Agenda: Quantum Statistics

- Concepts in quantum mechanics
  - Quantal traveling waves and translational motion
  - Quantum model for vibrations (also Bosons)
  - Quantum model for vibrations
- Quantum partition functions for Fermions
- Quantum Fermi gas
- Bose radiation gas

Indistinguishable Particles

Ensembles of N identical and independent particles: each can access many s.p. states without restriction→ partition function is product of s.p. partition functions

Classical ***N***-body problem → classical ***1***-body problem*:*

$$\text{If particles are distinguishable} \rightarrow Q(N,V,T) = q^N$$

$$\text{If particles are indistinguishable} \rightarrow Q(N,V,T) \approx q^N / N!$$

Boltzmann
high-T limit

Condition for classical Boltzmann limit
high-T, large *m,* low density.
Often applicable for most @300K

$$\frac{V}{\lambda^3_{therm}} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \left(\frac{eV}{N}\right) \gg 1$$

For identical, indistinguishable particles, phase space restrictions,
Pauli blocking for Fermions: no two identical Fermions on same qu. state,
No restrictions on Bosons (any # bosons per state possible).

Dependence on N → use grand canonical ensemble $\Xi(V, T, \mu)$

GPF for Indistinguishable Particles

Ensembles of *N* identical and independent particles → PF product structure

$$\textit{Grand partition function } \left(\beta = 1/k_B T\right)$$

$$\Xi(V,T,\mu) = \sum_{N=0}^{\infty} Q(N,V,T)\cdot e^{-\beta\cdot\mu\cdot N} = \sum_{N=0}^{\infty} \lambda^N \cdot Q(N,V,T)$$

$$\textit{Activity } \lambda := e^{-\beta\cdot\mu}$$

$$\textit{Canonical pf for } N-\textit{particle ensembles } Q_N := Q(N,V,T)$$

Relation between Free Energy μ and @ particles

$$\textit{Helmholtz free energy } A_N = -k_B T\cdot Ln Q_N \rightarrow Q_N = e^{-A_N/k_B T}$$

$$\frac{1}{\beta}\frac{\partial A_N}{\partial N} = \mu = -k_B T\left\{\frac{Ln Q_{N+1} - Ln Q_N}{(N+1)-N}\right\} = k_B T\cdot Ln\left(\frac{Q_N}{Q_{N+1}}\right) \rightarrow$$

$$\boxed{Q_{N+1} = e^{-\mu/k_B T}\cdot Q_N}$$

Fermion State Populations

Ensembles of *N* identical and independent particles→ PF product structure

$$Q_N = e^{-\mu/k_BT} \cdot Q_{N-1} \quad \text{also: } Q_N = \sum_j^{\{N\}} e^{-\beta \cdot E_j^{(N)}} = \sum_j^{\{N\}} \prod_i e^{-\beta \cdot n_i(j) \cdot \varepsilon_i}$$

$$j \in \left\{ \begin{matrix} N \text{ particle} \\ \text{states} \end{matrix} \right\}$$

N-particle energy $E_j^{(N)} = \sum_i^{\{N\}} n_i(j) \cdot \varepsilon_i;$

Fermions : $n_i = 0, 1$ *for any s.p. state i*

Consider one specific state i : $Q_N = Q_N(n_i = 1) + Q_N(n_i = 0)$

1 particle in state *i* removed

$$Q_N(n_i = 1) = \sum_j^{\{N\}} \prod_i e^{-\beta \cdot n_i(j) \cdot \varepsilon_i} = e^{-\beta \cdot \varepsilon_i} \sum_j^{\{N-1\}} \prod_i e^{-\beta \cdot n_i(j) \cdot \varepsilon_i} = e^{-\beta \cdot \varepsilon_i} Q_{N-1}(n_i = 0)$$

$$\langle n_i \rangle = \frac{Q_N(1)}{Q_N(1) + Q_N(0)} = \frac{e^{-\beta \cdot \varepsilon_i} Q_{N-1}(0)}{e^{-\beta \cdot \varepsilon_i} Q_{N-1}(0) + Q_N(0)} = \frac{e^{-\beta \cdot \varepsilon_i} Q_{N-1}}{e^{-\beta \cdot \varepsilon_i} Q_{N-1} + Q_N}$$

Q_N , Q_{N-1} no info on state *i*

Fermi-Dirac and Bose-Einstein State Populations

Ensembles of N identical and independent particles→ PF product structure

$$Q_N = e^{-\mu/k_B T} \cdot Q_{N-1}$$ also: $$Q_N = \sum_j^{\{N\}} e^{-\beta \cdot E_j^{(N)}} = \sum_j^{\{N\}} \prod_i e^{-\beta \cdot n_i(j) \cdot \varepsilon_i}$$ $$j \in \left\{ \begin{matrix} N \text{ particle} \\ \text{states} \end{matrix} \right\}$$

$$\langle n_i \rangle = \frac{e^{-\beta \cdot \varepsilon_i} Q_{N-1}}{e^{-\beta \cdot \varepsilon_i} Q_{N-1} + Q_N} = \frac{e^{-\beta \cdot \varepsilon_i} Q_{N-1}}{e^{-\beta \cdot \varepsilon_i} Q_{N-1} + e^{-\beta \cdot \mu} Q_{N-1}} = \frac{e^{-\beta \cdot \varepsilon_i}}{e^{-\beta \cdot \varepsilon_i} + e^{-\beta \cdot \mu}}$$

Fermion occupation number for state i

$$\langle n_i \rangle = \frac{1}{e^{\beta \cdot (\varepsilon_i - \mu)} + 1}$$

Fermi-Dirac statistics

Boson occupation number for state i

$$\langle n_i \rangle = \frac{1}{e^{\beta \cdot (\varepsilon_i - \mu)} - 1}$$

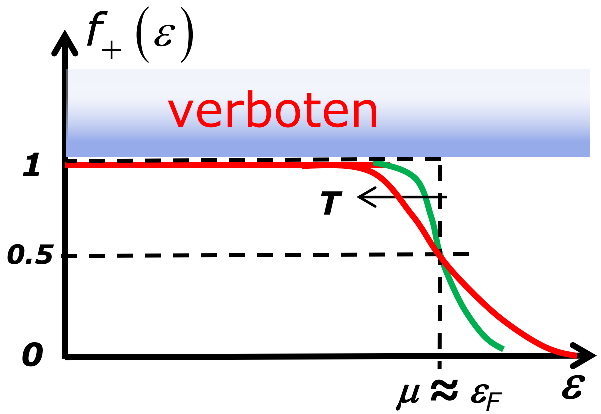
Bose-Einstein statistics From unrestricted partition sum *terms* $e^{\alpha} \ll 1$

Boltzmann High-T Limit State Populations

Fermi-Dirac or Bose-Einstein statistics $A := e^{\beta\cdot\mu} = e^{\mu/k_BT}$

Energy gain per particle added: $G = \mu\cdot N \rightarrow \mu = k_BT\cdot Ln\,A$

@ high T → $\langle n_i\rangle = f_\pm(\varepsilon_i) = \dfrac{1}{e^{\beta\cdot(\varepsilon_i-\mu)}\pm 1} \xrightarrow[\beta\to 0]{} e^{-\beta\cdot(\varepsilon_i-\mu)} = e^{-(\varepsilon_i-\mu)/k_BT}$



Boltzmann high T Limit for FD & BE $\xrightarrow[T\to\infty]{}$ $\langle n_i\rangle \propto e^{-\varepsilon_i/k_BT}$

$\mu : f_+(\mu) = 1/2$

$f_+(\varepsilon_i) = 1 \rightarrow$ *state i is occupied by 1 Fermion*

Pauli – blocked for other Fermions

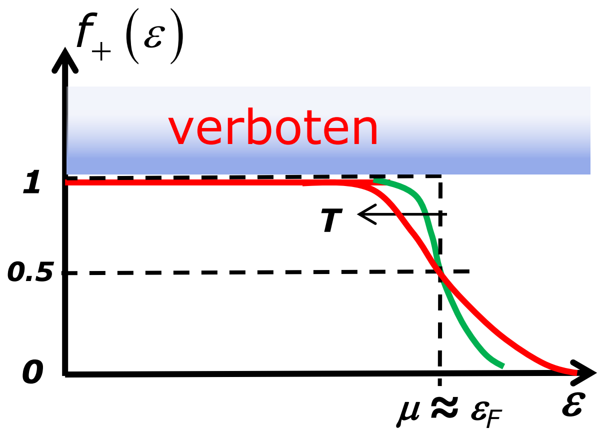
Degenerate Fermi gas : $T = 0,\ S = 0$

$$f_+(\varepsilon_i) = \begin{cases} 0 \text{ for } \varepsilon_i > \varepsilon_F \\ 1 \text{ for } \varepsilon_i < \varepsilon_F \end{cases}$$

Fermi-Dirac State Populations

Boltzmann high T Limit for FD & BE $\xrightarrow[T\to\infty]{} \boxed{\langle n_i \rangle \propto e^{-\varepsilon_i/k_B T}}$

$$Pauli-blocking: \quad f_+(\varepsilon_i) = 1 \rightarrow \text{state } i \text{ is occupied, not accessible to other Fermions}$$



Degenerate Fermi gas: $T = 0,\ S = 0$

$$f_+(\varepsilon_i) = \begin{cases} 0 \text{ for } & \varepsilon_i > \varepsilon_F \\ 1 \text{ for } & \varepsilon_i < \varepsilon_F \end{cases}$$

$$\mu : f_+(\mu) = 1/2$$

Sommerfeld expansion

$$\mu(T) = \mu(T=0)\left[1 - \frac{\pi}{12}\left(\frac{k_B T}{\mu(T=0)}\right)^2\right]$$

Task: Partition function → have general expression for probability term, equivalent to Boltzmann factors → apply to microscopic model systems:

→ Free electrons, electrons in solids, plasmas,…, nucleons in nuclei,…

→ Task: provide energy levels ε_i and degeneracies $g(\varepsilon_i)=(2s+1)\cdot\omega(\varepsilon_i)$

Grand Canonical Partition Function of FG

For degenerate FG, $\mu \gg k_B T \approx 0 \;\rightarrow$ mean (zero – point) energy :

Ground state : $T = 0 \rightarrow \langle E_0 \rangle = \frac{3}{5}\varepsilon_F > 0$ also $S = S_{min} = 0$

$\varepsilon_F = \varepsilon_F(N,V) \rightarrow$ calculate zero – point pressure $\langle p_0 \rangle = -\frac{\partial}{\partial V}(E)_{S,N}$

For properties of non – degenerate FG, need Partition Function Ξ

Have derived from qm particle – in – a – box model

Mean occupancy of μstate i $\langle n_i \rangle = \dfrac{e^{-\beta\cdot\varepsilon_i}}{e^{-\beta\cdot\varepsilon_i} + e^{-\beta\cdot\mu}}$

Grand Canonical PF

$$Ln\,\Xi = -\sum_i Ln\left\{1 + e^{\beta\cdot(\mu-\varepsilon_i)}\right\}$$

$$Ln\,\Xi = +\sum_i Ln\left\{1 - p_i\right\}$$

Thermodynamic Properties of FG

$$\text{Statistical Entropy}: S = -k_B \sum_{n=1}^{\Omega_N} p_n \cdot Ln\, p_n \qquad p_n = \text{probability of } \mu\text{state } n$$

Sum over all μ*states of* $N-$*particle system,*

each constructed of s.p. states with energy $\varepsilon_i \rightarrow p_n = p_n\left(\{n_i\}\right)$,

S is extensive $\rightarrow$ *sum over terms for s.p. states*

One s.p. state ε_i *contributes to* $N-$*particle* μ*state twice!*

$$p_+ = \langle n_i \rangle \text{ and } p_- = 1 - \langle n_i \rangle$$

$$p_+(\varepsilon) = \frac{1}{e^{\beta\cdot(\varepsilon-\mu)}+1}$$

$$p_-(\varepsilon) = 1 - \frac{1}{e^{\beta\cdot(\varepsilon-\mu)}+1} = \frac{1}{e^{-\beta\cdot(\varepsilon-\mu)}+1}$$

$$\text{Contribution to } S: \frac{-s_\varepsilon}{k_B} = p_+(\varepsilon) Lnp_+(\varepsilon) + p_-(\varepsilon) Lnp_-(\varepsilon)$$

$$\frac{+s_\varepsilon}{k_B} = \frac{1}{1+e^{\beta\cdot(\varepsilon-\mu)}} Ln\left(1+e^{\beta\cdot(\varepsilon-\mu)}\right) + \frac{1}{1+e^{-\beta\cdot(\varepsilon-\mu)}} Ln\left(1+e^{-\beta\cdot(\varepsilon-\mu)}\right)$$

Thermodynamic Properties of FG

$$\text{Statistical Entropy}: S = -k_B \sum_{n=1}^{\Omega_N} p_n \cdot Ln\, p_n \qquad p_n = \text{probability of } \mu\text{state } n$$

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$$\boxed{\frac{+s_\varepsilon}{k_B} = \frac{1}{1+e^{\beta\cdot(\varepsilon-\mu)}} Ln\left(1+e^{\beta\cdot(\varepsilon-\mu)}\right) + \frac{1}{1+e^{-\beta\cdot(\varepsilon-\mu)}} Ln\left(1+e^{-\beta\cdot(\varepsilon-\mu)}\right)}$$

$$\text{Evaluate in classical limit } e^{-\beta\cdot(\varepsilon-\mu)} \ll 1 \text{ small populations}$$

$$\frac{+s_\varepsilon}{k_B} \approx \beta\cdot(\varepsilon-\mu) e^{-\beta\cdot(\varepsilon-\mu)} + e^{-\beta\cdot(\varepsilon-\mu)}$$

$$s_\varepsilon \approx \left(k_B + \frac{(\varepsilon-\mu)}{T}\right) e^{-\beta\cdot(\varepsilon-\mu)} \rightarrow S = \sum_{Particles}^{1\ldots N} \sum_i s_{\varepsilon_i} = Nk_B + \frac{1}{T}\langle E\rangle - N\cdot\frac{\mu}{T}$$

$$G(N,\mu) = \left(Nk_B T + \langle E\rangle\right) - T\cdot S$$

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