Lecture 7

06.02.2018

Classical free particles
Maxwell-Boltzmann distribution

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

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

Free particles

- Mutual interactions between particles is negligible:

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

  - ideal classical gases
  - ideal quantum gases

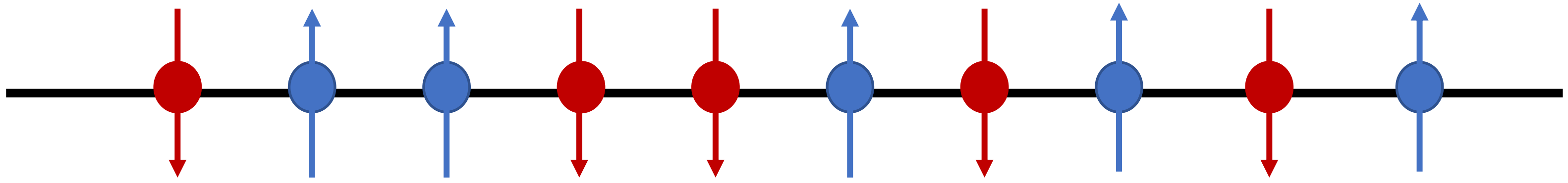
  } ➢ **indistinguishable particles**

Free spins

- Consider a paramagnetic solid composed of N *identical* spin ½ particles *localized* on a lattice

- Each particle is described by a spin $s = \pm\frac{1}{2}$ and a magnetic moment

$m = 2\mu s = \pm\mu$, where μ is the Bohr magneton.

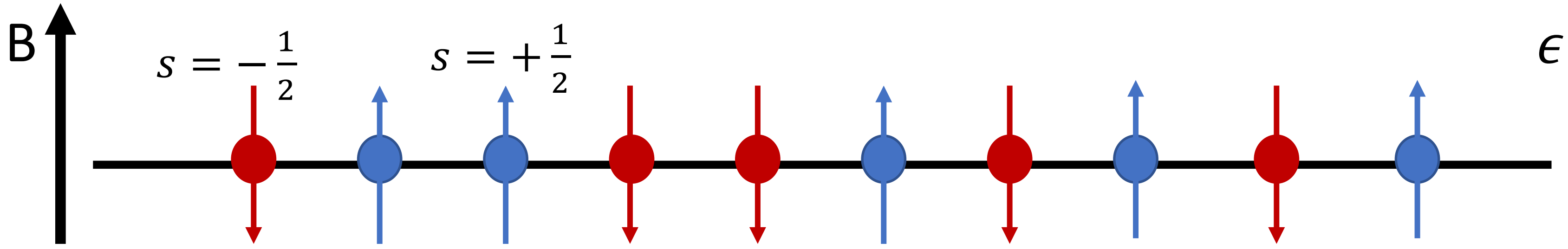


Free spins: microstates

- Each particle is described by a spin $s = \pm\frac{1}{2}$ and a magnetic moment $m = 2\mu s = \pm\mu$, where μ is the Bohr magneton.

- Spin in a magnetic field B has a potential energy

$$\epsilon = -\boldsymbol{m} \cdot \boldsymbol{B} = -2\mu s B$$



$\epsilon = -\mu B$, for $s = +\frac{1}{2}$

$\epsilon = +\mu B$, for $s = -\frac{1}{2}$

Free spins: equilibrium macrostate

- Number of spins N

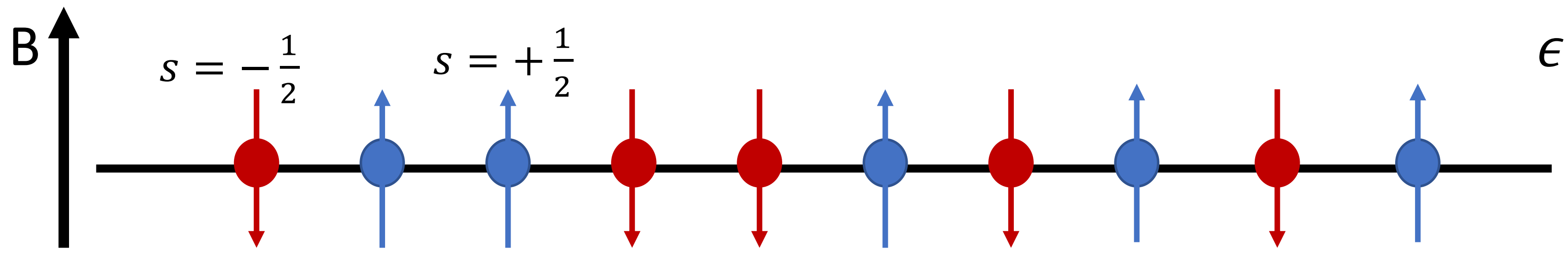
$$N = n_+ + n_-$$

- Total internal energy:

$$E = -\mu B(n_+ - n_-)$$

- Total magnetic moment:

$$M = \mu(n_+ - n_-)$$



$$\epsilon = -\mu B, \text{ for } s = +\frac{1}{2}$$

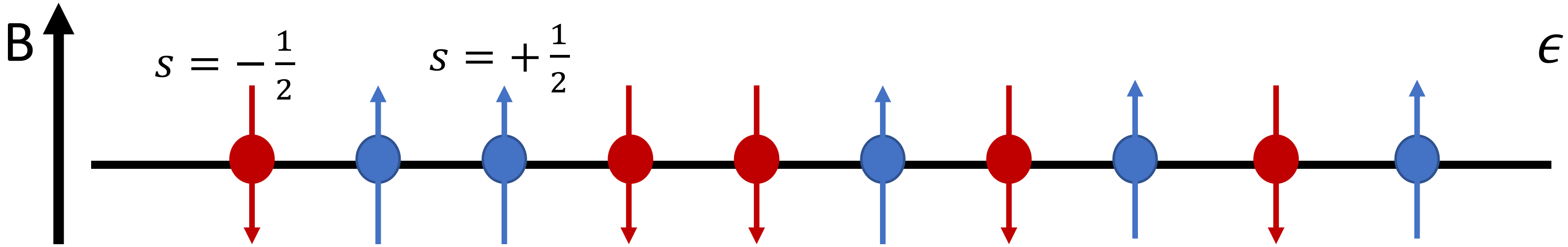
$$\epsilon = +\mu B, \text{ for } s = -\frac{1}{2}$$

Microcanonical ensemble of free spins

$$N = n_+ + n_-, \qquad U = -\mu B(n_+ - n_-), \qquad M = \mu(n_+ - n_-)$$

Free spins+ the external magnetic field = isolated system

Total energy is conserved. The equilibrium macrostate is determined by total (discrete) number of possible spin configurations (microstates) or its ***multiplicity*** $\boldsymbol{W(U,N)}$ *(the equivalant of the phase space volume for systems with a continuum number of microstates).*



$\epsilon = -\mu B$, for $s = +\frac{1}{2}$

$\epsilon = +\mu B$, for $s = -\frac{1}{2}$

Basic rules of combinatorics

- Number of ways (permutations) in which we can arrange N *distrinct* objects in a *row*

$$N \cdot (N-1) \cdots 2 \cdot 1 \equiv N!$$

- Ordered selection of r out of N distinct objects

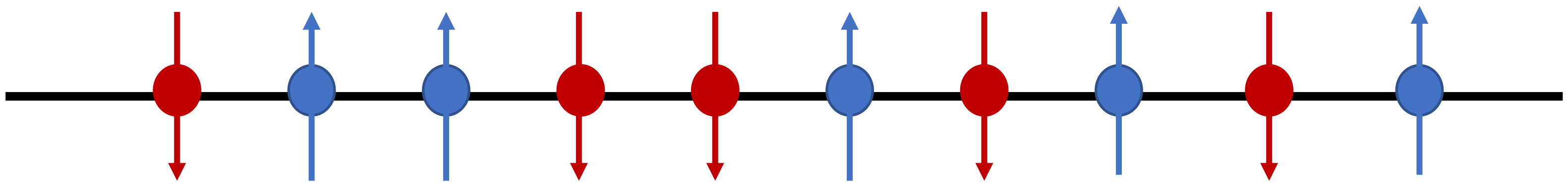
$$N \cdot (N-1) \cdots (N-r+1) \equiv \frac{N!}{(N-r)!}$$

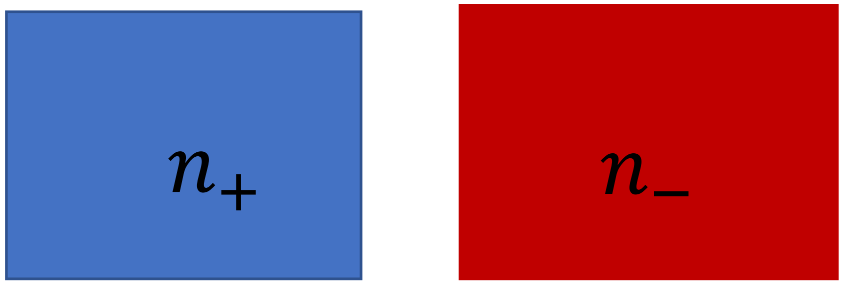
- When the selection is **unordered**, $\frac{N!}{r!(N-r)!}$

Microcanonical ensemble of free spins

Number of spin configurations with n_+ spins up and n_- spins down out of N spins is

$$\boldsymbol{W(n_+, N) = \frac{N!}{n_+!\, n_-!} = \frac{N!}{n_+!\,(N - n_+)!}}$$





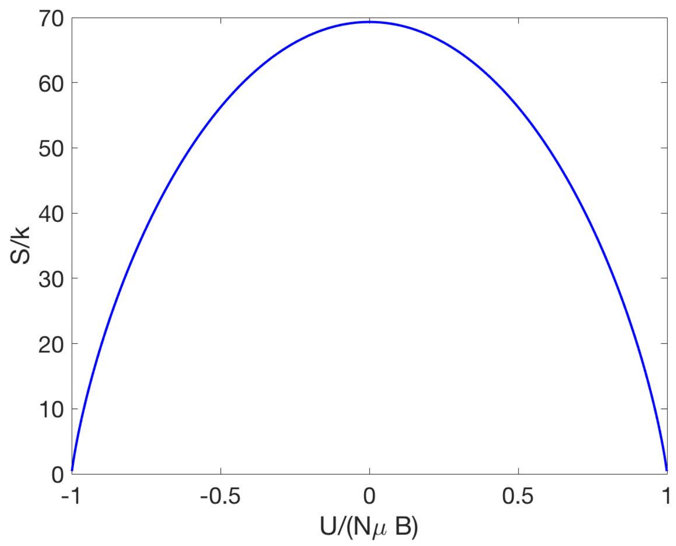
Microcanonical ensemble of free spins: Macrostate

- Boltzmann' entropy $S = k \ln W$

$$S(n_+, N) = k(\mathrm{N} \log N - n_+ \ln n_+ - (N - n_+) \ln(N - n_+))$$

- Energy $U(n_+, N) = -\mu B(2n_+ - N)$
- Temperature $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N = \frac{\partial S}{\partial n_+} \frac{\partial n_+}{\partial U} = k \ln\left(\frac{n_+}{N - n_+}\right) \frac{1}{2\mu B}$

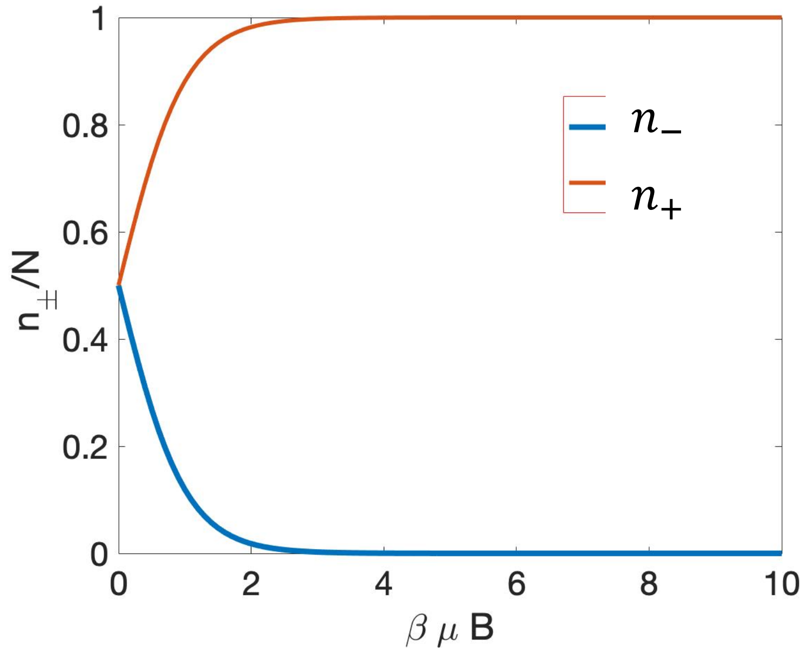
$$\frac{n_+}{N - n_+} = e^{2\beta\mu B}$$



Microcanonical ensemble: Maxwell-Boltzmann distribution

$$\frac{n_+}{N} = \frac{e^{\frac{\mu B}{kT}}}{e^{\frac{\mu B}{kT}} + e^{-\frac{\mu B}{kT}}}, \qquad \frac{n_-}{N} = \frac{e^{-\frac{\mu B}{kT}}}{e^{\frac{\mu B}{kT}} + e^{-\frac{\mu B}{kT}}}$$

- As temperature T gets lower, the distribution of spins up increases
- Thermal fluctuations increase the likelyhood that spins may align in the opposite directions with the applied magnetic field



Thermodynamics of paramagnets

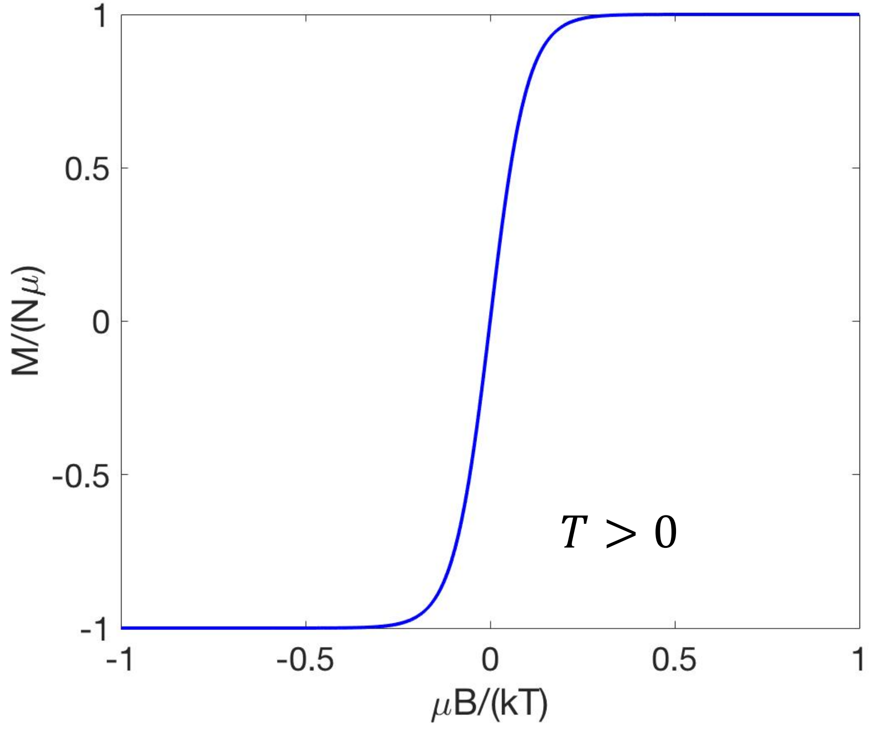
$$\frac{n_+}{N} = \frac{e^{\frac{\mu B}{kT}}}{e^{\frac{\mu B}{kT}} + e^{-\frac{\mu B}{kT}}}, \qquad \frac{n_-}{N} = \frac{e^{-\frac{\mu B}{kT}}}{e^{\frac{\mu B}{kT}} + e^{-\frac{\mu B}{kT}}}$$

- Total magnetization

$$M = \mu(n_+ - n_-) = N\mu \tanh\frac{\mu B}{kT}$$

- Susceptibility

$$\chi = \left(\frac{\partial M}{\partial B}\right)_T = \frac{N\mu^2}{kT}\frac{1}{\cosh^2\left(\frac{\mu B}{kT}\right)}$$



Canonical ensemble of free spins at fixed T and N

Energy change upon flipping a +1/2 spin into a -1/2 spin due to thermal fluctuations: $n_+ \to n_+ - 1,\ n_- \to n_- + 1,$

$$U_1 = -\mu B(n_+ - n_-) \to U_2 = -\mu B\,(n_+ - 1\ - n_- - 1)$$

$$\Delta U = 2\mu B$$

Change in entropy upon a spin flipping

$$\Delta S = k(\log W_2 - \log W_1) = k\left(\log\frac{N!}{(n_+ - 1)!\,(n_- + 1)!} - \log\frac{N!}{(n_+)!\,(n_-)!}\right)$$

$$\Delta S \approx k\log\frac{n_+}{n_-}$$

Changes in energy and entropy are linked by the fixed temperature of the thermal bath

$$\frac{\Delta S}{\Delta U} = \frac{1}{T} \to \frac{n_+}{n_-} = e^{\frac{2\mu B}{kT}} \to \frac{n_+}{N} = \frac{e^{\frac{\mu B}{kT}}}{e^{\frac{\mu B}{kT}} + e^{-\frac{\mu B}{kT}}}$$

Canonical ensemble of free spins: MBD

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

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

- 1-particle partition function $Z_1(T) = \sum_{s=\pm 1} e^{-\frac{\epsilon_s}{kT}} = 2\cosh\left(\frac{\mu B}{kT}\right)$

- N-partition function $Z_N(T) = Z_1^N = 2^N \cosh^N\left(\frac{\mu B}{kT}\right)$

Canonical ensemble of free spins: macrostate

- Average spin energy $\langle \epsilon \rangle = \frac{1}{Z_1} \sum_s \epsilon_s \, e^{-\frac{\epsilon_s}{kT}} = -\mu B \tanh\left(\frac{\mu B}{kT}\right)$

- Average total energy $\mathrm{U} = \mathrm{N}\langle \epsilon \rangle = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$

- Helmholtz free energy $\mathbf{F}(\mathbf{T}, \mathbf{M}(\mathbf{B}, \mathbf{T})) = -\boldsymbol{NkT} \log\left(\mathbf{2} \cosh\left(\frac{\boldsymbol{\mu B}}{\boldsymbol{kT}}\right)\right)$

- Gibbs free energy $\mathbf{G}(\mathbf{T}, \mathbf{B}) = \boldsymbol{F} - \boldsymbol{MB}$

Maxwell-Boltzmann statistics: generic case

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

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

- Each energy state ϵ_i has a «degeneracy» g_i which is the density of states, i.e. density of microstates at that energy level

Microcanonical: 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 participles in g_i degenerate states.

- The total number of microstates with the particle configurations $\{n_i\}$

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

- Total multiplicity of a macrostate is dominated by the equilibrium distribution, hence

$$S = k \log\left(W(\{n_i^{(eq)}\})\right)$$

Canonical ensemble

- Thermal fluctuation: a particle changes its energy from ϵ_j to ϵ_i

$$n_i \to n_i + 1, \qquad n_j \to n_j - 1$$

- Change in energy $\Delta U = \epsilon_i - \epsilon_j$

- Change in entropy $\Delta S = k\left(\log \frac{g_i^{n_i+1}}{(n_i+1)!}\frac{g_j^{n_j-1}}{(n_j-1)!} - \log \frac{g_i^{n_i}}{n_i!}\frac{g_j^{n_j}}{n_j!}\right) \approx k \log \frac{g_i n_j}{n_i\, g_j}$

$$\frac{\Delta S}{\Delta U} = \frac{1}{\mathrm{T}} \to \frac{g_i n_j}{n_i\, g_j} = \mathrm{e}^{-\beta(\epsilon_i - \epsilon_j)}$$

Maxwell-Boltzmann distribution

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

- 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

$$F = -kT\ln\, Z_1^N$$

- Entropy

$$\frac{S}{k} = N\log Z_1 + \frac{U}{kT}$$

Indistinguishable, free particles particles

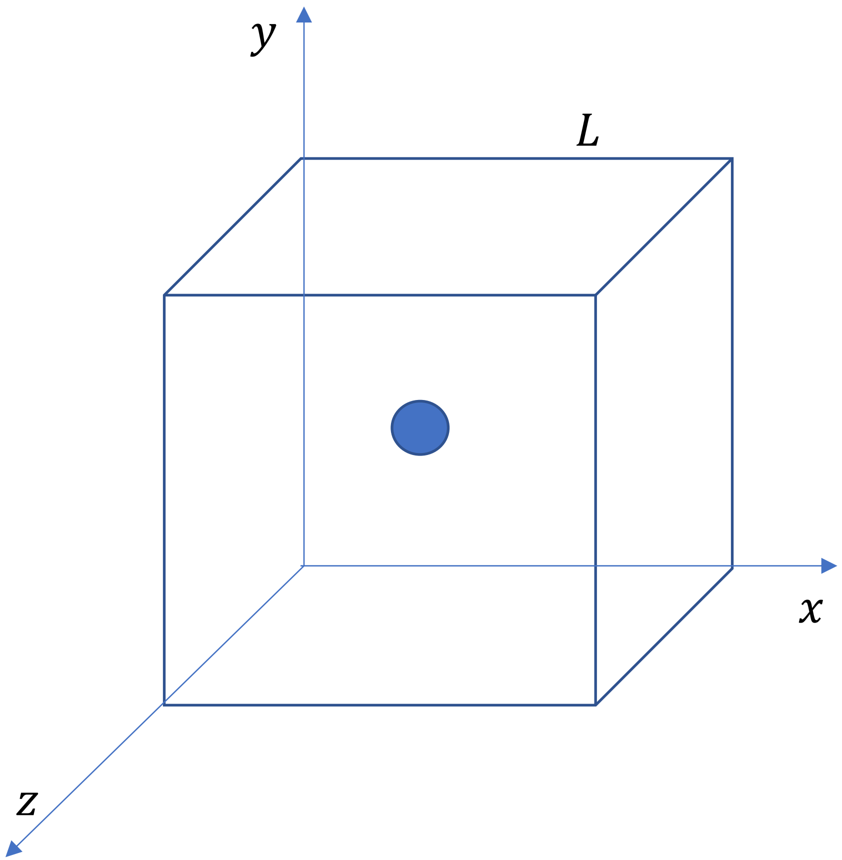
- Number of configurations $W_{\text{disting}} = N! \prod_i \frac{g_i^{n_i}}{n_i!}$

$$W_{\text{indisting}} = \prod_i \frac{g_i^{n_i}}{n_i!}$$

Ideal gas

- Find the energy levels ϵ_s for free particles in a box, so we can compute the partition function using the generic formula from M-B statistics

$$Z_N = \frac{Z_1^N}{N!}, \qquad Z_1 = \sum_s e^{-\beta\epsilon_s}$$



- Hamiltonian of one particle $\hat{H} = \frac{\hat{p}^2}{2m}$ with the momentum operator $\hat{p} = -i\hbar\nabla$

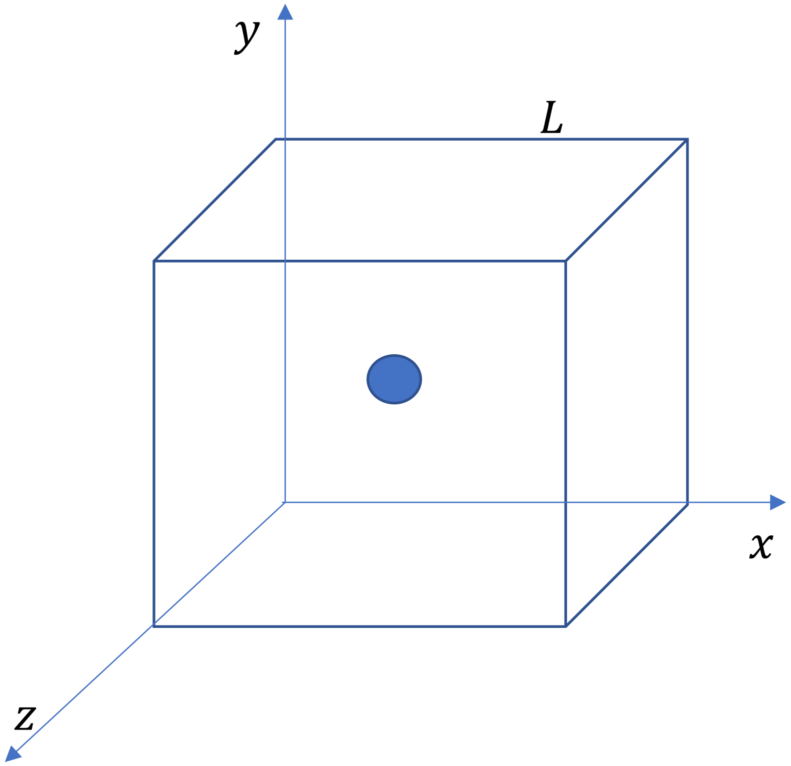
- The particle's wavefunction satisfies the $Schrödinger$ equation

$$\hat{H}\psi = \epsilon\psi \rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi = \epsilon\psi$$

Ideal gas

Eigenfunctions of the *Schrödinger* equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \epsilon\psi$$ with periodic boundary conditions



- $\psi_{\mathrm{n}} = \mathrm{e}^{2\pi i\frac{\boldsymbol{n}\cdot\boldsymbol{x}}{L}}, \boldsymbol{n} = (n_x, n_y, n_z), n_i = 0, \pm 1, \pm 2, \cdots$

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

Ideal gas: Z_1

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

$$Z_1 = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (n_x^2+n_y^2+n_z^2)} = \left(\sum_n e^{-\beta\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2}\right)^3$$

$$Z_1 \approx \left(\int_{-\infty}^{\infty} dn\, e^{-\beta\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2}\right)^{\mathbf{3}} = L^3\left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3}{2}}$$

$$Z_1 = \frac{V}{\Lambda^3}, \qquad \text{thermal wavelength } \Lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$$

Ideal gas

$$Z_1(T) = \frac{V}{\Lambda^3(T)}, \qquad \text{thermal wavelength } \Lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$$

- Maxwell-Boltzmann statistics is valid in the classical limit:

$$\Lambda^3(T) \ll \frac{L^3}{N} \rightarrow T \gg \left(\frac{h^2}{2\pi mk}\right)\frac{N^{\frac{2}{3}}}{L^2}$$

Ideal gas: **(p,q)**-phase space vs. **n**-space

Connection to the integral over the momentum phase space

$$Z_1 = \int d^3\boldsymbol{n}\, e^{-\beta\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\boldsymbol{n}^2}$$

The momentum coordinate $\boldsymbol{p} = \frac{2\pi\hbar}{L}\boldsymbol{n} \rightarrow d^3\boldsymbol{p} = \frac{(2\pi\hbar)^3}{V}d^3\boldsymbol{n}$

$$Z_1 = V\int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3}e^{-\beta\frac{\boldsymbol{p}^2}{2m}} = 4\pi V\int \frac{p^2dp}{(2\pi\hbar)^3}e^{-\beta\frac{p^2}{2m}}$$

$$Z_1 = 4\pi V\int \frac{p^2dp}{(2\pi\hbar)^3}e^{-\beta\frac{p^2}{2m}} \underset{\epsilon=\frac{p^2}{2m}}{=} \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int d\epsilon\,\epsilon^{1/2}e^{-\beta\epsilon} = \int d\epsilon \mathrm{D}(\epsilon)e^{-\beta\epsilon}$$

Ideal gas: density of states

$$\mathrm{Z}_1 = \int_0^\infty d\epsilon\, \mathrm{D}(\epsilon) e^{-\beta\epsilon}$$ (Laplace transform)

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

$D(\epsilon)d\epsilon$ 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

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

- Pressure $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V}$

- Chemical potential $\mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \ln \frac{Z_1}{N} = kT \ln \frac{N\Lambda^3}{V} = kT \ln \frac{P\Lambda^3}{kT}$

- Internal energy $U = -\frac{\partial}{\partial \beta} \log Z_N = \frac{3}{2} NkT$

- Entropy $\mathrm{S} = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk\left[\frac{5}{2} - \log \frac{N}{V}\Lambda^3\right]$