X. Non-interacting Particles : Fermi-Dirac and Bose-Einstein Distributions

Motivation: Interacting Systems are difficult to handle, though interesting

Classical ideal gas physics breaks down when

$$\left(\frac{V}{N}\right)^{1/3} \sim \frac{h}{\sqrt{2\pi m k T}}$$

Metals at room temperature

10^{23} electrons in $1\ cm^3$ of metal $\Rightarrow$ $\underbrace{\left(\frac{V}{N}\right)^{1/3}}_{\text{separation between electrons}} \sim 10^{-8}\ cm$

but mass of electron ($\sim 10^{-30}$ Kg) (tiny)

$\lambda_{th}(T_{room}) > \left(\frac{V}{N}\right)^{1/3}$ $\Rightarrow$ must take fermionic nature of electrons into account for metal physics

room temperature

(even assuming electrons are not interacting)

A. Single-Particle States

- No interacting $U(\vec{x}_i - \vec{x}_j)$ term in Hamiltonian
- $\hat{H}_N = \sum_{i=1}^{N} \hat{h}_i$ ← single-particle Hamiltonian $\hat{h}_i = \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{U(\vec{x}_i)}$

  even with a potential energy term, it depends only on $\vec{x}_i$
- Statistical Mechanics Problems become two-step problems:

(i) Solve $\hat{h}\,\psi(\vec{r}) = \varepsilon\,\psi(\vec{r})$ QM problem

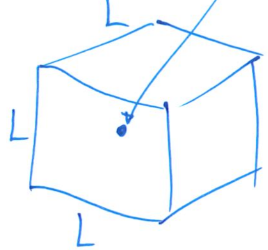
$\psi_i(\vec{r}) \leftrightarrow \varepsilon_i$ pairs

single-particle (s.p.) states; energy of state i

[i labels different states]

e.g. particle-in-a-BIG-box[+]

m = mass



$$\psi_{\underbrace{n_x n_y n_z}}(x,y,z) = \sqrt{\frac{8}{V}}\,\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{L}\right)\sin\left(\frac{n_z \pi y}{L}\right)$$

pairs; labels s.p. state

$$\epsilon_{n_x, n_y, n_z} = (n_x^2 + n_y^2 + n_z^2)\frac{\pi^2 \hbar^2}{2mL^2}$$

$n_x = 1, 2, \dots$
$n_y = 1, 2, \dots$
$n_z = 1, 2, \dots$

[+] $\hat{h} = -\frac{\hbar^2}{2m}\nabla^2$ in $0 < x, y, z < L$

energy (axis)

dot $\varepsilon_{n_x, n_y, n_z}$ in (very dense)

buffer $d\varepsilon$ — count s.p. states in $\varepsilon \to \varepsilon + d\varepsilon$

Use continuum description

$\Rightarrow$ $\boxed{g(\varepsilon)\,d\varepsilon = \#\text{ s.p. states in the interval } \varepsilon \to \varepsilon + d\varepsilon}$

$\boxed{\text{What is } g(\varepsilon)?}$ Q1

(ii) Fill the particles into s.p. states

N particles → how to fill them into s.p. states?

→ what is the rule for fermions/ bosons? Q2

(fermions/ bosons: assumed non-interacting because we invoked s.p. states)

We have two questions Q1 and Q2.

Take-Home Messages

Q1: Single-particle states, can be treated as basic QM problem, are densely packed on energy axis. Need to invoke $g(\varepsilon)d\varepsilon$ to describe them. (This is NOT a thermal/statistical physics problem)

Q2: How to fill particles into s.p. states?

- Rules? [Fermions, Bosons]
- Different temperatures?

We will answer Q2 first.

B. Set up the Problem of finding the Most Probable Distribution

Recall the Most Probable Distribution Problem (Ch. VIII)

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The Problem of Finding the Most Probable Distribution

Idea 1

$$S = k \ln W = k \ln \Big[\underbrace{\sum_{\text{distributions}} W(\text{distribution})}_{\text{one term } W(\text{most probable}) \text{ dominates}} \Big] \quad \text{exact}$$

(out numbered sum of other terms)

$$\approx k \ln W(\text{most probable}) \quad \text{(should be an excellent approximation)}$$

$$= k \ln W_{mp}$$

Question becomes: Set up formalism for obtaining the most probable distribution

Idea 2 [Key concepts here]

Most Probable distribution: A string of yet-to-be-determined occupation numbers

(a) $\{n_i\}_{mp} = \{n_1, n_2, n_3, n_4, \cdots\}_{mp}$

symbol for a string $\updownarrow$ $\boxed{\text{unknowns}}$ $\updownarrow$

energy : $\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \cdots$

(b) Count # microstates corresponding to $\{n_i\}_{mp}$

$W(\{n_i\}_{mp})$ = a function of the unknowns $\{n_i\}_{mp}$

(c) there are constraints (Eq. (19))

$$\sum_i n_i = N \quad ; \quad \sum_i n_i \varepsilon_i = E \qquad (19)$$

(d) Mathematical Statement of finding $\{n_i\}_{mp}$

Find $\{n_i\}_{mp}$ such that $W(\{n_i\}_{mp})$ or $\ln W(\{n_i\}_{mp})$ is a maximum subject to the constraints

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \varepsilon_i = E \tag{20}$$

- A topic† in partial differentiation (using Lagrange multiplers)
- $W(\{n_i\})$ depends on further details of the non-interacting particles
  - a single-particle state can either be empty or occupied at most by one particle (fermions)

    (the result is the "Fermi-Dirac distribution")

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† Eq.(20) is finding the extremum of a function $\mathcal{F}(n_1, n_2, \cdots)$ under constraints. Naturally, we would vary each n_i, i.e. δn_i's, but the constraints say not all δn_i's are independent.

- a single-particle state can be empty or occupied by any number of particles (bosons)

  (the result is the Bose-Einstein distribution)

All particles are either fermions (spin 1/2, 3/2, ...) or bosons (spin 0, 1, ...)

- There are cases in which we don't need to care about fermionic or bosonic nature of particles ("classical particles")

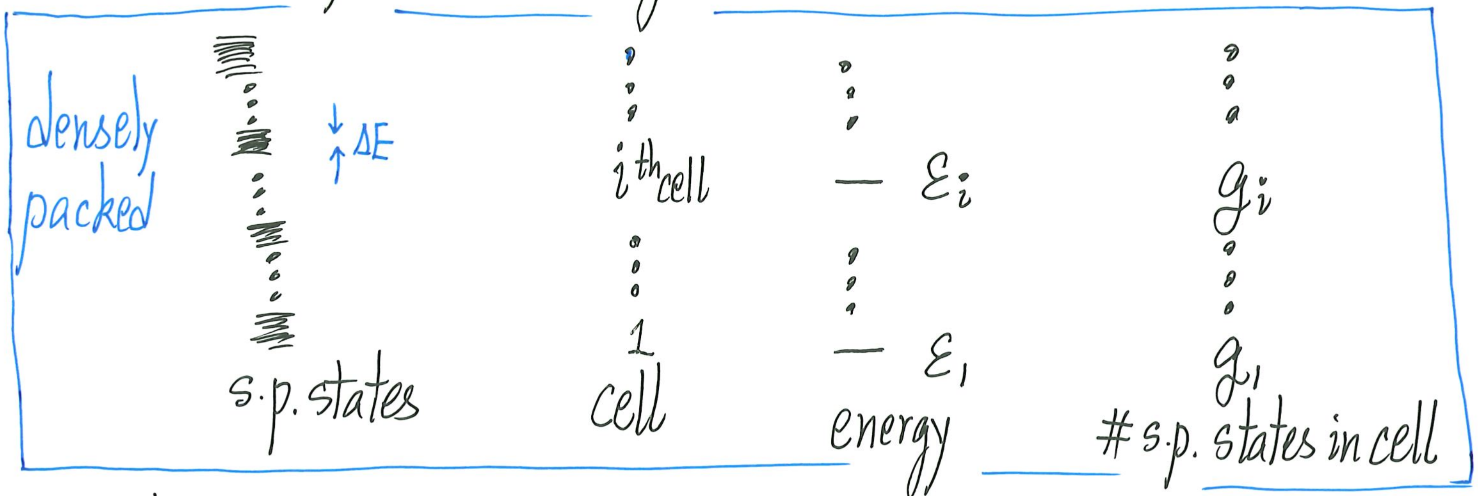
  Why?

  $$\text{when } \underbrace{\#\text{ particles } (\text{"}n_i\text{"}) \text{ per single-particle states}}_{\text{many s.p. states available to one particle}} \ll 1$$

  (never need to worry having more than 1 particle in a s.p. state)

Let's set up the problems†

- For convenience (and for using Stirling's approximation), we group s.p. states of nearly same energies into CELLS.



i.e. Cell i has g_i s.p. states all of energy ε_i

strings: $\{n_1, n_2, \cdots, n_i, \cdots\}$

$\downarrow$

particles in Cell 1, Cell 2, ⋯, Cell i, ⋯

$$N = \sum_i n_i$$

$$E = \sum_i \varepsilon_i n_i$$

constraints

$$\boxed{\text{Find } \{n_i\} \text{ that maximizes } W(\{n_i\}) \text{ under the constraints}}$$

† This will answer the question Q2.

(a) Counting $W_{FD}(\{n_i\})$ for Fermions

Given a string $\{n_1, \cdots, n_i \cdots\}$ for fermions

Cell energy: $\varepsilon_1, \cdots, \varepsilon_i, \cdots$
s.p. states in Cell: $g_1, \cdots, g_i, \cdots$

- For fermions, $n_i \leq g_i$ (otherwise violate Pauli exclusion rule)
- For cell i, we have $\begin{cases} n_i \text{ (out of } g_i\text{) states with one particle} \\ (g_i - n_i) \text{ states with no particle} \end{cases}$

How many ways for cell i?

↳ divide g_i s.p. states into two groups

↳ $\begin{cases} n_i \text{ in one group (occupied)} \\ (g_i - n_i) \text{ in another group (empty)} \end{cases}$

(it is picking n_i out of g_i)

\# ways of arranging n_i <u>fermions</u> into g_i s.p. states $= \dfrac{g_i!}{n_i!\,(g_i-n_i)!}$

key step for fermions

- Repeat argument for every cell

- For a string $\{n_1, n_2, \cdots, n_i \cdots\}$,

  Number of microstates $$W_{FD}(\{n_i\}) = \prod_i \frac{g_i!}{n_i!\,(g_i-n_i)!} \quad (1)$$

  product over cells

  Find $\{n_i\}$ that maximizes $\ln W_{FD}(\{n_i\})$ under the constraints

  $$\left.\begin{aligned} \sum_i n_i &= N \\ \sum_i \varepsilon_i n_i &= E \end{aligned}\right\} \quad (2)$$

This defines the <u>Fermions</u> problem

(3)

[Recall: The Most Probable Distribution problem is formulated within fixed E, V, N.]

(b) Counting $W_{BE}(\{n_i\})$ for Bosons

Given a string $\{n_1, \ldots, n_i, \ldots\}$ for bosons

$\updownarrow \quad \updownarrow$

Cell energy: $\varepsilon_1, \ldots, \varepsilon_i, \ldots$

s.p. states in Cell: $g_1, \ldots, g_i, \ldots$

- For cell i, n_i bosons in g_i s.p. states

  no restriction on number of bosons in ONE s.p. state

  # ways of arranging n_i bosons into g_i groups (use $(g_i - 1)$ sticks)

  $$= \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \approx \frac{(n_i + g_i)!}{n_i!\, g_i!}$$

  key step for bosons

  $(g_i \gg 1)$

  g_i is in the set up (can make sure that it is the case)

- Repeat argument for every cell

- For a string $\{n_1, n_2, \cdots, n_i \cdots\}$

Number of microstates $W_{BE}(\{n_i\}) = \prod_i \frac{(g_i + n_i)!}{n_i!\, g_i!}$ (4)

product over cells

Find $\{n_i\}$ that maximizes $\ln W_{BE}(\{n_i\})$ under the constraints (5)

$$\left.\begin{aligned} \sum_i n_i &= N \\ \sum_i \varepsilon_i n_i &= E \end{aligned}\right\} \quad (2)$$

This defines the Bosons problem.

C. Summary on Procedure of Method of Lagrange Multipliers[+]

Find extremum of $W(x_1, x_2, \cdots, x_n)$ under constraints $\begin{cases} g_1(x_1, \cdots, x_n) = \text{constant} \\ g_2(x_1, \cdots, x_n) = \text{constant} \end{cases}$

Introduce one multiplier for each constraint, thus 2 multipliers

Optimal $(x_1, x_2, \cdots x_n)$ satisfies

$$\frac{\partial W}{\partial x_i} - \lambda_1 \frac{\partial g_1}{\partial x_i} - \lambda_2 \frac{\partial g_2}{\partial x_i} = 0 \quad \text{all } i = 1, \cdots, n$$

$$g_1(x_1, \cdots, x_n) = \text{constant} \qquad (6)$$

$$g_2(x_1, \cdots, x_n) = \text{constant}$$

give $(n+2)$ equations for the optimal $\underbrace{(x_1^{op}, x_2^{op}, \cdots, x_n^{op})}_{n \text{ unknowns}}$ AND $\underbrace{\lambda_1, \lambda_2}_{2 \text{ unknowns}}$

that maximize $W(\{n_i\})$

[+]See Essential Math Skills for detail

D. The Fermi-Dirac Distribution

Maximize $\ln W_{FD}(\{n_i\}) = \ln\left[\prod_i \frac{g_i!}{n_i!(g_i-n_i)!}\right] = \sum_i \ln\left(\frac{g_i!}{n_i!(g_i-n_i)!}\right)$

$$= \sum_i \left(g_i \ln g_i - n_i \ln n_i - (g_i-n_i)\ln(g_i-n_i)\right)$$

Stirling approximation

Preparing for Eq. (6):

$$\frac{\partial \ln W_{FD}(\{n_i\})}{\partial n_j} = -\ln n_j - 1 + \ln(g_j-n_j) + 1 = \ln\left(\frac{g_j-n_j}{n_j}\right)$$

one of n_i's

Constraint #1 : $\underbrace{\sum_i n_i = N}_{\text{this is "}g_1\text{" in Eq. (6)}}$ → introduce multiplier α

→ $\frac{\partial}{\partial n_j}\left(\sum_i n_i\right) = 1$

Constraint #2 : $\underbrace{\sum_i \varepsilon_i n_i = E}_{\text{this is "}g_2\text{" in Eq. (6)}}$ → introduce multiplier β

→ $\frac{\partial}{\partial n_j}\left(\sum_i \varepsilon_i n_i\right) = \varepsilon_j$

Applying Method of Lagrange Multipliers:
Optimal distribution $\{n_i\}$ satisfies

$$\ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha - \beta\varepsilon_i = 0 \qquad i = 1, \cdots, n \quad \text{(plus the two constraints)} \tag{7}$$

$$\Rightarrow \boxed{n_i = g_i \cdot \frac{1}{e^{\alpha} e^{\beta\varepsilon_i} + 1}} \tag{8}$$

OR

$$\boxed{\frac{n_i}{g_i} = \frac{1}{e^{\alpha} e^{\beta\varepsilon_i} + 1}} \tag{9}$$

Key Results & Important Physics here

Note meaning

$$\boxed{\frac{n_i}{g_i} = \text{\# fermion per single-particle state of energy } \varepsilon_i} \tag{10}$$

This is the physical meaning of the "Fermi-Dirac Distribution"

Formally, α should be fixed by $\sum_i n_i = N$; β should be fixed by $\sum_i \varepsilon_i n_i = E$

Here, we just claim the results : $\beta = 1/kT$; $\alpha = -\mu/kT$ (μ is chemical potential)

$$\therefore \boxed{\underbrace{n_i}_{\substack{\#\text{ fermions}\\ \text{in s.p. states}\\ \text{of energy } \varepsilon_i}} = \underbrace{g_i}_{\substack{\#\text{ s.p. states}\\ \text{with energy } \varepsilon_i}} \cdot \underbrace{\frac{1}{e^{(\varepsilon_i-\mu)/kT}+1}}_{\substack{\#\text{ fermion PER single-particle state of energy } \varepsilon_i\\ \text{when system is in equilibrium at temp. } T \text{ and chemical potential } \mu}}} \quad (11) \quad [\text{Key Result}]$$

Taking energy ε_i as continuous [ε_i are densely packed]

$$\boxed{f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT}+1}} \quad (12)$$

is the Fermi-Dirac Distribution

always remember its meaning! It is # fermion per s.p. state of energy ε

[if there is/are s.p. state(s) at that energy (given by $g(\varepsilon)$)]

Taking energy as continuous, Eq. (11) becomes

$$\underbrace{n(\varepsilon)\,d\varepsilon}_{\substack{\#\text{ fermions}\\ \text{with energy in}\\ \text{interval } \varepsilon\to\varepsilon+d\varepsilon}} = \underbrace{g(\varepsilon)}\,\overbrace{f_{FD}(\varepsilon)}\,\underbrace{d\varepsilon} \qquad (13)$$

fermion PER s.p. state

s.p. states in interval $\varepsilon \to \varepsilon + d\varepsilon$

It follows that (from the constraints):

$$\boxed{\int_0^\infty \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/kT}+1}\,d\varepsilon = N \;;\; \int_0^\infty \frac{\varepsilon\, g(\varepsilon)}{e^{(\varepsilon-\mu)/kT}+1}\,d\varepsilon = E} \qquad (14)$$

These are the key equations for study Ideal Fermi Gas!

We need the information $\underbrace{g(\varepsilon)}_{\text{density of s.p. states}}$ to proceed.

Pause: What have we done?

We found that $\dfrac{n_i}{g_i} = \dfrac{1}{e^{(\varepsilon_i-\mu)/kT}+1}$ for $i=1,2,\ldots$

are the optimal way to fill fermions into s.p. states, i.e. this way will maximize the microstate number W and $\ln W(\{n_i\})$

i.e.

$$S = k \ln\left[W\{n_i^{\text{optimal}}\}\right]$$

from which we can construct $F = E - TS$, $-pV = E - TS - \mu N$, etc. for an Ideal Fermi Gas (see later section)

Physics of Metals (how electrons contribute to electric current, heat capacity) all follows from Eq.(14)

Physics of degenerate pressure (opposing gravitational pull in stars and dying stars) all follows from Eq.(14)

Information on systems, e.g. 1D wire, 2D electron gas, 3D piece of metal, neutron stars is embedded in $g(\varepsilon)$

E. The Bose-Einstein Distribution

Stirling approximation

Maximize $\ln W_{BE}(\{n_i\}) = \ln\left[\prod_i \frac{(g_i+n_i)!}{g_i!\, n_i!}\right] \overset{\downarrow}{\approx} \sum_i \left[(g_i+n_i)\ln(g_i+n_i) - n_i \ln n_i - g_i \ln g_i\right]$

Preparing for Eq.(6):

$$\frac{\partial \ln W_{BE}(\{n_i\})}{\partial n_j} = \ln(g_j+n_j) + 1 - \ln n_j - 1 = \ln\left(\frac{g_j+n_j}{n_j}\right)$$

one of n_i's

Constraint #1 : $\sum_i n_i = N$ → introduce multiplier α

→ $\frac{\partial}{\partial n_j}\left(\sum_i n_i\right) = 1$

Constraint #2 : $\sum_i \varepsilon_i n_i = E$ → introduce multiplier β

→ $\frac{\partial}{\partial n_j}\left(\sum_i \varepsilon_i n_i\right) = \varepsilon_j$

Applying Method of Lagrange Multipliers, optimal distribution satisfies

$$\ln\left(\frac{g_i+n_i}{n_i}\right) - \alpha - \beta\varepsilon_i = 0\,, \quad i=1,\cdots,n \qquad \text{(plus the two constraints)} \qquad (15)$$

$$\boxed{n_i = g_i \cdot \frac{1}{e^{\alpha} e^{\beta \varepsilon_i} - 1}} \quad (16) \qquad \text{OR} \qquad \boxed{\underbrace{\frac{n_i}{g_i}} = \frac{1}{e^{\alpha} e^{\beta \varepsilon_i} - 1}} \quad (17)$$

meaning is number of bosons PER s.p. state of energy ε_i

Claiming $\beta = 1/kT$, $\alpha = -\mu/kT$

$$n_i = g_i \cdot \underbrace{\frac{1}{e^{(\varepsilon_i - \mu)/kT} - 1}} \qquad (18) \qquad \text{[Key Result]}$$

n_i: # bosons in s.p. states of energy ε_i

g_i: # s.p. states with energy ε_i

bosons PER s.p. state of energy ε_i when system is in equilibrium at temp. T and chemical potential μ.

Taking energy ε_i as continuous

$$\boxed{f_{BE}(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/kT} - 1}} \qquad (19)$$

is the Bose-Einstein Distribution

always remember its meaning! It is # bosons per s.p. state of energy ε
[if there is/are s.p. state(s) at that energy (given by $g(\varepsilon)$)

Taking energy as continuous, Eq. (16) becomes

$$\underbrace{n(\varepsilon)\,d\varepsilon}_{\substack{\text{\# Bosons}\\ \text{with energy in}\\ \text{interval } \varepsilon \to \varepsilon+d\varepsilon}} = g(\varepsilon)\, f_{BE}(\varepsilon)\, d\varepsilon \qquad (20)$$

\# bosons PER s.p. state

\# s.p. states in interval $\varepsilon \to \varepsilon + d\varepsilon$

It follows that (from the constraints):

$$\boxed{\int_0^\infty \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/kT}-1}\, d\varepsilon = N \quad ; \quad \int_0^\infty \frac{\varepsilon\, g(\varepsilon)}{e^{(\varepsilon-\mu)/kT}-1}\, d\varepsilon = E} \qquad (21)$$

These are the key equations for study Ideal Bose Gas!

We need the information $\underbrace{g(\varepsilon)}_{\text{density of s.p. states}}$ to proceed.

Pause: What have we done?

We found that $\dfrac{n_i}{g_i} = \dfrac{1}{e^{(\varepsilon_i-\mu)/kT} - 1}$ for $i = 1, 2, \ldots$

are the optimal way to fill Bosons into s.p. states, i.e. this way will maximize the microstate number W and

$$\ln W(\{n_i\})$$

i.e.

$$S = k \ln\left[W\{n_i^{\text{optimal}}\}\right]$$

from which we can construct $F = E - TS$, $-pV = E - TS - \mu N$, etc. for an Ideal Bose Gas

Physics of Bose-Einstein Condensation

["cooling" bosons to $\sim 10^{-8}$ K range]

Liquid (superfluid) helium

Gas of phonons [collection of oscillators in solids]

Gas of photons [thermal radiation]

⋮

All follow from Eq. (21)

Again, we need information on $g(\varepsilon)$ to proceed.