Recall: in chapter 6, when deriving the partition function of many particles

Distinguishable:

$$Z_N = Z_1^N$$

Indistinguishable

$$Z_N = \frac{1}{N!} Z_1^N$$

Where did $N!$ come from?

- $Z_N$ is the sum over all possible states

- If particles are indistinguishable, we over count the possible states

Ex: Two particles, A + B

Each particle can have one of 5 possible energies

| $E_1$ | $E_2$ | $E_3$ | $E_4$ | $E_5$ |
|---|---|---|---|---|
| A | B | | | |
| A | | B | | |
| A | | | B | |
| A | | | | B |
| B | A | | | |
| B | | A | | |
| B | | | A | |
| B | | | | A |

⋮

If particles are distinguishable:

25 states

Indistinguishable

$$\frac{1}{N!}(25) = \frac{1}{2} \cdot 25 = 12.5 \quad ?$$

Can't be right

Count more carefully

End up with 15 states

$Z_N = \frac{1}{N!} Z_1^N$ is only an approximation

In this chapter, we will see

- How to count states more carefully
- Why it matters & when the approx is OK

Our task: Obtain the partition function for systems of indistinguishable particles

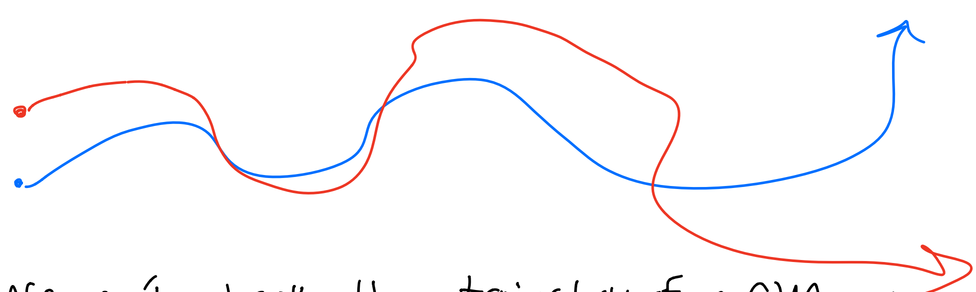
First: what does indistinguishable really mean?

- Fundamentally quantum-mechanical

- Just like an individual particle does not have a well defined position or momentum, one electron in a group of electrons does not even have a well defined <u>identity</u>

We can't just follow an electron around with a microscope.

Ex: Two classical particles, we distinguish them by trajectories



We can't track the trajectory of a QM particle

No such thing as "this electron" or "that electron"

Before we proceed to the partition function, let's explore some of the quantum mechanical implications of identical particles

Suppose: I have two particles

The wave function depends on the states of the two particles

$\vec{s}_1$ means the first of my enumerated states, not state of particle 1

$$\psi = \psi(\vec{s}_1, \vec{s}_2)$$

First particle is in state $\vec{s}_1$, second is in $\vec{s}_2$

$\vec{s}$: position, momenta, spin, etc

Distinguishable:

$$\psi(\vec{s}_1, \vec{s}_2) \neq \psi(\vec{s}_2, \vec{s}_1)$$

- If I swap particles so that the first is in state $\vec{s}_2$, second in $\vec{s}_1$, I get a new $\psi$

Identical:

Swapping particles does not alter the overall state

$$\psi(\vec{s}_1, \vec{s}_2) = \psi(\vec{s}_2, \vec{s}_1)$$

Actually (QFT)

Take particle 1 & put it into state 2

2 1

$$\psi(\vec{s}_1, \vec{s}_2) = \pm\, \psi(\vec{s}_2, \vec{s}_1)$$

Two possibilities:

For particles with integer spin

$$\psi(\vec{s}_1, \vec{s}_2) = \psi(\vec{s}_2, \vec{s}_1)$$

Switching particles does not alter the system

Bosons

Particles w/ $\frac{1}{2}$ integer spin

$$\psi(\vec{s}_1, \vec{s}_2) = -\psi(\vec{s}_2, \vec{s}_1)$$

If I switch two particles, the state is antisymmetric

$\boxed{\text{Fermions}}$

What if both particles are in the same state, $\vec{s}$?

$$\psi(\vec{s}, \vec{s}) = -\psi(\vec{s}, \vec{s})$$

$$\Rightarrow \psi(\vec{s}, \vec{s}) = 0$$

For fermions: both particles cannot be in the same state

Generally: If there are N many, no 2 can be in the same state

(all N must occupy different states)

Pauli Exclusion Principle

Example: electron orbitals

Each electron is in the state

$$\vec{S} = \langle n, l, m_l, m_s \rangle$$

$n$: energy $(1, 2, 3, \ldots)$

$l$: ang momentum $(0, \ldots n-1)$

$m_l$: $l_z$ $(-l, \ldots 0, \ldots l)$

$m_s$: spin $(-\frac{1}{2}, \frac{1}{2})$

| $n$ | $l$ | $m_l$ | $m_s$ | # unique states |
|---|---|---|---|---|
| 1 | 0 | 0 | $-\frac{1}{2}, \frac{1}{2}$ | 2 |
| 2 | 0 | 0 | $-\frac{1}{2}$ $\frac{1}{2}$ | 2 |
| 2 | 1 | $-1, 0, 1$ | $-\frac{1}{2}, \frac{1}{2}$ | 6 |

This effects how we count states!

Ex: system of 2 particles, A + B

3 possible states

1) Classical (distinguishable)

| S | 1 | 2 | 3 |
|---|---|---|---|
| | AB | – | – |
| | – | AB | – |
| | – | – | AB |
| | A | B | – |
| | B | A | – |
| | A | – | B |
| | B | – | A |

| | | |
|---|---|---|
| — | A | B |
| — | B | A |

2) Bosons

$AB \rightarrow AA$

| S | 1 | 2 | 3 |
|---|---|---|---|
| | AA | — | — |
| | — | AA | — |
| | — | — | AA |
| | A | A | — |
| | A | — | A |
| | — | A | A |

3) Fermions

| S | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | – |
| | A | – | A |
| | – | A | A |

Let's start counting states, so we can construct the partition function

We know: the possible states of the system

the energy of each state

the # of particles in the state

Notation:

- The set of single particle states is $\vec{S}$

$\vec{S} = (S_1, S_2, S_3, \ldots)$

Ex: 2-state paramagnet, each particle can be up or down

So: $\vec{S} = \langle \uparrow, \downarrow \rangle$

Ex: Harmonic oscillator, state is characterized by energy level $n$

$\vec{S} = \langle 0, 1, 2, \ldots \rangle$

- The energy of a particle in a given state

State is labeled by $S$, energy is $\epsilon_s$

Ex: if $s = \uparrow$, $\epsilon_s = -\mu B$

if $s = (n=3)$ $\epsilon_s = (3+\frac{1}{2})\hbar\omega$

- The number of particles in state $s$ is $n_s$

- The current state of the entire system is $\vec{R}$

$$\vec{R} = \{2 \text{ spin up}, \; 4 \text{ spin down}\}$$

$$\vec{R} = \{2 \times (n=1), \; 0 \times (n=2), \; 4 \times (n=3)\}$$

OK

If the entire system is in some state $R$:

The total energy is

$$E_R = n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \dots$$

$$= \sum_s n_s \epsilon_s$$

Sum over all possible single-system states

(could be infinite)

| $s$ | $n_s$ | $\epsilon_s$ |
|---|---|---|
| $n=0$ | 5 | $\frac{1}{2}\hbar\omega$ |
| $n=1$ | 2 | $\frac{3}{2}\hbar\omega$ |
| $n=2$ | 6 | $\frac{5}{2}\hbar\omega$ |
| $\vdots$ | 0 | $\vdots$ |

Even if the number of allowed single-particle states is infinite, the total number of particles is not

$$\sum_s n_s = N$$

The partition function is:

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

$\sum_R$ is over all possible states of the entire system

| s | 1 | 2 | 3 | |
|---|---|---|---|---|
| | AA | — | — | $R_1$ |
| | — | AA | — | $R_2$ |
| | — | — | AA | $R_3$ |
| | A | A | — | $R_4$ |
| | A | — | A | $R_5$ |
| | — | A | A | $R_6$ |

$\sum_R$

Before going forward, let's consider the implications of fermions vs bosons

- Consider a system of $N$-many particles

If $T \to 0$, what happens?

Boson: All particles want to occupy the lowest energy state

- For harmonic oscillators

$$U \approx N\left(\tfrac{1}{2}\hbar\omega\right) \quad \text{(ground state)}$$

every particle is in the ground state

$\downarrow$

Fermions: Only one particle can occupy the lowest energy state

First particle occupies the ground state, next one the $n=1$ state

| $n$ | # |
|---|---|
| 0 | 1 |
| 1 | 1 |
| 2 | 1 |
| 3 | 1 |
| ⋮ | ⋮ |

First particle has energy $\frac{1}{2}\hbar\omega$

highest energy particle has energy $\sim (N+\frac{1}{2})\hbar\omega$

Even at $T \approx 0$, the fermion gas has considerable energy

What is the expected number of particles in state "s" $(n_s)$

$n_0$ = # in ground state

$n_1$ = # in next state

etc...

$$\langle n_s \rangle = \sum_R n_s P(n_s)$$

$$= \frac{\sum_R n_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots + n_s\epsilon_s + \ldots)}}{\sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots + n_s\epsilon_s + \ldots)}}$$

Example: 3 harmonic oscillators, 5 states

| $n_1$ | $n_2$ | $n_3$ | $n_4$ | $n_5$ | $N$ |
|---|---|---|---|---|---|
| 3 | 0 | 0 | 0 | 0 | 3 |
| 0 | 3 | 0 | 0 | 0 | 3 |
| 0 | 0 | 3 | 0 | 0 | 3 |
| | | ⋮ | | | |
| 2 | 1 | 0 | 0 | 0 | |
| 2 | 0 | 1 | 0 | 0 | |
| | | ⋮ | | | |
| 1 | 1 | 1 | 0 | 0 | |
| 1 | 1 | 0 | 1 | 0 | |
| | | ⋮ | | | |

$$\sum_R n_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots + n_s\epsilon_s + \dots)}$$

$s = 2$

$$0 \cdot e^{-\beta(3\epsilon_1)} + 3 \cdot e^{-\beta(3\epsilon_2)} + 0 e^{-\beta(3\epsilon_3)} +$$

$$\dots + 1 \cdot e^{-\beta(2\epsilon_1 + 1\cdot\epsilon_2)} + 2 e^{-\beta(\epsilon_1 + 2\epsilon_2)}$$

$$+ \dots$$

$$\epsilon_n = \left(n + \tfrac{1}{2}\right)\hbar\omega$$

$$\frac{\sum_R n_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots + n_s\epsilon_s + \ldots)}}{\sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots + n_s\epsilon_s + \ldots)}}$$

$$n_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots + n_s\epsilon_s + \ldots)}$$

$$= n_s e^{-\beta\sum_i n_i\epsilon_i} = n_s e^{-\beta\left(n_s\epsilon_s + \sum_{i\neq s} n_i\epsilon_i\right)}$$

$$= n_s e^{-\beta n_s\epsilon_s} e^{-\beta\sum_i^{(s)} n_i\epsilon_i}$$

$$\langle n_s\rangle = \frac{\sum_R n_s e^{-\beta n_s\epsilon_s} e^{-\beta\sum^{(s)} n_i\epsilon_i}}{\sum_R e^{-\beta\sum_i n_i\epsilon_i}}$$

$$\sum_R = \sum_{\{n_1, n_2, \ldots n_s, \ldots ; \sum n_i = N\}}$$

$$\langle n_s \rangle = \frac{\sum\limits_{n_s} n_s e^{-\beta n_s \epsilon_s} \sum\limits_{R_s} e^{-\beta \sum_i^{(s)} n_i \epsilon_i}}{\sum\limits_{n_s} e^{-\beta n_s \epsilon_s} \sum\limits_{R_s} e^{-\beta \sum_i^{(s)} n_i \epsilon_i}}$$

$$\sum_{R_s} = \sum_{\text{all possible values of } n \text{ for other states, given the value of } n_s}$$

$\sum\limits_{R_s} e^{-\beta \sum_i^{(s)} n_i \epsilon_i}$ : sum over all states <u>except</u> s. Subject to constraint that: $\sum\limits_i^{(s)} n_i = N - n_s$

$$Z(N - n_s) \equiv \sum_{R_s} e^{-\beta \sum_i^{(s)} n_i \epsilon_i}$$

$$\langle n_s \rangle = \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s} \cdot Z(N-n_s)}{\sum_{n_s} e^{-\beta n_s \epsilon_s} \cdot Z(N-n_s)}$$

For fermions: $n_s$ can be either 0 or 1

$$\langle n_s \rangle = \frac{0 + e^{-\beta \epsilon_s} \cdot Z(N-1)}{Z(N) + e^{-\beta \epsilon_s} Z(N-1)}$$

$$\langle n_s \rangle = \frac{1}{\frac{Z(N)}{Z(N-1)} e^{\beta \epsilon_s} + 1}$$

$$\ln Z(N-1) \approx \ln Z(N) - 1 \cdot \frac{\partial}{\partial N} \ln Z(N)$$

$$\frac{\partial}{\partial N} \ln Z(N) = \frac{\partial}{\partial N}\left(-\beta F\right) = -\beta\mu$$

$$\ln Z(N-1) \approx \ln Z(N) + \mu\beta$$

$$Z(N-1) \approx Z(N) e^{\mu\beta}$$

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

$$\boxed{\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}}$$