Summary.

· Canonical ensemble (CE):

→ fixed T, N, V

energy E fluctuates.

$$P_r = \frac{e^{-\beta E_r}}{Z}, \quad \beta = \frac{1}{T}, \quad r = \mu\text{-state}.$$

$$Z = \sum_r e^{-\beta E_r} \quad \text{partition fn.}$$

$$F = -T \ln Z \quad \text{free energy.}$$

· Grand canonical ensemble (GCE):

$$P_r = \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}}.$$

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)} \quad \text{grand partition fn.}$$

$$= \sum_N e^{\beta \mu N} Z_N$$

Z_N: N-particle canonical partition fn.

$$\Phi = -T \ln \mathcal{Z} \quad \text{grand potential.}$$

$$\rightarrow \bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \quad \text{mean particle \#.}$$

Quantum stat. mech. of ideal gases.

· Investigate stat. mech. of sys. at low T, where QM effects play an especially important role.

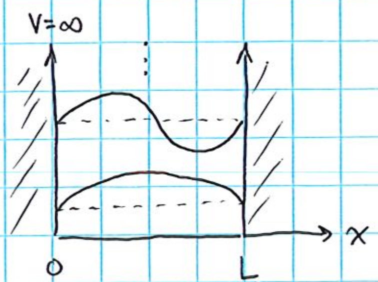
· New effects we will have to consider are associated w/ "exchange statistics" of identical particles.

· Discussion will be restricted to non-interacting particles → "ideal gas".

→ as we will see, even in absence of direct interaction force, effect of exch. stat. leads to a mutual coupling of particles.

· Before going into detailed formalism, we start w/ simple examples.

<u>Ex:</u> Two particles in a 1D box.



→ start w/ <u>distinguishable</u> particles, labelled "A" & "B".

$$\rightarrow \quad H = H_A + H_B, \qquad H_{A/B} = -\frac{\hbar^2}{2m}\frac{d^2}{dx_{A/B}^2}$$

$$\text{Sch. eqn:} \quad H\Psi(x_A, x_B) = E\,\Psi(x_A, x_B).$$

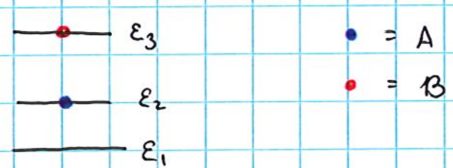
· particles non-int. ⇒ tot. energy is a sum of individual energies:

$$E \rightarrow E_{rs} = \varepsilon_r^{(A)} + \varepsilon_s^{(B)}, \qquad \varepsilon_r = \frac{\hbar^2}{2m}\left(\frac{\pi r}{L}\right)^2 \quad r = 1, 2, 3, \ldots$$

& same for ε_s

· in pictures:

(Ex: r=2, s=3)

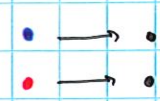


$$\rightarrow \quad E_{2,3} = \varepsilon_2^{(A)} + \varepsilon_3^{(B)}$$

· The wave fn. is $\Psi_{rs}(x_A, x_B) = \varphi_r(x_A)\,\varphi_s(x_B)$ w/ $\varphi_r(x) \sim \sin\left(\frac{\pi r}{L}\right)$

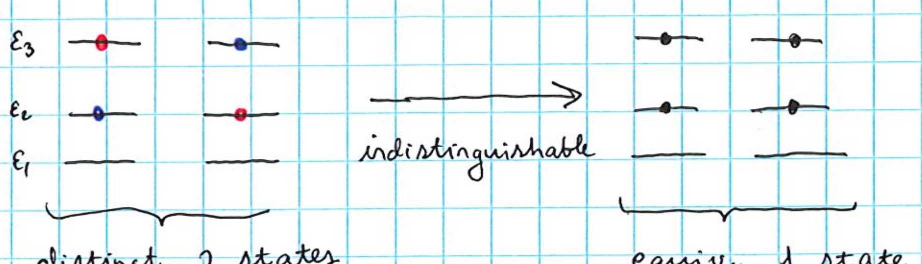
& same for φ_s.

· now suppose particles A & B are <u>indistinguishable</u>



⇒ states that were distinct become equivalent.

Ex:



In terms of wave fn.'s, we continue to use labels A & B, but now we impose a symmetry requirement on wave fn. under "exchange" of particles. There are two cases to consider:

<u>Bose-Einstein stat.</u> : · wave fn. symmetric under exchange
(BE)

$$\Psi_{rs}(x_A, x_B) = \Psi_{rs}(x_B, x_A).$$

$$\rightarrow \Psi_{rs}(x_A, x_B) \sim \varphi_r(x_A)\varphi_s(x_B) + \varphi_r(x_B)\varphi_s(x_A).$$

· particles w/ wave fn.'s symmetric under exchange have integer spin

$S = 0, \hbar, 2\hbar, \ldots$ & are called "bosons"

<u>Ex</u>: photons, Higgs particle, He^4 atoms, ...

<u>Fermi-Dirac stat.</u>: wave fn. antisymm. under exchange
(FD)

$$\Psi_{rs}(x_A, x_B) = -\Psi_{rs}(x_B, x_A)$$

$$\rightarrow \Psi_{rs}(x_A, x_B) \sim \varphi_r(x_A)\varphi_s(x_B) - \varphi_r(x_B)\varphi_s(x_A)$$

· particles w/ wave fn.'s antisymm. under exch. have $\frac{1}{2}$-integer spin

$S = \frac{\hbar}{2}, \frac{3\hbar}{2}, \ldots$ & are called "fermions".

<u>Ex</u>: e^-, protons/neutrons, He^3 atoms, ...

→ suppose $s = r$: $\Psi_{rr}(x_A, x_B) \sim \varphi_r(x_A)\varphi_{\cancel{s}\,r}(x_B) - \varphi_r(x_B)\varphi_r(x_A) = 0.$

⇒ ~~no~~ a given state may not be occupied by more than one identical particle. This is the "Pauli exclusion principle".

Note that no similar restriction applies for bosons.

For N particles:

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

$Q = (\vec{x}\, s)$ = spatial + spin coord.'s

Make the situation more explicit by considering the case of 2 particles & 3 accessible single-particle states $\varepsilon_1, \varepsilon_2, \varepsilon_3$.

(i) distinguishable particles A & B

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

→ 9 states.

(ii) bosons A = B (BE stat.)

	ε_1	ε_2	ε_3	$\{n_1, n_2, n_3\}$
1.	AA	x	x	$\{2, 0, 0\}$
2.	x	AA	x	$\{0, 2, 0\}$
3.	x	x	AA	$\{0, 0, 2\}$
4.	A	A	x	$\{1, 1, 0\}$
5.	A	x	A	$\{1, 0, 1\}$
6.	x	A	A	$\{0, 1, 1\}$

# of particles in each single-particle state.
= "occupation #'s".

→ 6 states.

(iii) fermions A = B (FD stat.)

	ε_1	ε_2	ε_3	$\{n_1, n_2, n_3\}$
1.	A	A	x	$\{1, 1, 0\}$
2.	A	x	A	$\{1, 0, 1\}$
3.	x	A	A	$\{0, 1, 1\}$

→ 3 states.

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- Now consider general situation:

  - N particles w/ single-particle states labelled by r & corresponding energy ε_r. (e.g., $\varepsilon_r = \frac{\hbar^2}{2m}\left(\frac{\pi r}{L}\right)^2$ r=1, 2, ...).

  → when particles are indistinguishable, what is relevant is the # of particles in each state (since it is not meaningful to ask which particle is in which state).

  → "occupation #'s" n_r = # of particles in single-particle state r.

  - Since particles are non-int., tot. energy of state w/ occ. #'s $\{n_1, n_2, \ldots\}$ is:

$$E_{\{n_1,n_2,\ldots\}} = n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots = \sum_r n_r \varepsilon_r .$$

  & we have constraint of fixed particle #:

$$\sum_r n_r = N.$$

⇒ In CE, the partition fn. is:

$$Z = \sum_{\{n_1 n_2 \ldots\}}{}' e^{-\beta E_{\{n_1 n_2 \ldots\}}} = \sum_{\{n_1 n_2 \ldots\}}{}' e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}$$

↑ sum over strings of occ. #'s. s.t. $\sum_r n_r = N$. (see previous ex.)

→ In BE stat., allowed occ. #'s are $n_r = 0, 1, 2, \ldots$ $\forall r$ s.t. $\sum_r n_r = N$.

→ In FD stat., allowed occ. #'s are $n_r = 0, 1$ $\forall r$ s.t. $\sum_r n_r = N$

↑ ☆ Pauli exclusion principle.