Agenda: Quantum Statistics

- Principal concepts in quantum mechanics
  Wave functions for free and bound particles,
  Uncertainty Relation, spectroscopy with photons,

- Quantum molecular models for translation, rotations &
  vibrations, particle-in-a-box model
  Maxwell-Boltzmann energy distribution

  Application to gas phase rxns, dissociation
  Qu rot. partition functions,
  Qu vib. partition function, diatomic molecules

- Quantum partition function for indistinguishable particles,
  Bosons, Fermions, Application elm. radiation.
  Fermions and quantum Fermi Gas,

Reading Assignments

LN IV.4, 6

McQ Ch. 1,4

Kond Ch. 20

Indistinguishable Particles (Bosons & Fermions)

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

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

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 $0 \leq N < \infty$ identical and independent quantal particles distributed in all different ways over single-particle states at energy ε_i. → PF has product structure

$$\text{Grand partition function } \left(\beta = 1/k_B T;\ \mu = \partial G/\partial N\right)$$

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

$$\text{Activity } \lambda := e^{-\beta\cdot\mu} \rightarrow \text{uniform shift of all levels } \varepsilon_i$$

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

Relation between Free Energy μ and number of particles ***N*** in given volume ***V,***
→ *Hierarchy of canonical PFs*.

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

$$\mu = \frac{1}{\beta}\frac{\partial A_N}{\partial N} \approx -k_B T\left\{\frac{Ln Q_{N+1} - Ln Q_N}{\underbrace{(N+1)-N}_{=1}}\right\} = k_B T\cdot Ln\left(\frac{Q_N}{Q_{N+1}}\right) \rightarrow \boxed{Q_{N+1} = e^{-\mu/k_B T}\cdot Q_N}$$

Equiv. change in reference energy due 1 extra particle.

Grand Canonical State Boson Populations

Ensembles of $0 \leq N < \infty$ identical and independent Bosons (photons, phonons) distributed in all different ways over single-particle states at energy $\boldsymbol{\varepsilon_i}$. → PF has product structure. $\boldsymbol{n_i}$=#of photons in s.p. state @$\boldsymbol{\varepsilon_i}$.

$$E_j^{(N)} = \sum_i n_i(j)\cdot\varepsilon_i \rightarrow \{n_1, n_2, n_3, \ldots\}_j = a\ partition\ of\ N$$

$j \in 1,\ldots,\Omega_N$ N – particle states

$$Massive\ Bosons \rightarrow normalize\ \ N = \sum_i n_i(j)$$

$$Q_N = \sum_j^{\{N\}} e^{-\beta\cdot E_j^{(N)}} = \sum_j^{\{N\}} e^{-\beta\cdot\sum_i n_i(j)\cdot\varepsilon_i} = \sum_{n_1,n_2,n_3,\cdots}^{\{N\}} e^{-\beta\cdot\sum_i n_i\cdot\varepsilon_i} = \prod_i \left(\sum_{n_i=0}^{\infty} e^{-\beta\cdot\varepsilon_i\cdot n_i}\right)$$

$$\left(e^{-\beta\cdot\varepsilon_i}\right)^{n_i}$$

Mean Boson occupation for ε_i

$$Q_N = \prod_i \left(\frac{1}{1-e^{-\beta\cdot\varepsilon_i}}\right) \Rightarrow \langle n_i\rangle = -\frac{1}{\beta}\frac{\partial LnQ_N}{\partial\varepsilon_i} = \frac{e^{-\beta\cdot\varepsilon_i}}{1-e^{-\beta\cdot\varepsilon_i}} \Rightarrow \boxed{\langle n_i\rangle = \frac{1}{e^{+\beta\cdot\varepsilon_i}-1}}$$

Massive bosons e.g. *He,…,W*$^+$

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

Grand Canonical State Fermion Populations

Ensembles of N identical and independent Fermions → PF product structure

Particle j contribution to N-particle energy

$$E_j^{(N)} = \sum_i n_i(j)\cdot\varepsilon_i \qquad j \in 1,\ldots\ldots,\Omega_N \quad N - particle\ states$$

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

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

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

1 particle in state x removed

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

Do this for any $x=i$ →

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

$n_x=1$ (in $Q_N(1)$), $n_x=0$ (in $Q_N(0)$)

Fermi-Dirac and Bose-Einstein State Populations

Ensembles of N identical and independent particles→ PF product structure

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

$j \in 1,......,\Omega_N$

N – particle states

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

Occupation number for state i = *probability for i to be occupied*

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

Fermi-Dirac statistics

Massive Bosons➔ normalize $\boldsymbol{n_x}$

$$n_x = 0, 1, 2, \cdots \rightarrow Q_N(n_x) = Q_N(0) + Q_N(1) + Q_N(2) + Q_N(3) + \cdots$$

Boson occupation number for state i

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

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

Grand Canonical Partition Function of FG

For equil. properties of *Fermion/Boson gases* *need Partition Function* Ξ

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

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

Grand Canonical Fermion PF

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

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

Grand Canonical Bose PF

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

$$\Xi = +k_B T \sum_i Ln\left\{1 + p_i\right\}$$

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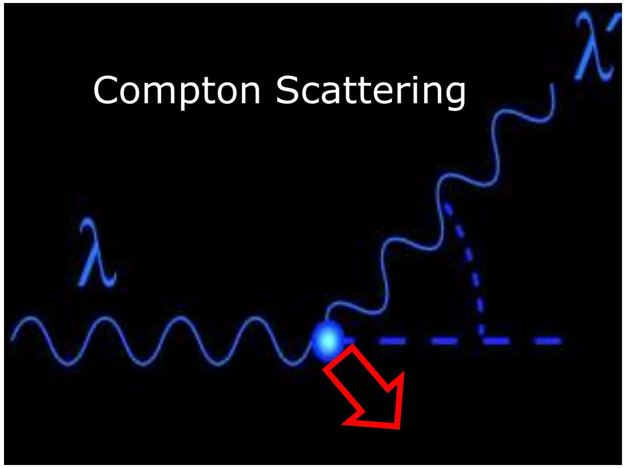
Electromagnetic Cavity Radiation: Photons

Electromagnetic radiation 3D waves materialize as photons = energy packets

Radiation frequency ν, *circular frequency* $\varpi = 2\pi \cdot \nu$, *wave length* λ

speed of light $c = \lambda \cdot \nu$



Energy quantum $\varepsilon = h \cdot \nu = \hbar \cdot \varpi$,

linear momentum $p = \varepsilon / c$

Angular momentum $(spin = 1\hbar) \rightarrow$ *Boson*

2 polarizations degeneracy $= 2$, *mass* $m_{ph} = 0$,

relativistic $\varepsilon = \sqrt{(p \cdot c)^2 + (m_{ph} c)^2} = p \cdot c$

Occupation Probability of ε : $f(\varepsilon) = \dfrac{1}{e^{\beta \cdot (\varepsilon - \mu)} - 1}$

Phase space density (waves in a cavity = box)

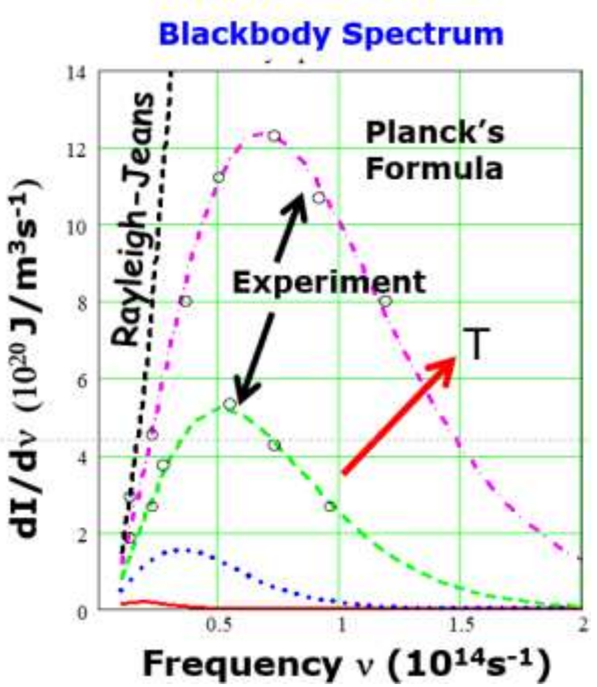
$$dn(\nu) = 2 \frac{1}{h^3} d^3\vec{p} \cdot d^3\vec{r} = 2 \frac{dV}{h^3} 4\pi p^2 dp = 2 \frac{dV}{c^3} 4\pi \cdot \nu^2 d\nu$$

Planck's Elm. Radiation Law

$$\frac{d^2n(\nu)}{dV\,d\nu} = \frac{8\pi}{c^3}\nu^2 \rightarrow Energy \text{ "radiance"}$$

$Planck's\ constant$

$h = 6.626 \cdot 10^{-34}\,Js$



$$\frac{dI(\nu,T)}{d\nu} = \frac{d^2n(\nu)}{dV\,d\nu} \cdot f(\nu,T) \cdot (h\nu)$$

#states occupancy energy

$$\frac{dI(\nu,T)}{d\nu} =: u(\nu,T) = \frac{8\pi h}{c^2}\frac{\nu^3}{e^{h\nu/k_BT} - 1}$$

Energy density

Mean thermal frequency $\langle\nu\rangle \sim T$

Stefan – Boltzmann Law : $Rad\,energy/time \cdot area$

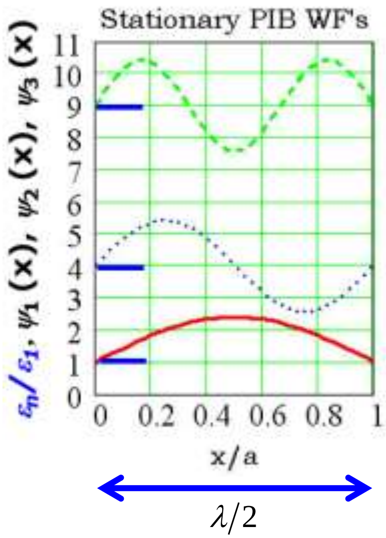
$$R = \frac{c}{4}I(T) = \frac{\pi^2 k_B^4}{60c^2\hbar^3}T^4 = \sigma_{SB} \cdot T^4$$

Stefan – Boltzmann constant

$$\sigma_{SB} = \frac{\pi^2 k_B^4}{60c^2\hbar^3} = 5.67 \cdot 10^{-8}\,Jm^{-2}s^{-1}K^{-4}$$

Radiation Pressure

Radiation field enclosed in a cavity=container (box, cube side length a)



$$Generally: \langle p\rangle = -\left(\frac{\partial}{\partial V}\langle E\rangle\right)_S \quad \text{with} \quad \langle E\rangle = \sum_i \langle n_i\rangle \cdot \varepsilon_i$$

$$\langle p\rangle = -\sum_i \langle n_i\rangle \cdot \left(\frac{\partial}{\partial V}\varepsilon_i\right)_S \qquad \varepsilon_i = i\cdot h\cdot \nu = i\cdot h\cdot c/\lambda = 2i\cdot h\cdot c/a$$

$$\varepsilon_i = 2i\cdot h\cdot c\cdot V^{-1/3} \rightarrow \left(\frac{\partial}{\partial V}\varepsilon_i\right)_S = -\frac{2}{3}i\cdot h\cdot c\cdot V^{-4/3} = -\frac{1}{3}\frac{\varepsilon_i}{V}$$

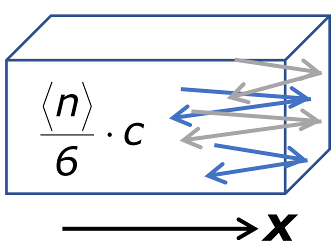
Boson pressure

$$\langle p\rangle = \frac{1}{3}\cdot u(T) = \frac{1}{3}\frac{\langle E\rangle}{V}$$

Classical gas pressure

$$\langle p\rangle_{cl} = \frac{2}{3}\frac{\langle E\rangle}{V}$$

Pressure (momentum transfer to wall)

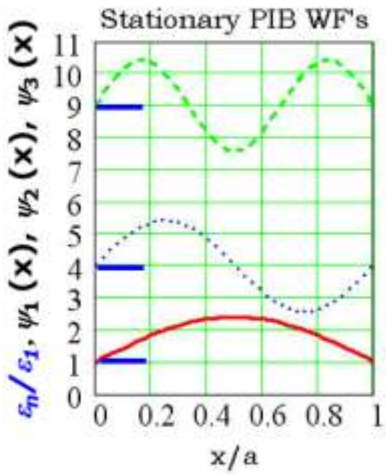


$$p(\nu,T) = \left(\frac{1}{6}c\right)\cdot\left[\frac{d^2n(\nu)}{dV\,d\nu}\cdot f(\nu,T)\right]\cdot\left(2\frac{h\nu}{c}\right)$$

$$= \frac{1}{3}\frac{dI(\nu,T)}{d\nu} \rightarrow p(T) = \frac{1}{3}I(T)$$

Partition Function and Radiation Pressure

Radiation field enclosed in a container (box, volume ***V***) → phase space !



$$Photon\ number\ dN = 2\cdot\frac{V}{h^3}d^3\vec{p}\ (2\ polarizations)$$

$$\rightarrow d^3\vec{p} = 4\pi\left|\vec{p}\right|^2\cdot d\left|\vec{p}\right| = \frac{4\pi}{c^3}h^3\nu^2 d\nu$$

$$Ln\,\Xi = -2\cdot\frac{V}{h^3}\int d^3\vec{p}\cdot Ln\left(1-e^{-\beta\cdot|\vec{p}|\cdot c}\right)$$

$$= \frac{-8\pi}{\beta^3h^3c^3}V\cdot\int_0^\infty(\beta h\nu)^2\cdot Ln\left(1-e^{-\beta\cdot h\nu}\right)d(\beta h\nu)$$

$$Ln\,\Xi = \left(\frac{\pi^4}{45}\frac{8\pi k_B^3}{(hc)^3}\right)\cdot V\cdot T^3 = \left(\frac{4}{3}\frac{\sigma_{SB}}{k_B\cdot c}\right)\cdot V\cdot T^3$$

Can calculate all thermodynamic quantities

Examples:

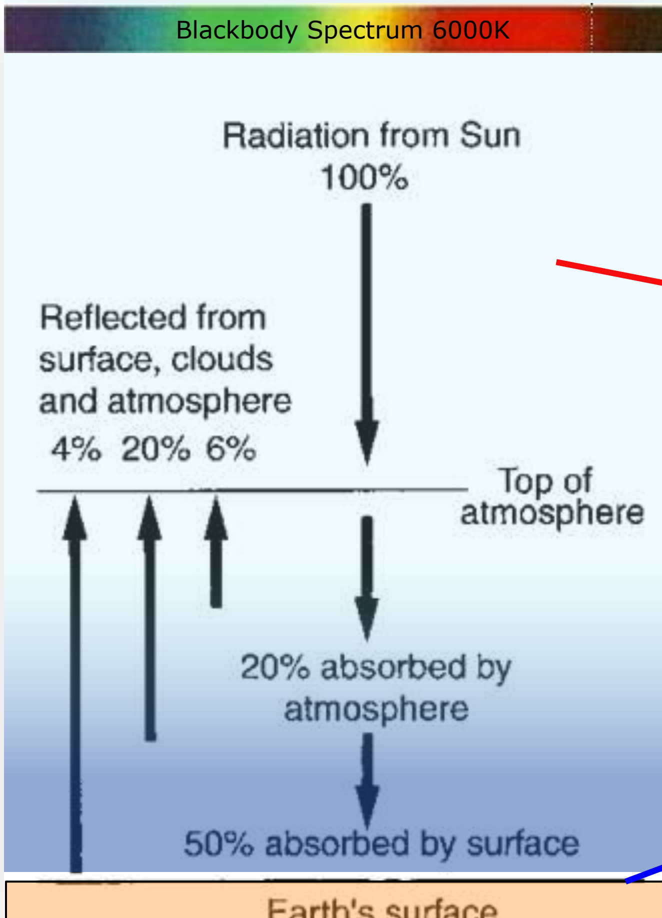
$$E(T,V) = V\cdot u(T) = \langle E\rangle = -\frac{\partial}{\partial\beta}Ln\,\Xi = \left(\frac{4\cdot\sigma_{SB}}{c}\right)\cdot V\cdot T^4$$

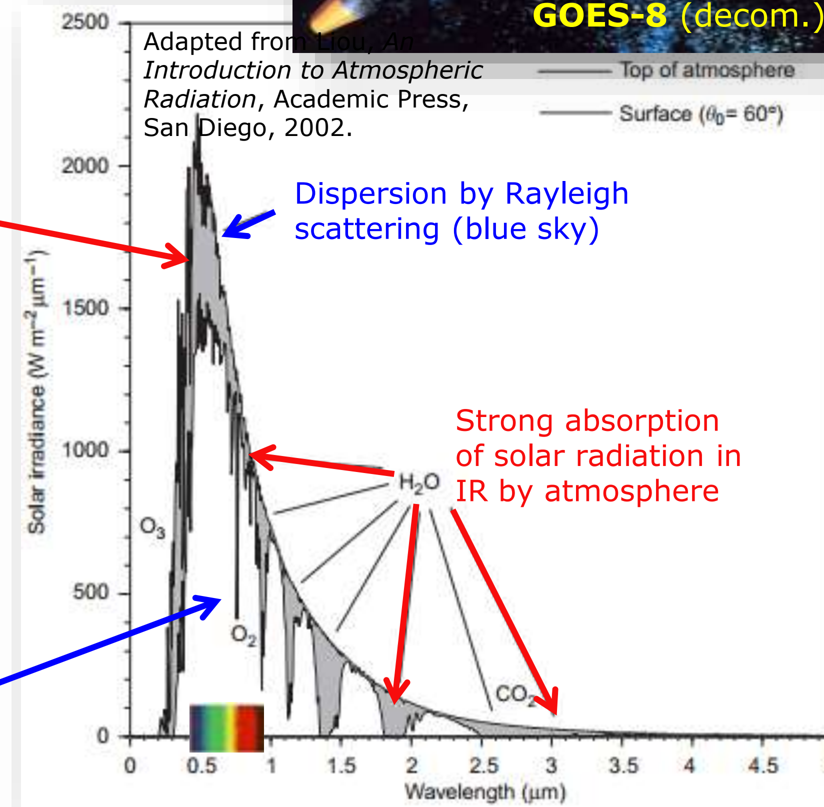
$$Pressure\ \ p = \left(\frac{4\cdot\sigma_{SB}}{3\cdot c}\right)\cdot T^4$$

Planetary Electromagnetic Photon Flux

Absorption of solar radiation by the atmosphere is determined using spectroscopic satellite, aircraft, and surface data. See recent Atmospheric Radiation Measurement Enhanced Shortwave Experiment (ARESE)

See, e.g., F. P. J. Valero et al., J. GEOPHYS. RES., 105, 4743 (2000)





Scattered or absorbed radiation not available for warming Earth surface. → T_E < 255K !!???

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  Expanded discussion Bose-Einstein populations,
  Fermions and quantum Fermi Gas.

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Expanded: Bose-Einstein State Populations

Expand procedure used for Fermions

any s.p. state $i = x : n_x = 0,1 \rightarrow Q_N(n_x) = Q_N(n_x = 0) + Q_N(n_x = 1)$

to Bosons $n_x = 0,1,2,\cdots \rightarrow Q_N(n_x) = Q_N(0) + Q_N(1) + Q_N(2) + Q_N(3) + \cdots$

$\cdots + \exp\{-3\beta\varepsilon_x\} + \cdots$

$$Take\ out\ BF\ e^{-\beta\varepsilon_x} = Q_N(1)/Q_N(0)$$

$$Take\ out\ BF\ e^{-\beta\mu} = Q_N(0)/Q_{N-1}(0) \rightarrow Q_N(0)/Q_M(0) = e^{\beta(N-M)\cdot\mu};$$

$\mu \approx constant,\ as\ long\ as\ N \sim M$ same order

$$\langle n_x \rangle = \frac{Q_N(0)}{Q_N(n_x)}\left\{e^{-\beta\varepsilon_x}\frac{Q_{N-1}(0)}{Q_N(0)} + 2e^{-2\beta\varepsilon_x}\frac{Q_{N-2}(0)}{Q_N(0)} + 3e^{-3\beta\varepsilon_x}\frac{Q_{N-3}(0)}{Q_N(0)} + \cdots\right\}$$

$$\langle n_x \rangle = \frac{Q_N(0)}{Q_N(n_x)}\left\{\underbrace{e^{\beta(\mu-\varepsilon_x)}}_{=x} + 2e^{2\beta(\mu-\varepsilon_x)} + 3e^{3\beta(\mu-\varepsilon_x)} + \cdots\right\} = \frac{Q_N(0)}{Q_N(n_x)}\left\{x + 2x^2 + 3x^3 + \cdots\right\}$$

Bose-Einstein State Populations

Expand procedure used for Fermions

any s.p. state $i = x : n_x = 0,1 \rightarrow Q_N(n_x) = Q_N(n_x = 0) + Q_N(n_x = 1)$

to Bosons $n_x = 0,1,2,\cdots \rightarrow Q_N(n_x) = Q_N(0) + Q_N(1) + Q_N(2) + Q_N(3) + \cdots$

$$\langle n_x \rangle = \frac{Q_N(0)}{Q_N(n_x)}\left\{\underbrace{e^{\beta(\mu-\varepsilon_x)}}_{=x} + 2e^{2\beta(\mu-\varepsilon_x)} + 3e^{3\beta(\mu-\varepsilon_x)} + \cdots\right\} = \frac{Q_N(0)}{Q_N(n_x)}\left\{x + 2x^2 + 3x^3 + \cdots\right\}$$

$$\frac{Q_N(n_x)}{Q_N(0)} = 1 + e^{\beta(\mu-\varepsilon_x)} + 2e^{2\beta(\mu-\varepsilon_x)} + 3e^{3\beta(\mu-\varepsilon_x)} + \cdots = 1 + x + 2x^2 + 3x^3 + \cdots$$

$$\langle n_x \rangle = \frac{x + 2x^2 + 3x^3 + \cdots}{1 + x + 2x^2 + 3x^3 + \cdots} = \frac{x\left(1 + 2x + 3x^2 + \cdots\right)}{(1-x)\left(1 + 2x + 3x^2 + ..\right)} \approx \frac{x}{1-x} = \frac{e^{\beta(\mu-\varepsilon_x)}}{1 - e^{\beta(\mu-\varepsilon_x)}}$$

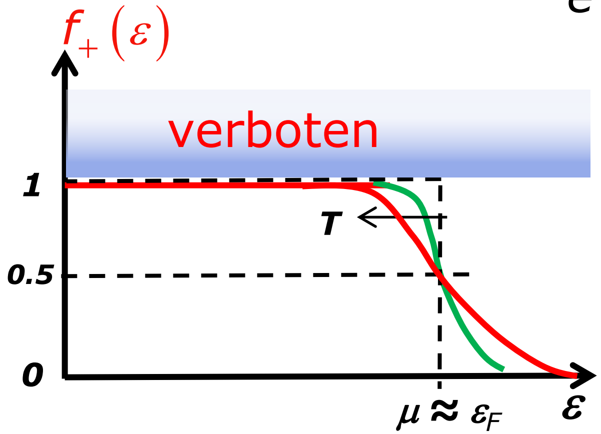
Boson state ***i*** population $\boxed{\langle n_i \rangle = \dfrac{1}{e^{\beta(\varepsilon_i-\mu)} - 1}}$ mean number of Bosons

Boltzmann High-T Limit State Populations

Canonical Fermi-Dirac or Bose-Einstein statistics $Q_{N-1}/Q_N = e^{\beta\cdot\mu} = e^{\mu/k_BT}$

Energy gain per particle added: $\mu = k_BT \cdot Ln\left(Q_{N-1}/Q_N\right) = k_BT \cdot \left(A_N - A_{N-1}\right)$

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



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

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

Box-shape of degenerate Fermi gas
Thermal excitations diffuse the Fermi Surface.
Diffuseness parameter = temperature T

Definition Fermi energy

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

"High-T limit"

$$\beta\cdot\left(\varepsilon_i - \mu\right) \gg 1 \rightarrow f_{\pm}\left(\varepsilon_i\right) \propto e^{-\beta\cdot\left(\varepsilon_i-\mu\right)}$$

$$\langle n_i \rangle \propto e^{-\varepsilon_i/k_BT}$$

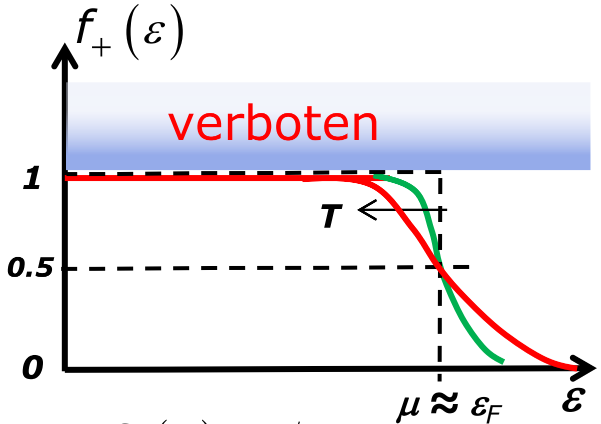
Boltzmann high T
Limit for FD & BE

Fermi-Dirac State Populations

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

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

Boltzmann high T Limit for FD & BE $\xrightarrow{\beta\cdot(\varepsilon_i - \mu) \gg 1}$ $\langle n_i \rangle \propto e^{-\varepsilon_i / k_B T}$



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

Sommerfeld expansion

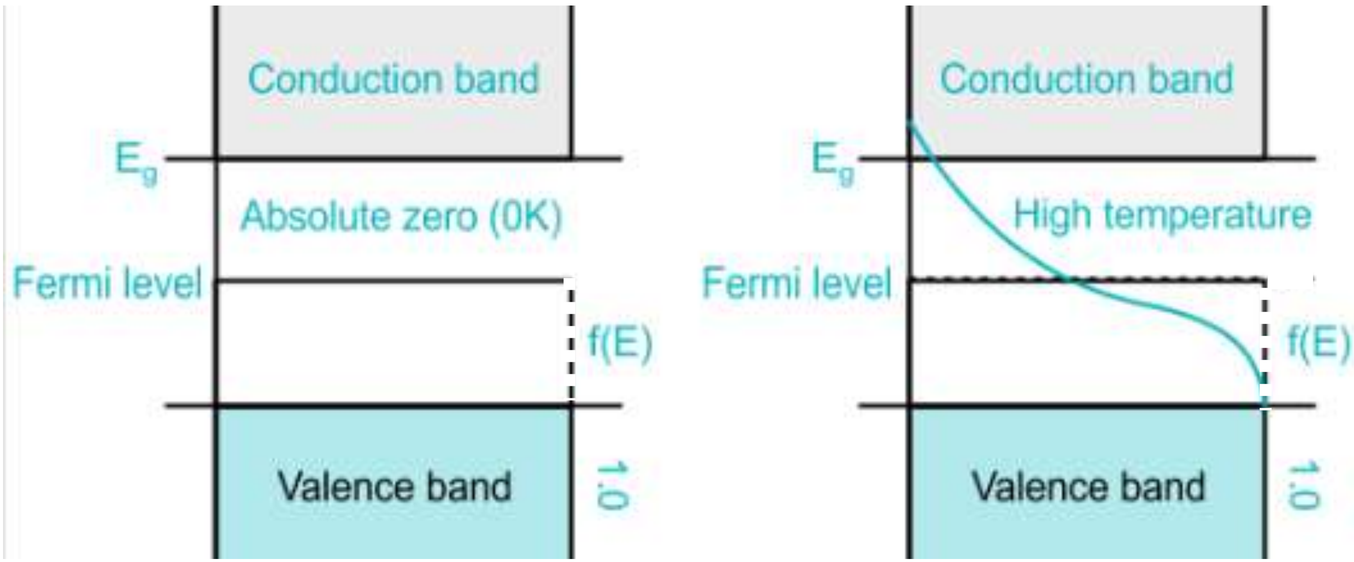
$$\mu(T) = \mu(T=0)\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\mu(T=0)}\right)^2\right]$$

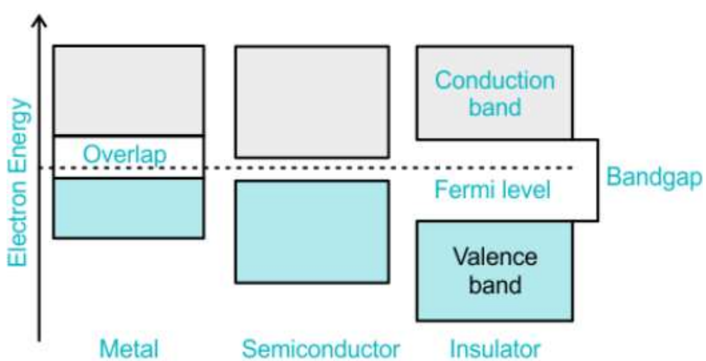
Task: Partition function → have general expression for probability term, equivalent to Boltzmann factors → apply to microscopic model systems:

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

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

Electron Energy Distribution in Solid State Materials





The gap of energy levels between continuous bands of energy states

- is large for insulator materials
- is small for semi-conductors,
- is essentially absent for metals

Properties of Metal Electron Fermi Gases

Metal	Name	Valency	$n/10^{28}\,m^{-3}$	r_S/pm	r_S/r_B	E_F/eV	$T_0/10^4$ K	$k_F/10^{10}\,m^{-1}$	$v_F/10^6\,m\,s^{-1}$
Li[a]	Lithium	1	4.70	172	3.25	4.74	5.51	1.12	1.29
Na[b]	Sodium	1	2.65	208	3.93	3.24	3.77	0.92	1.07
K[b]	Potassium	1	1.40	257	4.86	2.12	2.46	0.75	0.86
Rb[b]	Rubidium	1	1.15	275	5.20	1.85	2.15	0.70	0.81
Cs[b]	Cesium	1	0.91	298	5.62	1.59	1.84	0.65	0.75
Cu	Copper	1	8.47	141	2.67	7.00	8.16	1.36	1.57
Ag	Silver	1	5.86	160	3.02	5.49	6.38	1.20	1.39
Au	Gold	1	5.90	159	3.01	5.53	6.42	1.21	1.40
Be	Beryllium	2	24.7	99	1.87	14.3	16.6	1.94	2.25
Mg	Magnesium	2	8.61	141	2.66	7.08	8.23	1.36	1.58
Ca	Calcium	2	4.61	173	3.27	4.69	5.44	1.11	1.28
Sr	Strontium	2	3.55	189	3.57	3.93	4.57	1.02	1.18
Ba	Barium	2	3.15	196	3.71	3.84	4.23	0.98	1.13
Nb	Niobium	1	5.56	163	3.07	5.32	6.18	1.18	1.37
Fe	Iron	2	17.0	112	2.12	11.1	13.0	1.71	1.98
Mn[c]	Manganese	2	16.5	113	2.14	10.9	12.7	1.70	1.96
Zn	Zinc	2	13.2	122	2.30	9.47	11.0	1.58	1.83
Cd	Cadmium	2	9.27	137	2.59	7.47	8.88	1.40	1.62
Hg[a]	Mercury	2	8.65	140	2.65	7.13	8.29	1.37	1.58

$T_0 = \varepsilon_F / k_B$

Bohr radius r_B

Elementary Volume

$$\frac{V}{N_e} = \frac{4\pi}{3} r_s^3$$

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