F. Classical Gases: Ideal and Non-ideal

- Canonical Ensemble works well, of course
- See later chapter on classical statistical mechanics within canonical ensemble with a discussion on phase transitions due to presence of interaction
- Monatomic Gases [or translation motions of CM of molecules]

$$Z(T,V,N) = \frac{1}{N!\,h^{3N}} \underbrace{\int d^3x_1 \int d^3p_1 \cdots \int d^3x_N \int d^3p_N}_{\text{sum over all N-particle states becomes integrate over 6N phase space}} e^{-\frac{H(\{x_i,p_i\})}{kT}}$$

correction for over-counting

$$\underset{\text{Hamiltonian}}{H(\{x_i,p_i\})} = \underbrace{\underbrace{\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}}_{\text{k.e. of N particles}}}_{\text{"ideal gas" part of Hamiltonian}} + \underbrace{U(\{x_i\})}_{\text{possible particle-particle interaction and effect of external field}}$$

- Non-ideal gases and liquid state physics begin here!

G. Ideal Quantum Gas: Formal Discussions - Canonical Ensemble

Gas of identical particles
- indistinguishable
- bosons / fermions [QM]

- "Perfect" or "ideal": Non-interacting
  ⇒ can discuss the problem using single-particle states
- Fermions / Bosons

Fermions → cannot have two or more particles occupying the same single-particle state

Bosons → no such restriction

(i) What do we know?

- For a N-particle system, the probability of finding the system in a state of energy E_r when the system is in equilibrium at temperature T is:

$$P_r = \frac{1}{Z} e^{-\beta E_r}$$

- $Z = Z(T,V,N) = \sum_{\underbrace{\text{all states } i}_{N\text{-particle states}}} e^{-\beta E_i}$ Partition function of the whole system

This works all the time! The point is: When we consider a system of N (fixed N) bosons/fermions, $\sum_{\text{all states } i}$ should include the states with the proper symmetry requirement imposed by quantum mechanics on the N-fermion OR N-boson states.

QM

Bosons: Wavefunction should be symmetric with respect to interchanging two particles

Fermions: Wavefunction should be anti-symmetric w.r.t. interchanging two particles

→ Regardless the fermions/bosons are interacting

With $Z(T,V,N)$, other thermodynamic quantities follow.

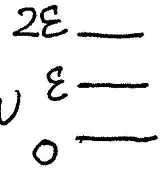
The points are:

- $Z = \sum_{\text{all } N\text{-particle states } i} e^{-\beta E_i}$ works for quantum gases
- Listing out all the states in $\sum_{\text{all states } i}$ is difficult, even for non-interacting fermions/bosons!

(ii) Nature of Particles affects the Partition Function

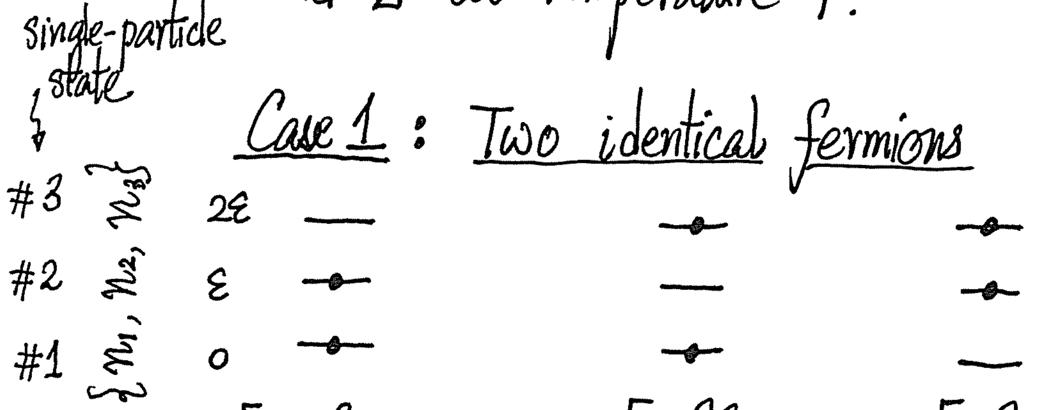
Example: Two non-interacting particles

Each particle has a single-particle energy spectrum



Find Z at temperature T.

Case 1 : Two identical fermions

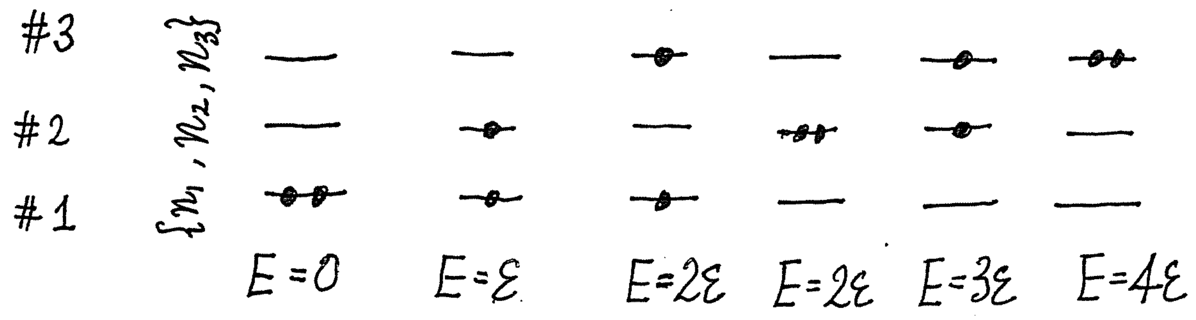


	$E = \varepsilon$	$E = 2\varepsilon$	$E = 3\varepsilon$
occupation numbers:	$\{1,1,0\}$	$\{1,0,1\}$	$\{0,1,1\}$

A total of three 2-particle states to be included in Z

$$Z_{\text{fermion}} = e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} = e^{-\frac{\varepsilon}{kT}} + e^{-\frac{2\varepsilon}{kT}} + e^{-\frac{3\varepsilon}{kT}}$$

Case 2: Two identical bosons



Six 2-particle states to be included in Z

Occupation numbers: {2,0,0} {1,1,0} {1,0,1} {0,2,0} {0,1,1} {0,0,2}

$$Z_{bosons} = e^{-\beta\cdot 0} + e^{-\beta\varepsilon} + e^{-\beta 2\varepsilon} + e^{-\beta 2\varepsilon} + e^{-\beta 3\varepsilon} + e^{-\beta 4\varepsilon}$$

$$= 1 + e^{-\frac{\varepsilon}{kT}} + 2e^{-\frac{2\varepsilon}{kT}} + e^{-\frac{3\varepsilon}{kT}} + e^{-\frac{4\varepsilon}{kT}}$$

Obviously, $Z_{fermions} \neq Z_{bosons} \neq Z_{distinguishable}$

Case 3: Two distinguishable particles

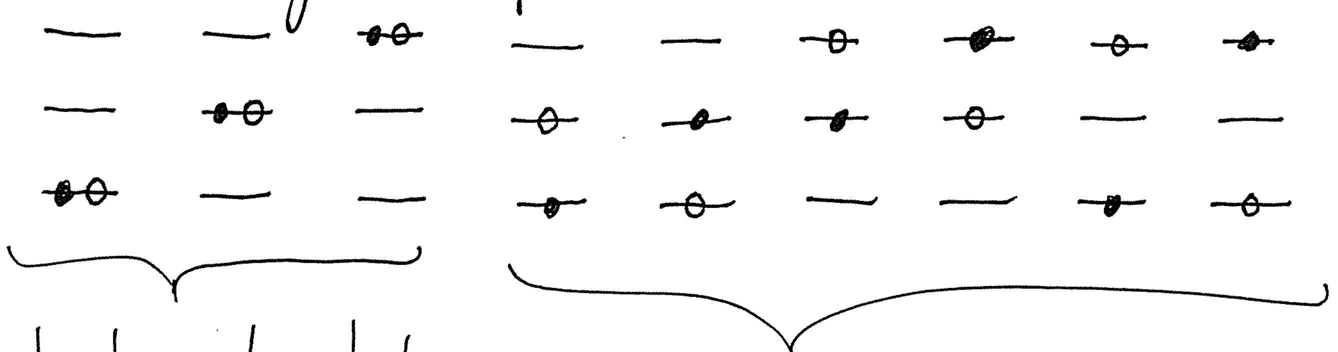
$$Z_{distinguishable} = z^2 \qquad \text{(Why?)}$$

$$= \underbrace{\left(1 + e^{-\frac{\varepsilon}{kT}} + e^{-\frac{2\varepsilon}{kT}}\right)^2}_{} \qquad \text{(Why?)}$$

9 terms ⇒ Nine 2-particle states in Z

Notes: In general, cannot use $\frac{1}{N!}$ $(=\frac{1}{2}$ here) to turn distinguishable-particle results into useful results!
[Only works in classical situations]
Fermionic/Bosonic nature of particle is important!
For many-fermion(boson) systems, Z is hard to write down!

Two distinguishable particles (Nine 2-particle states)



- $\frac{1}{2!}$ does not work!
- $\frac{1}{2!}$ "over-corrected" the counting!
- When such situations amount to a tiny negligible fraction of all states, then $\frac{1}{N!}$ works! This is the case for classical indistinguishable particles.

$\frac{1}{2!}$ works OK to correct for over-counting when particles become indistinguishable

(iii) Occupation number representation: Book-keeping method

- Non-interacting: Work with single-particle states (solving 1-particle Schrödinger Equation)
- Indistinguishable: Specifying number of particle(s) in each single-particle state

[See previous Sec. (ii) for examples]

E.g.

single-particle state	#1	#2	#3
energy of s.p. state	$\varepsilon_1 = 0$	$\varepsilon_2 = \varepsilon$	$\varepsilon_3 = 2\varepsilon$
consider a 2-particle state	$\{1,$	$0,$	$1\}$
	one particle in state #1	no particle in state #2	one particle in state #3

$N = \sum_i n_i$ as $2 = 1 + 0 + 1$

$E = \sum_i n_i \varepsilon_i$ as $2\varepsilon = 1\cdot 0 + 0\cdot(\varepsilon) + 1\cdot(2\varepsilon)$

Generally, the single-particle states can be labelled by $1, 2, \cdots, r, \cdots$ with energies $\varepsilon_1 \leq \varepsilon_2 \leq \cdots \leq \varepsilon_r \leq \cdots$

It is convenient to specify a set of occupation numbers $\{n_1, n_2, \cdots, n_r, \cdots\}$

where n_r = number of particles in single-particle state r in describing a N-particle state.

$\sum_r n_r = N$ for N-particle states

Partition Function Z

- In a state specified by $\{n_1, n_2, \cdots, n_r, \cdots\}$, the energy is $E(\{n_1, n_2, \cdots\}) = \sum_r n_r \varepsilon_r$

- We have $\sum_r n_r = N$ ——— (a)
- We have $\begin{cases} n_r = 0 \text{ or } 1 & \text{for fermions} \text{ — (b)} \\ n_r = 0, 1, 2, 3, \cdots & \text{for bosons} \text{ — (c)} \end{cases}$

$$Z(T,V,N) = \sum_{\text{allowed } \{n_r\}} e^{-\beta\left(\sum_r \varepsilon_r n_r\right)} = \sum_{\text{allowed } \{n_r\}} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots + n_r\varepsilon_r + \cdots)}$$

Important: $\sum_{\text{allowed } \{n_r\}}$ is a sum over all sets of $\{n_i\}$ satisfying

$\begin{cases} \text{(a) AND (b)} & \text{for fermions} \\ \text{(a) AND (c)} & \text{for bosons} \end{cases}$

Note: If the requirement is (b) only or (c) only, it will be easy to do the sum. But [(a) AND (b)], [(a) AND (c)] make the calculation of Z hard to do!

- The Grand Canonical Ensemble approach simplifies the calculation.
- In some cases not dealing with "real" (matter) particles in which N is not fixed, Z can be calculated.

Ideal Fermi/Bose Gases

Z is not easy to get!

Ways out?

short cut

Go back to microcanonical ensemble (E, V, N) and look for most probable distributions for fermions/bosons

new formalism

Grand Canonical Ensemble

Idea:

Z is hard to get because of the "$\sum_r n_r = N$" requirement in listing out the states.

How about relaxing the requirement?

Physics is physics!

The same physics results!

- Fermi-Dirac distribution
- Bose-Einstein distribution

References for Sec. 6:

Mandl: Ch. 9

Bowley and Sanchez: Ch. 6