1

* quantum sn: the state itself is symmetrized correctly. There is only ONE state with n_k particles in state $|k\rangle$

$$\Rightarrow Z_c = \sum_{\{\sum_k n_k = N\}} e^{-\beta \sum_k n_k \varepsilon_k} \quad ; \ \varepsilon_k \text{ the energy of state } |k\rangle$$

$\Rightarrow$ No need to correct for overcounting afterwards, the trace includes what is needed.

* Still $\sum_k n_k = N$ leads to a somewhat painful constrained sum

$\Rightarrow$ grand canonical ensemble

Grand canonical partition function

$$Q = \mathrm{Tr}\left(e^{\beta\mu\hat{N} - \beta\hat{H}}\right) = \sum_{\{n_k\}} e^{\beta\mu\sum_k n_k - \beta\sum_k n_k\varepsilon_k} = \prod_k \sum_{n_k} \left[e^{\beta(\mu-\varepsilon_k)}\right]^{n_k}$$

Fermions: $n_k = 0,1$ $\quad Q_- = \prod_k \left(1 + e^{\beta(\mu-\varepsilon_k)}\right)$

Bosons: $n_k \in \mathbb{Z}^+$ $\quad Q_+ = \prod_k \dfrac{1}{1 - e^{\beta(\mu-\varepsilon_k)}}$

$$\left.\right\} \quad Q_\eta = \prod_k \left[1 - \eta e^{\beta(\mu-\varepsilon_k)}\right]^{-\eta}$$

Comment: Bosons require $\mu < \min_k \varepsilon_k$ for convergence of Q_+.

Then $\quad P_\eta(\{n_k\}) = \dfrac{1}{Q_\eta} \prod_k \exp\left[\beta(\mu-\varepsilon_k)n_k\right]$

occupation statistics:

$$\langle n_k\rangle = -\frac{\partial}{\partial(\beta\varepsilon_k)} \ln Q_\eta = \eta \frac{\partial}{\partial\beta\varepsilon_k} \ln\left(1 - \eta e^{\beta(\mu-\varepsilon_k)}\right) = \eta \frac{\eta e^{\beta(\mu-\varepsilon_k)}}{1 - \eta e^{\beta(\mu-\varepsilon_k)}}$$

$$\boxed{\langle n_k\rangle_\eta = \frac{1}{e^{\beta(\varepsilon_k-\mu)} - \eta}}$$

Ideal gas: a state $|k\rangle \Leftrightarrow$ wavevector $\vec{k}$ & spin $\sigma \in \{-S, \dots, S\}$

k vs $\vec{k} \Rightarrow$ dangerous notation!

$\hat{H} = \frac{\hat{P}^2}{2m} \Rightarrow$ eigenstates = plane waves & eigenvalues $= \frac{\hbar^2 \vec{k}^2}{2m}$

$$\underbrace{\langle n_k \rangle}_{\text{single state}} = \langle n_{\vec{k},\sigma} \rangle = \frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} - \eta} \Rightarrow \underbrace{\langle n_{\vec{k}} \rangle}_{\text{single } \vec{k}} = \frac{2S+1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} - 1}$$

Be careful...

Degeneracy: We often introduce $g = 2S+1$ to denote the degeneracy due to spin.

Thermodynamics:

Grand potential $G_\eta = -kT \ln Q_\eta = \eta kT \sum_{\vec{k},\sigma} \ln\left(1 - \eta e^{\beta(\mu - \varepsilon_k)}\right)$

$$\boxed{G_\eta = \eta k T g \sum_{\vec{k}} \ln\left[1 - \eta e^{\beta(\mu - \varepsilon_k)}\right]}$$

Pressure: Always true: $P = -\left.\frac{\partial G_\eta}{\partial V}\right|_{T,\mu}$.

If extensive system: $G = -PV \Rightarrow \boxed{P = -\frac{\eta k T g}{V} \sum_{\vec{k}} \ln\left[1 - \eta e^{\beta(\mu - \varepsilon_k)}\right]}$

Energy: $\boxed{E = g \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}} \rangle_\eta = g \sum_{\vec{k}} \frac{\varepsilon(\vec{k})}{e^{\beta(\varepsilon(\vec{k}) - \mu)} - \eta}}$

Particle number: $\boxed{\langle N \rangle_\eta = \sum_k \langle n_k \rangle_\eta = g \sum_{\vec{k}} \frac{1}{e^{\beta[\varepsilon(\vec{k}) - \mu]} - \eta}} = -\partial_\mu \langle G \rangle$

Let us now analyze separately the properties of bosons & fermions

6.3) The ideal Bose gas & the Bose Einstein condensation

Grand canonical ensemble, what happens when μ & T vary?

Occupation statistics $\quad \langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k-\mu)}-1}$

* $\vec{k}=\vec{0} \Rightarrow \epsilon_{\vec{0}}=0 \quad \langle n_0 \rangle \geq 0 \Rightarrow e^{-\beta\mu} > 1 \Rightarrow -\infty < \mu < 0$

⚠ $z = \mathfrak{z}$ … fugacity $\qquad \Leftrightarrow \quad 0 < z = e^{\beta\mu} < 1$

Classical limit: $\langle N \rangle = \frac{V}{\lambda^3} z = \frac{V}{\lambda^3} e^{\beta\mu} \Rightarrow \mu = k_B T \ln[\langle n \rangle \lambda^3]$

Classical stat mech requires distance between particles $\gg \lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$

$\Rightarrow \langle n \rangle \lambda^3 \ll 1 \Rightarrow \mu \ll -1 \Rightarrow \mu \to -\infty$, $z \to 0$ is the classical limit

What about $\mu \to 0$ & $z \to 1$?

* In a finite system, when $\mu \to 0$ $\quad \langle n_k \rangle = \frac{1}{e^{\beta\epsilon_k}-1} < \infty$ if $k \neq 0$

but

$$\left.\boxed{\begin{array}{l} \langle n_0 \rangle = \frac{1}{e^{-\beta\mu}-1} \xrightarrow[\mu \to 0^-]{} \infty \\ \langle n_0 \rangle = \frac{z}{1-z} \xrightarrow[z \to 1]{} \infty \end{array}}\right\} \Rightarrow \text{complicated limit!}$$

* How do the bosons occupy the energy levels in this limit?

$$\rho_0 = \frac{N}{V} = \frac{g}{V} \sum_{\vec{k}} \frac{1}{e^{\beta(\epsilon_k-\mu)}-1}$$

$$\boxed{\rho_0 = \underbrace{\frac{g}{V}\frac{1}{e^{-\beta\mu}-1}}_{\text{ground state} \quad \rho_{GS}} + \underbrace{\frac{g}{V}\sum_{\vec{k}\neq 0} \frac{1}{e^{\beta[\epsilon(\vec{k})-\mu]}-1}}_{\rho_{ES} \quad \text{excited states}}}$$

Excited states $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ with $\vec{n} \in \underbrace{\mathbb{Z}_0^+}_{\mathbb{Z}^+\cup\{0\}}$; $dk_\alpha = \frac{2\pi}{L}$

$$\rho_{ES} = \frac{g}{V}\cdot\left(\frac{L}{2\pi}\right)^3 \sum_{\vec{k}} d^3\vec{k}\, \frac{1}{z^{-1}e^{\beta\frac{\hbar^2k^2}{2m}}-1} = \frac{g}{8\pi^3}\int d^3\vec{k}\, \frac{1}{z^{-1}e^{\beta\frac{\hbar^2k^2}{2m}}-1}$$

$$\rho_{ES} = \frac{g}{2\pi^2}\int_0^\infty k^2 dk\, \frac{1}{z^{-1}e^{\beta\frac{\hbar^2k^2}{2m}}-1}$$

$x = \frac{\hbar^2k^2}{2mkT}$; $k = \frac{\sqrt{2mkT}}{\hbar}\sqrt{x}$

$dk = \frac{\sqrt{2mkT}}{\hbar}\,\frac{dx}{2\sqrt{x}}$

$$= \frac{g}{4\pi^2}\left(\frac{2mkT}{\hbar^2}\right)^{3/2}\int_0^\infty dx\, \frac{x^{1/2}}{z^{-1}e^x-1}$$

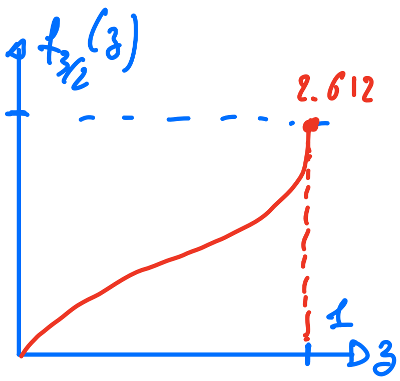
$$\rho_{ES} = g\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{2}{\sqrt{\pi}}\int_0^\infty dx\, \frac{x^{1/2}}{z^{-1}e^x-1}$$

$$\boxed{\rho_{ES}\cdot\Lambda^3 = g\, f^+_{3/2}(z)} ; \text{ where } f^\eta_m = \frac{1}{(m-1)!}\int_0^\infty dx\, \frac{x^{m-1}}{z^{-1}e^x-\eta}$$

Comment: $f^+_{3/2}(1) = \int_0^\infty dx\, \frac{x^{1/2}}{e^x-1} = 2.612$ finite

Mathematically, $\frac{x^{1/2}}{e^x-1}$ diverges as $x\to 0$, but it is integrable since $\frac{x^{1/2}}{e^x-1} \simeq x^{-1/2}$ so that $\int_\varepsilon \frac{x^{1/2}}{e^x-1} \underset{\varepsilon\to 0}{\sim} -2\sqrt{\varepsilon}$

$$\Rightarrow \boxed{\rho_{ES} \leq \frac{g}{\Lambda^3} f^+_{3/2}(1) = \rho_{ES}^{MAX} \simeq 2.612\, g\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}}$$



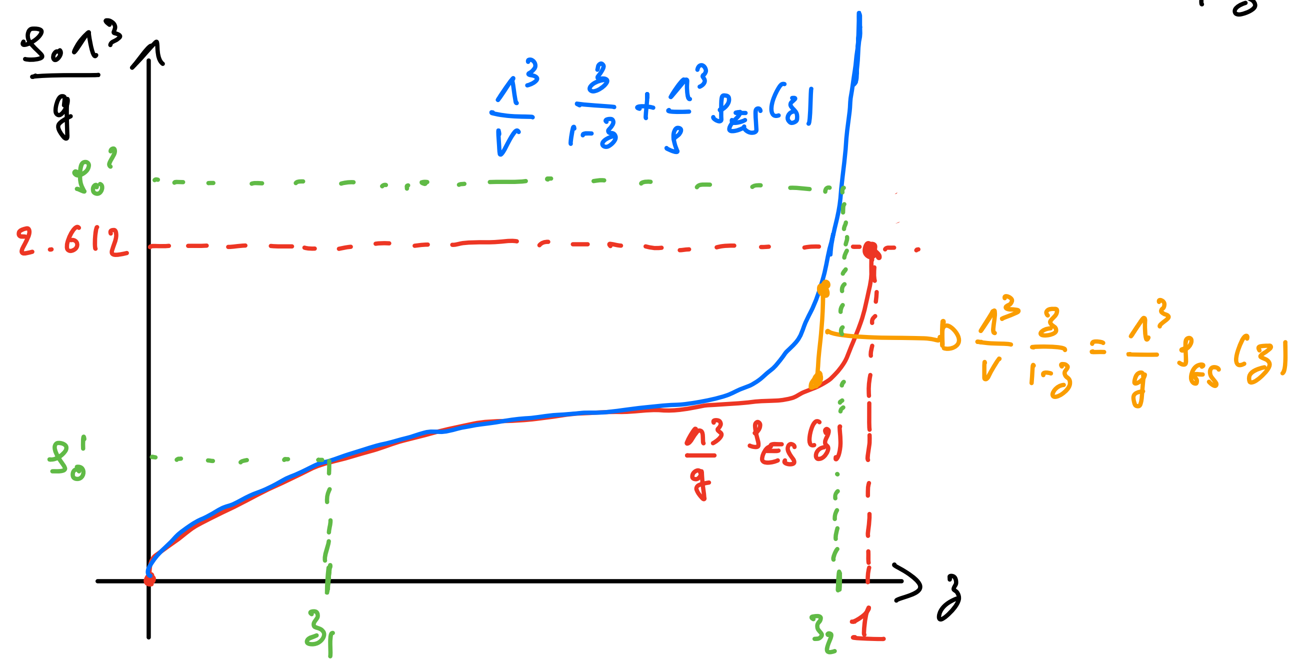
$$\rho_0 = \frac{g}{V}\,\frac{z}{1-z} + g\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2} f_{3/2}(z)$$

Conclusion: as $\mu \to 0$ & $z \to 1$, ρ_{ES} remains finite while $\rho_0 = \frac{g}{V}\frac{z}{1-z}$ diverges

$\Rightarrow$ the majority of atoms are in the ground state $\Rightarrow$ Bose Einstein condensation!

Detail on the $z \to 1$ limit

Let us illustrate this graphically by plotting $\rho_0(z) = \frac{g}{V}\frac{z}{1-z} + \rho_{ES}(z)$



As $z \to 1$, $\rho_0 > \rho_{ES}^{MAX}$ and the ground state is occupied by a finite fraction of atoms.

$$z = 1 - \frac{g}{\alpha V} \Rightarrow \rho_{GS} = \frac{g}{V}\,\frac{1 - \frac{g}{\alpha V}}{\frac{g}{\alpha V}} = \alpha - \frac{g}{V} \simeq \alpha \qquad \left[\rho_{GS} = \alpha \Leftrightarrow z = 1 - \frac{g}{g+\alpha V}\right]$$

For $\alpha \sim O(1)$, we necessarily have condensation as $V \to \infty$ since ρ_{GS} is finite. Everything happens in a boundary layer close to $z = 1$.

Canonical perspective For large systems, the description of intensive quantities like ρ & μ is expected to be equivalent in all ensembles. We can thus think about fixing ρ_0 & solving $\rho_0 = \rho_{GS}(z) + \rho_{ES}(z)$ to get z, ρ_{GS} & ρ_{ES}.