right)^n$$

$$\langle n^2\rangle_i = \frac{1}{\langle n_i\rangle + 1}\left(x\frac{d}{dx}\right)^2 \sum_{n=0}^{\infty} x^n$$

$$\langle n^2\rangle_i = \frac{1}{\langle n_i\rangle + 1}\left(x\frac{d}{dx}\right)^2\left(\frac{1}{1-x}\right), \qquad x = \frac{\langle n_i\rangle}{\langle n_i\rangle + 1}$$

$$\langle n^2\rangle_i = \langle n_i\rangle + 2\langle n_i\rangle^2$$

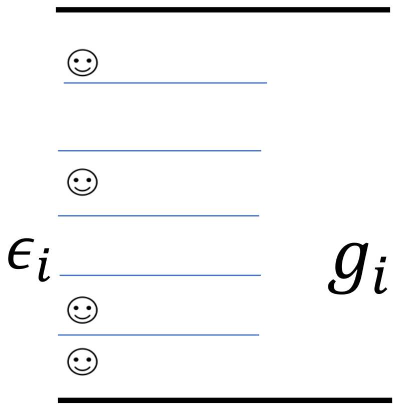
Relative number fluctuations $\quad \dfrac{\langle \Delta n^2\rangle_i}{n_i^2} = \dfrac{1}{n_i} + 1$

Increased number fluctuations relative to be MB statistics

Fermi-Dirac statistics

Equilibrium occupation number for an energy state

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



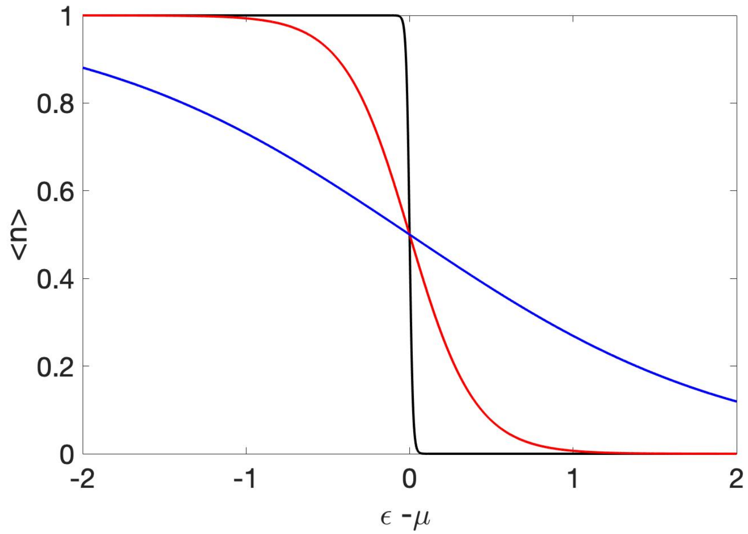
$$g_i > n_i$$

- Probability of a specific microstate at fixed T and μ in the equilibrium

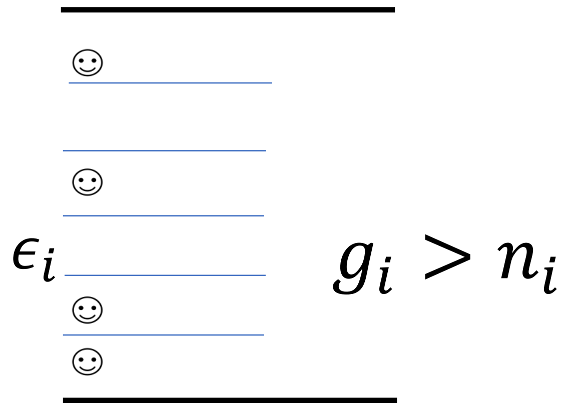
$$\boldsymbol{P(s) = \frac{1}{\Xi(T,\mu)} e^{-\beta(E_s - \mu N_s)}}, \qquad N_s = \sum_i n_i\,, \qquad E_s = \sum_i \epsilon_i n_i$$

- **Grand-canonical partition function**

$$\Xi(T,\mu) = \prod_i \left(\sum_{n_i} e^{-\beta n_i(\epsilon_1 - \mu)} \right) = \prod_i \left(1 + e^{-\beta(\epsilon_i - \mu)} \right)$$



Free fermions: Fermi-Dirac statistics



- **Probability for having n free fermions in a given energy state ϵ_i at fixed T and μ is the same as the average occupation number n_i**

$$P_i^{(FD)}(n) = \frac{\left(\lambda e^{-\beta\epsilon_i}\right)^n}{1+\lambda e^{-\beta\epsilon_i}} = \begin{cases} 1-n_i, & n=0 \\ n_i, & n=1 \end{cases}$$

- $\langle n^2\rangle_i = \sum_{i=0}^{1} n^2 P_i(n) = P_i(1) = n_i$

- Relative mean square fluctuations: as the occupation probability increases, fluctuations are suppressed

$$\frac{\langle \Delta n^2\rangle_i}{n_i^2} = \frac{1}{n_i} - 1 \to 0, as\ n_i \to 1$$

- *Negative statistical correlation– statistical repelling force*

Classical limit: $\epsilon_i \ll kT, \mu(T) \ll 0$ (high-T limit)

- Fermi Dirac/Bose-Einstein distribution:

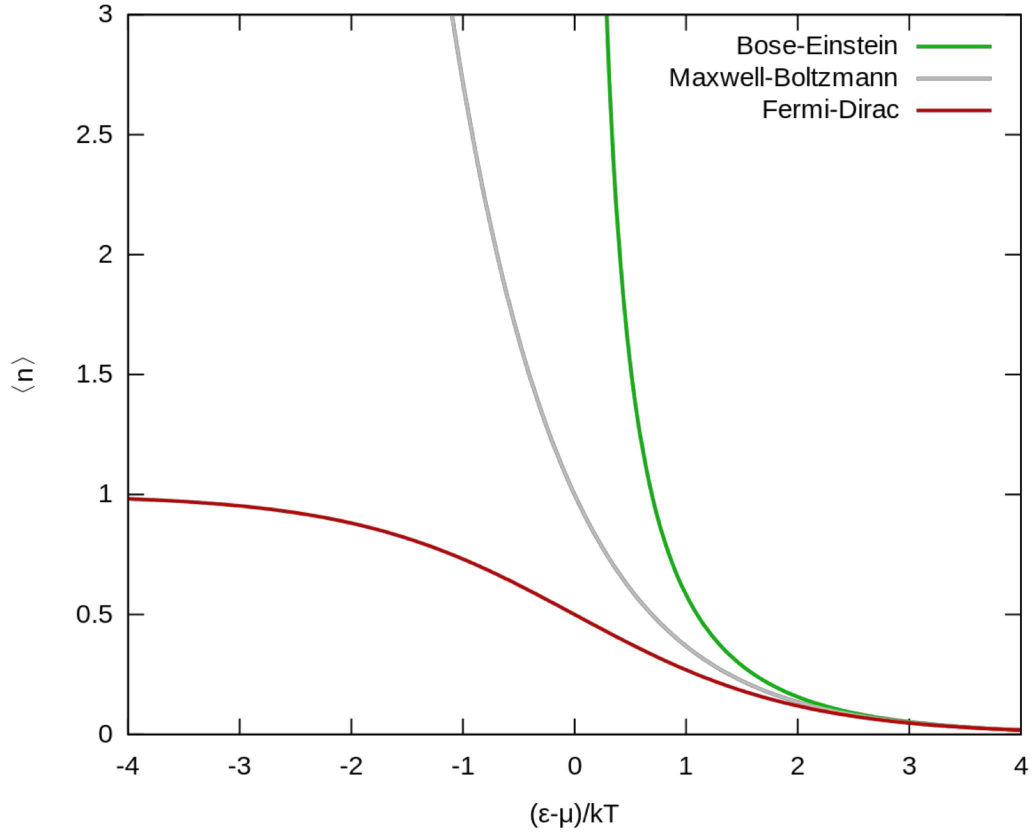
$$n_i = \frac{1}{e^{\beta(\epsilon_i-\mu)} \pm 1} = e^{\beta\mu} \frac{e^{-\beta\epsilon_i}}{1 \pm e^{-\beta\epsilon_i} e^{\beta\mu}} \approx e^{\beta\mu} e^{-\beta\epsilon_i}$$

- Maxwell Boltzmann distribution:

$$n_i^{MB} = \frac{N}{Z_1} e^{-\beta\epsilon_i} = e^{\beta\mu} e^{-\beta\epsilon_i}$$

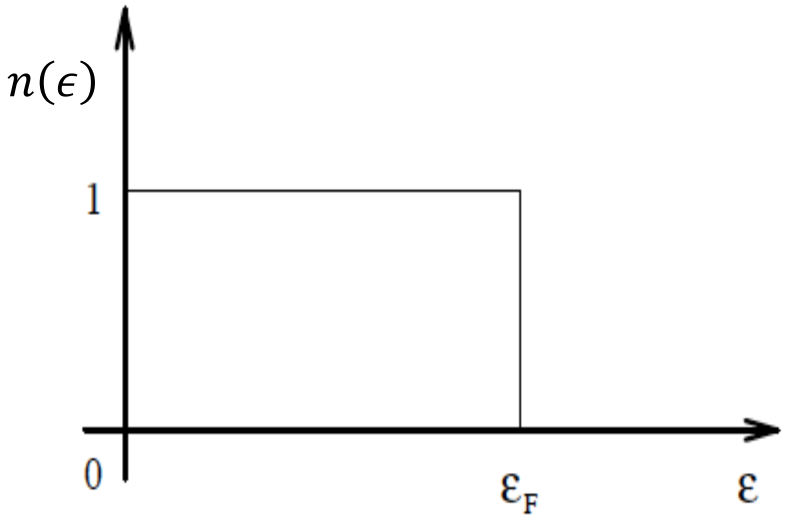
- Classical ideal gas limit: $\mu = -kT \ln \frac{V}{N\Lambda^3(T)} \ll 0 \rightarrow$

$$\boldsymbol{T \gg T^* = \left(\frac{h^2}{2\pi m k}\right)\rho^2, \qquad \rho = \frac{N}{V}}$$

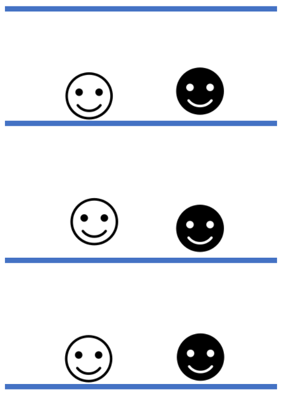


Fermi Dirac distribution at T=0 K

$$n(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}+1} \rightarrow_{T\rightarrow 0} \begin{cases} 1, & \epsilon < \mu \\ 0, & \epsilon > \mu \end{cases}$$

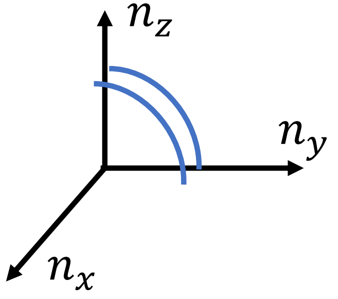


$\epsilon_F \equiv \mu$ Fermi energy level below which all states are occupied



Fermi energy is determined by the density of the Fermi gas $\epsilon_F = \epsilon_F(\rho)$

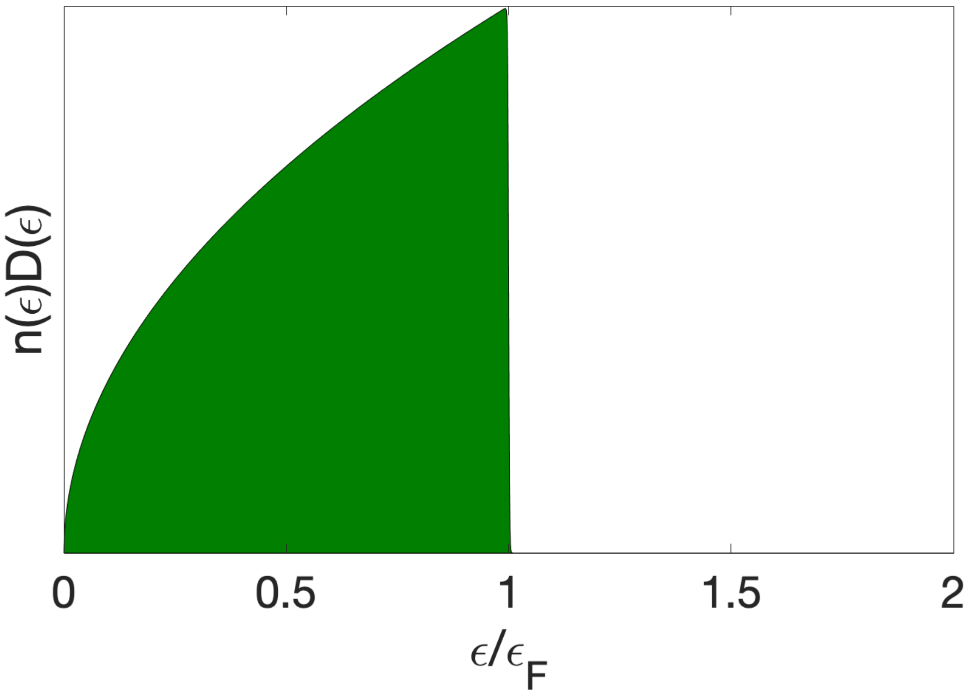
Fermi-Dirac statistics at T=0 K in 3D

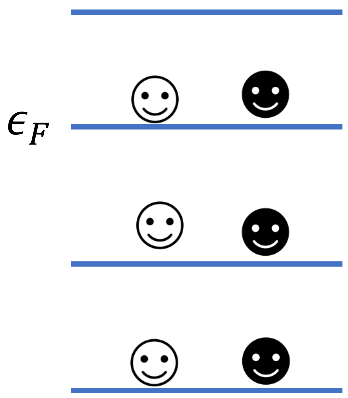


Ideal gas: $\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |n|^2$

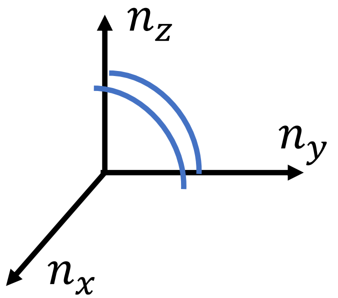
Density of states $D(\epsilon)d\epsilon = (4\pi n^2)dn \rightarrow$

$$D(\epsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{1/2}, \qquad V = L^3$$





Fermi-Dirac statistics at T=0 K in 3D



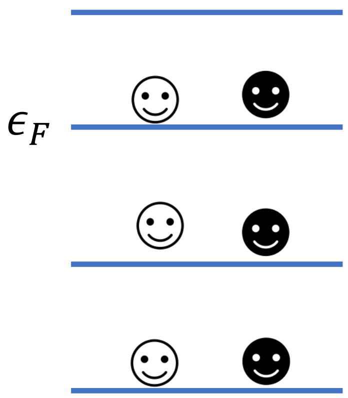
Ideal gas: $\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |n|^2$

Density of states $D(\epsilon)d\epsilon = (4\pi n^2)dn \rightarrow D(\epsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{1/2}, \quad V = L^3$

Number of particles

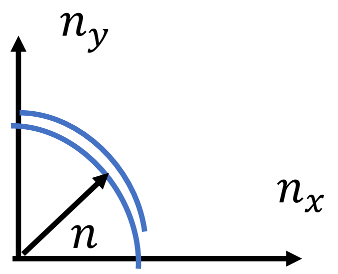
$$N = \sum_i \langle n \rangle(\epsilon_i) = 2\int_0^\infty d\epsilon\ D(\epsilon)H(\epsilon - \epsilon_F) = 2\int_0^{\epsilon_F} d\epsilon\ D(\epsilon)$$

$$N = 2\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^{\epsilon_F} d\epsilon\ \epsilon^{1/2} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3}\ \epsilon_F^{3/2}$$



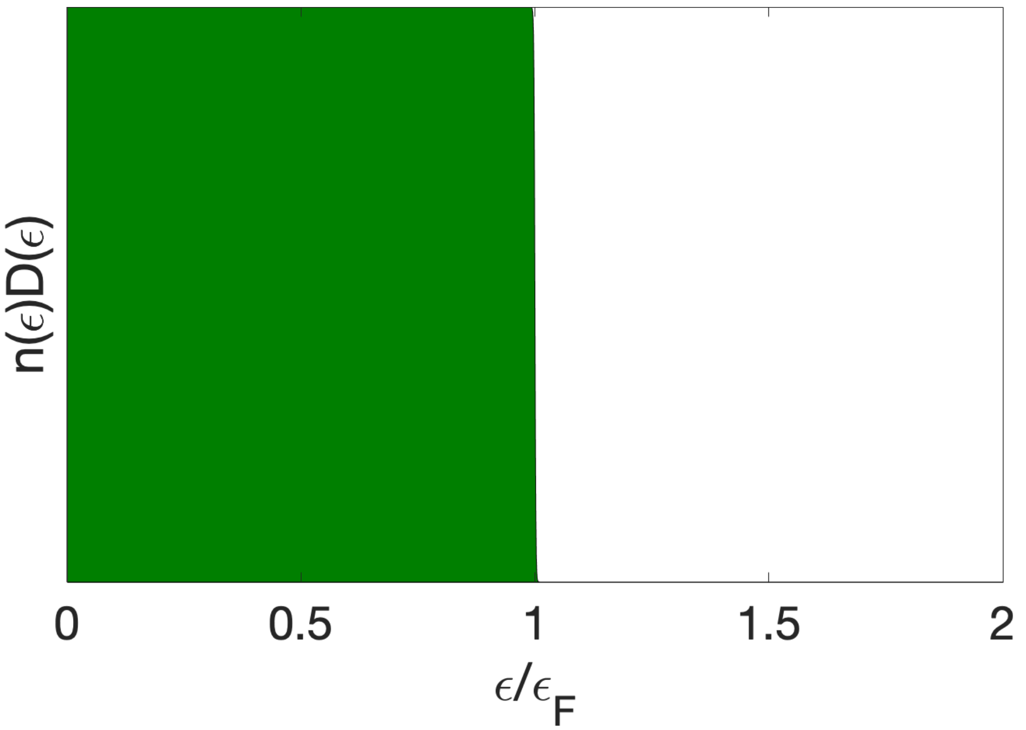
- Fermi energy $\boldsymbol{\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{\frac{2}{3}}}$
- Fermi temperature $\boldsymbol{T_F = \frac{\epsilon_F}{k} = \frac{\hbar^2}{2mk}(3\pi^2\rho)^{\frac{2}{3}} < T^* = \left(\frac{h^2}{2\pi mk}\right)\rho^2}$
- Electron gas in metals $\boldsymbol{T_F \sim 10^4 - 10^5\ K \gg 3\times10^2 K}$ (degenerate gas--- behaves as if it was $0K$ for a wide range of $T \ll T\_F$)

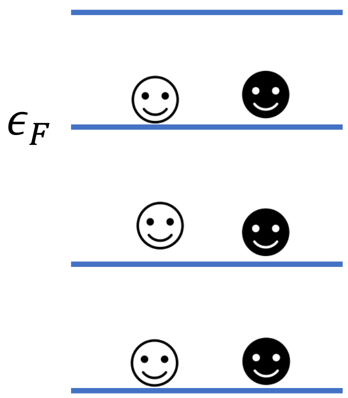
Fermi-Dirac statistics at T=0 K in 2D



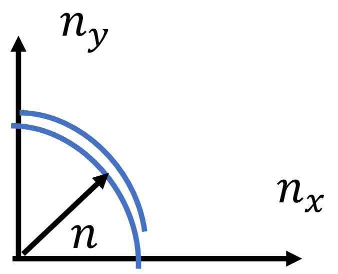
Ideal gas: $\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |n|^2$

Density of states $D(\epsilon)d\epsilon = (2\pi n)dn \rightarrow D(\epsilon) = \frac{L^2}{4\pi}\frac{2m}{\hbar^2}$





Fermi-Dirac statistics at T=0 K in 2D



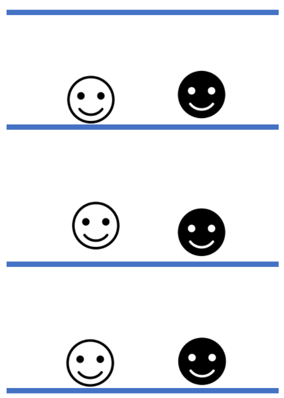
Ideal gas: $\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |n|^2$

Density of states $D(\epsilon)d\epsilon = (2\pi n)dn \rightarrow D(\epsilon) = \frac{L^2}{4\pi}\frac{2m}{\hbar^2}$

Number of particles

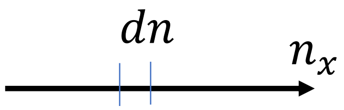
$$N = \sum_i \langle n \rangle(\epsilon_i) = 2\int_0^\infty d\epsilon\ D(\epsilon)H(\epsilon - \epsilon_F) = 2\int_0^{\epsilon_F} d\epsilon\ D(\epsilon)$$

$$N = \frac{L^2}{\pi}\frac{m}{\hbar^2}\int_0^{\epsilon_F} d\epsilon\ = \frac{L^2}{\pi}\frac{m}{\hbar^2}\epsilon_F$$



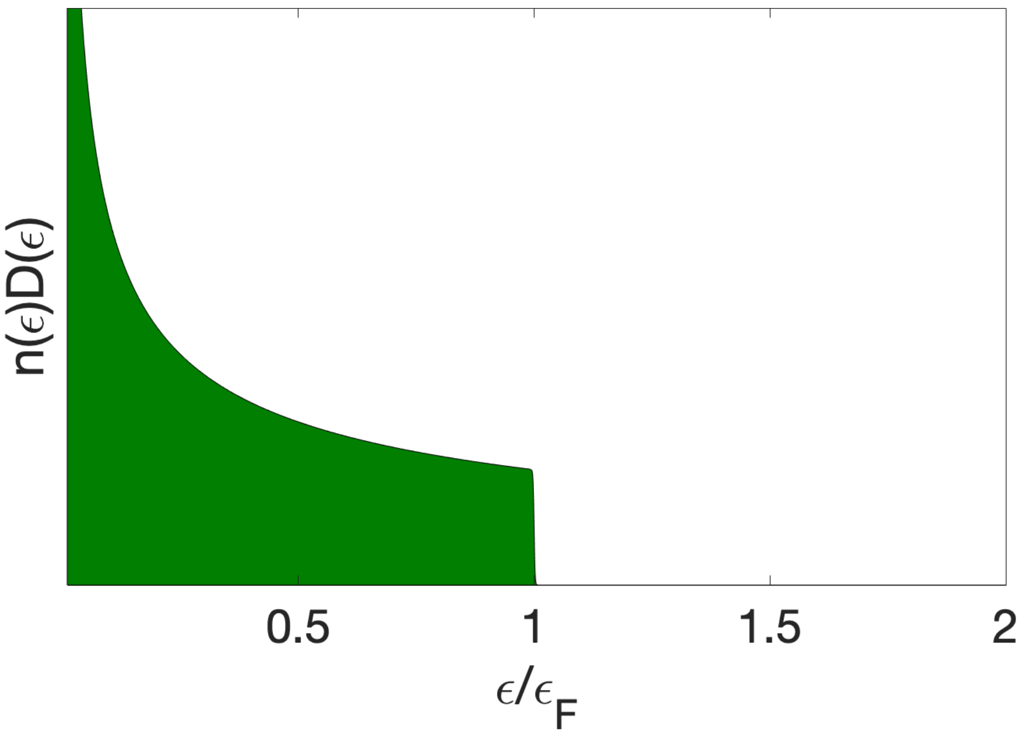
- Fermi energy $\boldsymbol{\epsilon_F = \frac{\hbar^2}{m}\pi\rho}$
- Fermi temperature $\boldsymbol{T_F = \frac{\epsilon_F}{k} = \frac{\hbar^2}{m}\pi\rho}$

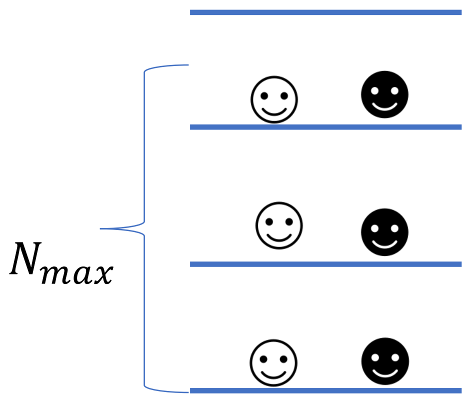
Fermi-Dirac statistics at T=0 K in 1D



Ideal gas: $\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |n|^2$

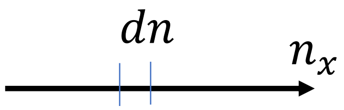
Density of states $D(\epsilon)d\epsilon = dn \rightarrow D(\epsilon) = \frac{L}{4\pi}\left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} \epsilon^{-1/2}$





Fermi-Dirac statistics at T=0 K in 1D

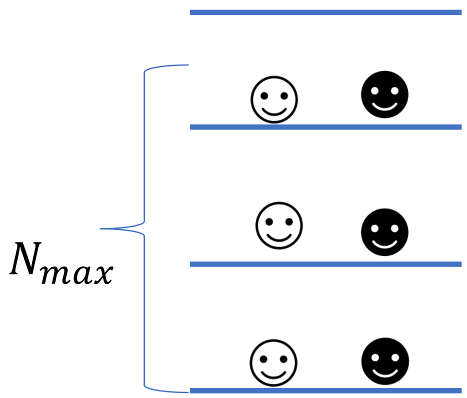
Ideal gas: $\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |n|^2$



Density of states $D(\epsilon)d\epsilon = dn \rightarrow D(\epsilon) = \frac{L}{4\pi}\left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} \epsilon^{-1/2}$

$$N = 2\int_0^{\epsilon_F} d\epsilon\ D(\epsilon) = \frac{L}{\pi}\left(\frac{2m}{\hbar^2}\right)^{\frac{1}{2}} \epsilon_F^{\frac{1}{2}} \rightarrow \epsilon_F = \frac{\hbar^2}{2m}(\pi\rho)^2$$

Number of particles $N = \sum_i \langle n \rangle(\epsilon_i) = 2N_{max}$

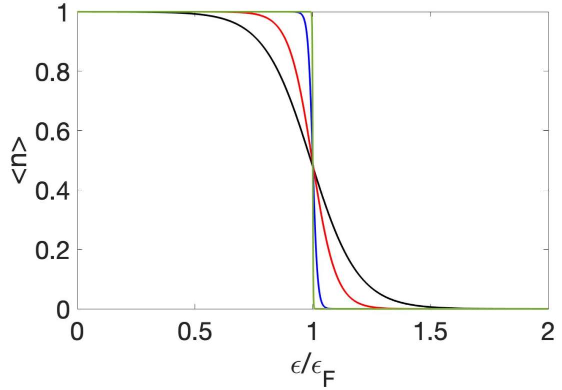


- Fermi energy $\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 N_{max}^2 \rightarrow$

$$\epsilon_F = \frac{\hbar^2}{2m}(\pi\rho)^2, \qquad \rho = \frac{N}{L}$$

Fermi temperature $\mathrm{T_F} = \frac{\hbar^2}{2mk}(\pi\rho)^2$

Fermi Dirac distribution at T>0 K



$$n(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}+1}, \qquad \mu(\epsilon_F, T)$$

Energy states above the Fermi level are occupied by excited fermions