Physics 415 - Lecture 27

March 31, 2025

Summary

Canonical Ensemble (CE)

- Fixed T, N, V.
- Probability of microstate r: $P_r = \frac{e^{-\beta E_r}}{Z}$, where $\beta = 1/T$ (T in energy units).
- Partition function: $Z = \sum_r e^{-\beta E_r}$.
- Energy E fluctuates.
- Helmholtz Free Energy: $F = -T \ln Z$.

Grand Canonical Ensemble (GCE)

- Fixed T, μ, V. (μ = chemical potential).
- Probability of microstate r (with N_r particles): $P_r = \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}}$.
- Grand partition function: $\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)} = \sum_N e^{\beta \mu N} Z_N$. ($Z_N$ = N-particle canonical partition function).
- Grand Potential: $\Phi = -T \ln \mathcal{Z}$.
- Mean particle number: $\overline{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$.

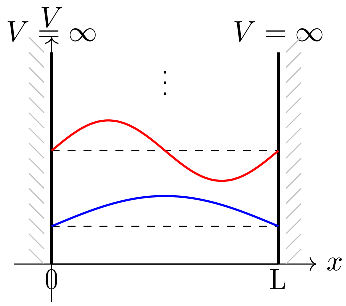
Quantum Statistical Mechanics of Ideal Gases

Investigate statistical mechanics of systems at low T, where QM effects play an especially important role.

- New effects are associated with "exchange statistics" of identical particles. We will have to consider identical particles.
- Discussion will be restricted to non-interacting particles ("ideal gas").
- As we will see, even in the absence of direct interaction forces, the effect of exchange statistics leads to a mutual coupling of particles.

Example: Two Particles in a 1D Box

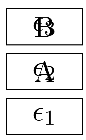
Before going into detailed formalism, we start with simple examples. Consider a 1D box of length L with infinite potential walls.



Start w/ distinguishable particles, labelled "A" & "B".

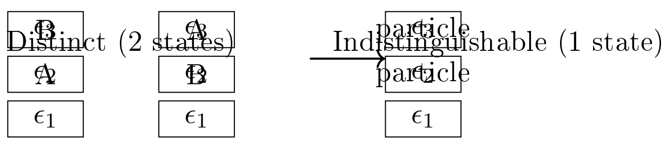
- Hamiltonian: $H = H_A + H_B$, where $H_{A/B} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2_{A/B}}$.
- Schrödinger equation: $H\Psi(x_A, x_B) = E\Psi(x_A, x_B)$.
- Since particles are non-interacting, total energy is a sum of individual energies: $E_{rs} = \epsilon_r^{(A)} + \epsilon_s^{(B)}$.
- Single-particle energy levels: $\epsilon_r = \frac{\hbar^2}{2m}\left(\frac{\pi r}{L}\right)^2$, $r = 1, 2, 3, \ldots$. Same for ϵ_s.
- The wave function is $\Psi_{rs}(x_A, x_B) = \varphi_r(x_A)\varphi_s(x_B)$ with $\varphi_r(x) \propto \sin\left(\frac{\pi r x}{L}\right)$.

Picture Example: $(r = 2, s = 3)$



$$E_{2,3} = \epsilon_2^{(A)} + \epsilon_3^{(B)}$$

Now suppose particles A & B are indistinguishable. States that were distinct become equivalent. **Example:**



Wave Functions for Identical Particles

In terms of wave functions, we continue to use labels A & B, but now we impose a symmetry requirement on the wave function under "exchange" of particles ($x_A \leftrightarrow x_B$). There are two cases:

Bose-Einstein Statistics (BE)

- Wave function is <u>symmetric</u> under exchange: $\Psi_{rs}(x_A, x_B) = +\Psi_{rs}(x_B, x_A)$.
- Form: $\Psi_{rs}(x_A, x_B) \propto \varphi_r(x_A)\varphi_s(x_B) + \varphi_r(x_B)\varphi_s(x_A)$.
- Particles with symmetric wave functions have integer spin ($S = 0, \hbar, 2\hbar, \ldots$) and are called "bosons".
- Examples: photons, Higgs particle, ^{4}He atoms, ...

Fermi-Dirac Statistics (FD)

- Wave function is antisymmetric under exchange: $\Psi_{rs}(x_A, x_B) = -\Psi_{rs}(x_B, x_A)$.
- Form: $\Psi_{rs}(x_A, x_B) \propto \varphi_r(x_A)\varphi_s(x_B) - \varphi_r(x_B)\varphi_s(x_A)$.
- Particles with antisymmetric wave functions have half-integer spin ($S = \frac{\hbar}{2}, \frac{3\hbar}{2}, \dots$) and are called "fermions".
- Examples: e^-, protons/neutrons, ^{3}He atoms, ...
- Suppose $r = s$: $\Psi_{rr}(x_A, x_B) \propto \varphi_r(x_A)\varphi_r(x_B) - \varphi_r(x_B)\varphi_r(x_A) = 0$.
- A given state may not be occupied by more than one identical fermion. This is the "**Pauli exclusion principle**".
- Note that no similar restriction applies for bosons (e.g., $\Psi_{rr} \propto 2\varphi_r(x_A)\varphi_r(x_B) \neq 0$).

Generalization for N particles: Let $Q_i = (\vec{r}_i, s_i)$ represent spatial and spin coordinates.

$$\Psi(\dots, Q_i, \dots, Q_j, \dots) = \begin{cases} +\Psi(\dots, Q_j, \dots, Q_i, \dots) & \text{BE stat. (Bosons)} \\ -\Psi(\dots, Q_j, \dots, Q_i, \dots) & \text{FD stat. (Fermions)} \end{cases}$$

Counting States Example: 2 Particles, 3 States

Make the situation more explicit by considering the case of 2 particles & 3 accessible single-particle states $\epsilon_1, \epsilon_2, \epsilon_3$.

(i) Distinguishable particles A & B

The possible states (distribution of A and B among $\epsilon_1, \epsilon_2, \epsilon_3$) are:

State #	ϵ_1	ϵ_2	ϵ_3
1.	AB	-	-
2.	-	AB	-
3.	-	-	AB
4.	A	B	-
5.	A	-	B
6.	-	A	B
7.	B	A	-
8.	B	-	A
9.	-	B	A

Total: 9 states.

(ii) Bosons (A=B, BE stat.)

Now particles are identical bosons. We characterize states by the number of particles in each single-particle state (n_r), the "occupation numbers". Total $N = \sum n_r = 2$.

State #	ϵ_1	ϵ_2	ϵ_3	(n_1, n_2, n_3)
1.	AA	-	-	(2, 0, 0)
2.	-	AA	-	(0, 2, 0)
3.	-	-	AA	(0, 0, 2)
4.	A	A	-	(1, 1, 0)
5.	A	-	A	(1, 0, 1)
6.	-	A	A	(0, 1, 1)

Total: 6 states.

(iii) Fermions (A=B, FD stat.)

Now particles are identical fermions. Occupation numbers n_r can only be 0 or 1 (Pauli exclusion).

State #	ϵ_1	ϵ_2	ϵ_3	(n_1, n_2, n_3)
1.	A	A	-	(1, 1, 0)
2.	A	-	A	(1, 0, 1)
3.	-	A	A	(0, 1, 1)

Total: 3 states.

General Situation: N Particles

Consider N particles with single-particle states labelled by r and corresponding energy ϵ_r (e.g., $\epsilon_r = \frac{\hbar^2}{2m}(\frac{\pi r}{L})^2$ for $r = 1, 2, \dots$).

- When particles are indistinguishable, what is relevant is the set of number of particles in each state, $\{n_1, n_2, \dots\}$, the "occupation numbers". ($n_r = \#$ of particles in single-particle state r).
- Since particles are non-interacting (ideal gas), the total energy of a state specified by $\{n_r\}$ is $E_{\{n_r\}} = \sum_r n_r \epsilon_r$.
- We have the constraint of fixed total particle number: $\sum_r n_r = N$.
- In the canonical ensemble (fixed T, N, V), the partition function is:

$$Z = \sum_{\{n_1, n_2, \dots\}}{}' e^{-\beta E_{\{n_r\}}} = \sum_{\{n_1, n_2, \dots\}}{}' e^{-\beta(\sum_r n_r \epsilon_r)}$$

  The prime $'$ indicates the sum over all sets of occupation numbers $\{n_r\}$ such that $\sum_r n_r = N$.

- Allowed occupation numbers depend on statistics:
  - **BE stat.:** $n_r = 0, 1, 2, \dots$ for all r, subject to $\sum_r n_r = N$.
  - **FD stat.:** $n_r = 0, 1$ for all r, subject to $\sum_r n_r = N$ (Pauli exclusion principle).