Bose-Einstein Statistics

Quantum Review: Bosons at $\vec{r}_1, \ldots, \vec{r}_N$

- Any wave function must be symmetric under interchange of particles:
  $$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \Psi(\vec{r}_{\pi(1)}, \vec{r}_{\pi(2)}, \ldots, \vec{r}_{\pi(N)})$$
  $$\text{with } \pi = \{P_1, P_2, \ldots, P_N\} \text{ a permutation of integers } 1 \ldots N.$$

- Hamiltonians act the same, act on symmetric $WF$:
  $$H \Psi_\alpha = E_\alpha \Psi_\alpha$$

- Statistical mechanics: trace over symmetric $WF$:
  $$Z = \text{Tr}(e^{-\beta H}) = \sum e^{-\beta E_\alpha}$$

- Non-symmetric eigenstate $\Phi_\alpha(\vec{r}_1, \ldots, \vec{r}_N)$ can be symmetrized:
  $$\Psi_\alpha(\vec{r}_1, \ldots, \vec{r}_N) = \{\text{Normalization}\} \sum_{\pi} \Phi_\alpha(\vec{r}_{\pi(1)}, \ldots, \vec{r}_{\pi(N)})$$
  If $\Psi_\alpha \neq 0$, it is also an eigenstate $H \Psi_\alpha = E_\alpha \Psi_\alpha$

- Mesons, He$^4$, photons, phonons, etc.
**Special Case: Non-Interacting Bosons**

- Many-body Quantum Hard
- Dilute Bose Gas, Bose Condensation
- Qualitative Features Shared with Super Fluids, Superconductors
- Phonons & Photons: Non-Interacting

\[
H^{\text{NI}} = \sum_{j=1}^{N} H^{\text{I}}(\vec{r}_{j}) = \sum_{j=1}^{N} \frac{\hbar^{2}}{2m} \nabla_{j}^{2} + V(\vec{r}_{j})
\]

**Single-particle eigenstates**

\[H^{\text{I}} \Psi_{k}(\vec{r}) = \varepsilon_{k} \Psi_{k}(\vec{r})\]

\[\Phi^{\text{NI}}(\vec{r}_{1}, ..., \vec{r}_{N}) = \prod_{j=1}^{N} \Psi_{k_{j}}(\vec{r}_{j})\]

**Distinctable eigenstates**

Product of single-particle eigenstates

\[\Phi^{\text{NI}}(\vec{r}_{1}, ..., \vec{r}_{N}) = \sum_{P} \prod_{j=1}^{N} \Psi_{k_{j}}(\vec{r}_{P_{j}})\]

**Examples:**

2 particles, states \(k_{1}, k_{2}\)

\[\Psi(\vec{r}_{1}, \vec{r}_{2}) = \frac{1}{\sqrt{2}} (\Psi_{k_{1}}(\vec{r}_{1}) \Psi_{k_{2}}(\vec{r}_{2}) + \Psi_{k_{2}}(\vec{r}_{1}) \Psi_{k_{1}}(\vec{r}_{2}))\]

2 particles, same \(k\)

\[\Psi(\vec{r}_{1}, \vec{r}_{2}) = \Psi_{k}(\vec{r}_{1}) \Psi_{k}(\vec{r}_{2})\]
Review: Maxwell–Boltzmann Quantum Statistics

Non-Interacting, Indistinguishable

Distinguishable: Particle \( j \) in state \( \varepsilon_{k_j} \), \( E = \varepsilon_{k_j} \)

\[
e^{-\beta E} = e^{-\sum_j \varepsilon_{k_j}} = \prod_j e^{-\beta \varepsilon_{k_j}}
\]

Canonical Ensemble: Trace over All Eigenstates = All ways of filling \( N \) single-particle states.

\[
Z_1 = \text{Tr} e^{-\beta H} = \sum_{\text{states}} e^{-\beta E_k}
\]

\[
Z_2 = \text{Tr} e^{-\beta H} = \sum_{k_1, k_2} e^{-\beta (E_{k_1} + E_{k_2})} = \left( \sum_k e^{-\beta E_k} \right)^2
\]

\[
Z_N^{\text{NF}} = \sum_{k_1, k_2, \ldots, k_N} e^{-\beta \left( E_{k_1} + E_{k_2} + \ldots + E_{k_N} \right)} = \left( \sum_k e^{-\beta E_k} \right)^N
\]

In classical stat mech, we imposed indistinguishability by dividing by the "Gibbs factor" \( \frac{1}{N!} \)

\[
Z_N^{\text{NF}} = \frac{1}{N!} \left( \sum_k e^{-\beta E_k} \right)^N = \frac{1}{N!} \sum_N^{\text{NF}}
\]

Indistinguishable?

Is that still OK, when we have discrete states?
Problems with the "Gibbs Factor"

Try 2 particles in 3 states

\[ Z_2 = \frac{1}{2!} \left( e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3} \right)^2 \]

\[ = \frac{1}{2} e^{-2\beta E_1} + \frac{1}{2} e^{-2\beta E_2} + \frac{1}{2} e^{-2\beta E_3} + e^{-\beta (E_1 + E_2)} + e^{-\beta (E_2 + E_3)} + e^{-\beta (E_1 + E_3)} \]

Unintuitive suppression of multiply occupied states?

\[ \frac{1}{N!} \] fixes weights of singly occupied states

Maxwell-Boltzmann distribution isn't sensible when multiple occupancy is important.

Two ways to fix:

- Don't suppress! equal weights

\[ Z_{\text{Boson}} = e^{-2\beta E_1} + e^{-2\beta E_2} + e^{-2\beta E_3} + e^{-\beta (E_1 + E_2)} + e^{-\beta (E_2 + E_3)} + e^{-\beta (E_1 + E_3)} \]

- Suppress Multiple Occupancy Entirely

\[ Z_{\text{Fermion}} = 0 + 0 + 0 + e^{-\beta (E_1 + E_2)} + e^{-\beta (E_2 + E_3)} + e^{-\beta (E_1 + E_3)} \]

Hard to do in canonical ensemble! Need grand canonical
Grand Canonical Maxwell Boltzmann Non-Interacting Indistinguishable

Grand Partition Function $Z = \sum_N Z_N e^{-NB/\mu}$

$Z^{NI} = \sum_N \frac{1}{N!} (e^{-\beta(E_k-\mu)})^N e^{\beta(E_k-\mu)}$

$= \sum_N \frac{1}{N!} \left( \frac{\beta(E_k-\mu)}{kT} \right)^N$

$= e^{\frac{\beta(E_k-\mu)}{kT}}$

$= \frac{1}{Z_k^{NI}} Z_k^{NI}$

Yikes! e^x!

Why does it factor?
Each eigenstate independent filling: bath of energy & particles.
Makes grand canonical easy for non-interacting.

Grand Free Energy

$\Phi^{NI} = -kT \log Z^{NI} = -kT \left( \sum_k e^{-(E_k-\mu)/kT} \right)$

$kT \left( \frac{1}{kT} e^{-(E_k-\mu)/kT} \right)$

$\Phi_k = -kT e^{-(E_k-\mu)/kT}$

Maxwell-Boltzmann ≡ Bosons or Fermions

when nondegenerate occupancy: $n_k = \# \text{ in state } k$

$n_k = -\frac{\partial \Phi_k}{\partial \mu} = kT \frac{d}{d\mu} e^{-(E_k-\mu)/kT}$

$kT \left( \frac{1}{kT} e^{-(E_k-\mu)/kT} \right) = e^{-(E_k-\mu)/kT}$

$n_k \gg\frac{1}{kT} e^{-(E_k-\mu)/kT}$

"Boltzmann Factor" "Maxwell Boltzmann Distribution"

If $\mu \ll E_k$ (dilute, high temperatures), Maxwell Boltzmann OK because $n_k \ll 1$. 