Part IV

- Quick set up of Equations for
  - ideal Fermi/Bose gas
- Most probable distribution
  - Fermi-Dirac distribution for fermions
  - Bose-Einstein distribution for bosons
  - Physical meaning of these "distributions"
- Mathematical Skill
  - Method of undetermined Lagrange multipliers

Background: See Ch. III for the most probable distribution and why it is important.

VII. Single-Particle States, The Most Probable Distribution, and all that

$$Z = \sum_{\text{all states } i} e^{-\beta E_i} = Z(T,V,N)$$

[general, good for interacting and non-interacting particles]

- for systems with non-interacting particles,

calculating $Z \Rightarrow$ calculating z ("easier") (exactly solvable) $\rightarrow$ [But could be hard to do the sum over states!]

Interacting: $\hat{H}_N \psi_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = E\, \psi_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$

A. Single-Particle States

Non-interacting or weakly interacting:

- 2-step process

$$\hat{H}_N = \sum_{i=1}^{N} \hat{h}_i$$

$\hat{h}_i$ ← single-particle Hamiltonian

$$\hat{h}_i = \frac{\hat{p}^2}{2m} + V(\vec{r}_i)$$

one-body potential energy function

non-interacting "=" equal

weakly interacting "≈" approximation

Step 1

Solve: $\hat{h}_i \psi(\vec{r}_i) = \varepsilon\, \psi(\vec{r}_i)$

energy of single-particle states

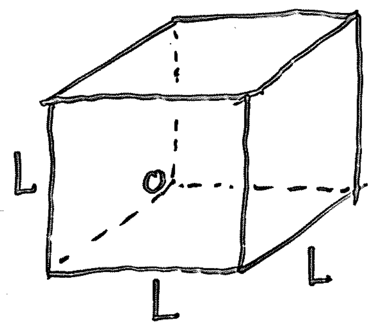
"single-particle states"

A single-particle QM problem.

e.g. Gas

- Each atom is a particle-in-a-BIG-box problem

[Formally, it can be treated quantum mechanically.]



$V = L^3$

N non- (or weakly)- interacting particles

then each particle is confined in a big box

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = \varepsilon\,\psi(x,y,z) \quad \text{inside box}$$

Boundary conditions are: $\psi(0,y,z) = \psi(L,y,z) = 0$

$\psi(x,0,z) = \psi(x,L,z) = 0$

$\psi(x,y,0) = \psi(x,y,L) = 0$

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

$$= \sqrt{\frac{8}{V}}\,\sin(k_x x)\,\sin(k_y y)\,\sin(k_z z)$$

$n_x = 1, 2, 3, \cdots$, $n_y = 1, 2, 3, \cdots$, $n_z = 1, 2, 3, \cdots$

Energy of single-particle states:

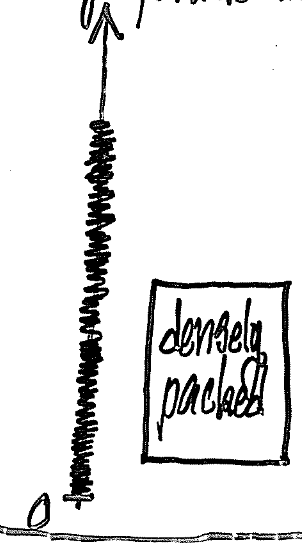
$$\epsilon(n_x, n_y, n_z) = \frac{\pi^2\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

OR $\epsilon(k_x, k_y, k_z) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}$

single-particle energies

For macroscopic systems, $L \sim$ cm,

- ϵ are densely populated on the energy axis
- degeneracy increases with ϵ



Often, a continuum description using a density of states $g(\epsilon)$ of single-particle states is useful.

Step 2

- Fill the N particles into the single-particle states according to some rules

e.g. Pauli Exclusion principle: Fermions

No restriction: Bosons

Slight chance of occupying a state: "Classical Particles"

Note: Atoms, molecules, solids are treated also in this way.

B. The most probable distribution of single-particle states

- Recall (in Ch. III) we considered the problem of distributing N (distinguishable) particles into single-particle states for a given (fixed) total energy E. This is the microcanonical ensemble problem, i.e., dealing with an isolated system of fixed (E, N, V).

- $$W(E,N,V) = \#\text{ accessible microstates} = \sum_{\text{distributions}} W(\text{distribution})$$

- In equilibrium, all W(E,N,V) states are equally probable.

- $S = k \ln W$

- S is a maximum in equilibrium

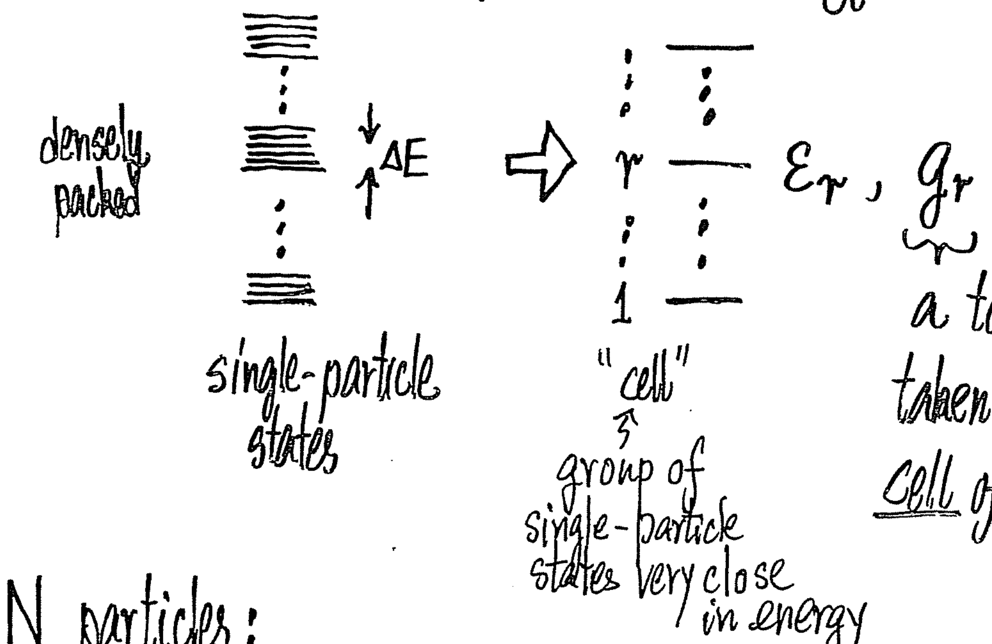
- Macroscopic system, W is huge!

- Most probable distribution

$$\{\underset{\varepsilon_1}{\overset{\downarrow}{n_1}},\ \underset{\varepsilon_2}{\overset{\downarrow}{n_2}},\ \underset{\varepsilon_3}{\overset{\downarrow}{n_3}}, \cdots\} \text{ such that } W(\{n_1, n_2, n_3, \cdots\}) \text{ is largest}$$

Question: Solve for the most probable distribution†

As discussed, single-particle states are often densely packed. We divide the allowed single-particle energies (including degeneracy) into CELLS of nearly the same energy.



a total of g_r states taken to be in the cell of energy ε_r

- N particles:

$$\{n_1, n_2, n_3, \cdots\}$$
$$\downarrow \quad \downarrow \quad \downarrow$$
in cell 1, cell 2, cell 3, ⋯

- What is the set $\{n_1, n_2, n_3, \cdots\}$ that gives the largest W?

[Idea: $W = \sum_{\text{distributions}} W(\text{distribution}) \approx W(\text{most probable distribution})$] and then everything follows!

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† Important to note that we are setting up the problem under the conditions of fixed (E, N, V), i.e. microcanonical ensemble.

If we know the most probable distribution $\{n_i\}_{mp}$, then $W_{mp}(\{n_i\})$ dominates W and

$$S = k \ln W_{mp}(\{n_i\})$$

and everything follows.

The result will depend on the nature of particles

- identical fermions
- identical bosons
- identical "classical particles"

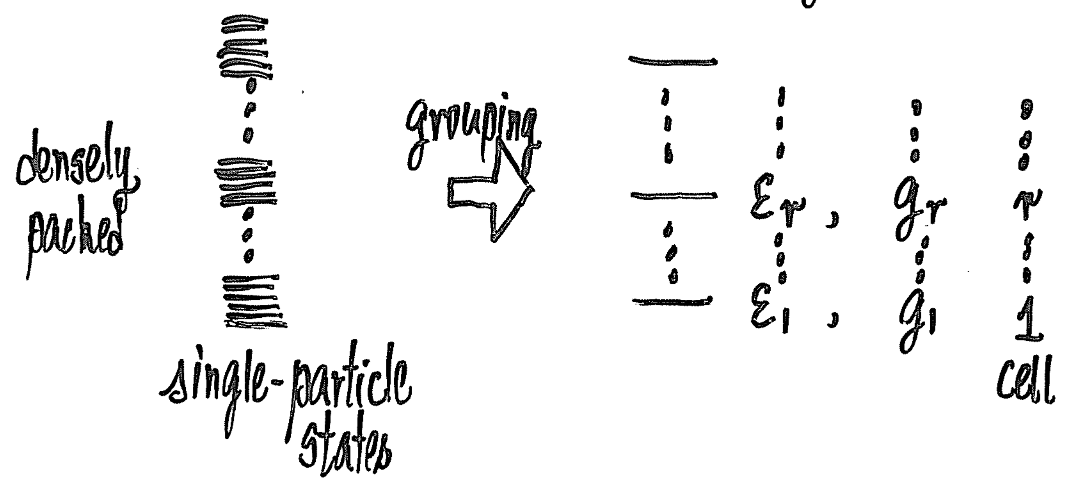
i.e. under situations where the quantum characteristics of particles can be ignored (but what are the situations?)

C. The most probable distribution

– Fermions and the Fermi-Dirac distribution

- What if we do the counting of $W(\{n_r\})$ more carefully?
- Let's jump into quantum statistics

Problem: N (identical, indistinguishable) fermions



- Fermions (Pauli Exclusion Principle)

$\Rightarrow$ $\underbrace{\text{no particle or one particle in each single-particle state}}_{\text{Count } W(\{n_r\}) \text{ including this restriction}}$

Total energy E

What is the most probable distribution?

- N particles:

$$\{n_1, n_2, n_3, \dots\}$$
$$\downarrow \quad \downarrow \quad \downarrow$$
in cell 1, cell 2, cell 3, ...

- What is the set $\{n_1, n_2, n_3, \dots\}$ that gives the largest $W(\{n_i\})$, subjected to

$$\sum_{\text{cells } r} n_r = N = \text{constant}$$

$$\sum_{\text{cells } r} \varepsilon_r n_r = E = \text{constant}$$

and the restriction that one state can only be occupied by one particle?

- Consider the n_r fermions in the cell (or group) r with g_r single-particle states

We have: n_r states with one particle
$(g_r - n_r)$ states with no particle
} Pauli Exclusion principle

$\therefore$ There are g_r objects (states). We want to divide them into two groups: n_r occupied states
$g_r - n_r$ unoccupied states

Number of ways to distribute n_r fermions among g_r states $= \dfrac{g_r!}{n_r!\,(g_r-n_r)!}$

- Repeat the arguments for each cell, the number of microstates $W_{FD}(\{n_r\})$ for a distribution $\{n_r\}$ is:

$$\underbrace{W_{FD}}_{\text{Fermi-Dirac}}(\{n_r\}) = \prod_r \frac{g_r!}{n_r!\,(g_r-n_r)!} \qquad \text{(Key step) (fermions)} \qquad (1)^{+}$$

The mathematical problem is:

$$\boxed{\begin{array}{l} \text{Find } \{n_r\} \text{ that maximizes } \ln W_{FD}(\{n_r\}), \\ \text{under the constraints:} \\ \qquad \sum_r n_r = N = \text{constant} \\ \qquad \sum_r \varepsilon_r n_r = E = \text{constant} \end{array}} \qquad (2)^{+}$$

$$\ln W_{FD} = \sum_r \ln \frac{g_r!}{n_r!\,(g_r-n_r)!} = \sum_r g_r \ln g_r - n_r \ln n_r - (g_r-n_r)\ln(g_r-n_r)$$

(Ex.)

$^{+}$ Note: Eqs. (1) & (2) set up a math. problem for fermions.

Any variations about the most probable distribution vanish.

$$\delta(\ln W_{FD}) = \sum_r \left[-\delta n_r \ln n_r - \delta n_r + \frac{(g_r - n_r)}{g_r - n_r}(+\delta n_r) + \delta n_r \ln(g_r - n_r)\right]$$

$$= \sum_r \ln\left(\frac{g_r - n_r}{n_r}\right)\delta n_r$$

$$\delta(\ln W_{FD}) = 0 \Rightarrow \boxed{\sum_r \ln\left(\frac{g_r - n_r}{n_r}\right)\delta n_r = 0}$$

Constraints:

$$\sum_r \delta n_r = 0 \qquad [\text{multiplier } \alpha]$$

$$\sum_r \varepsilon_r \delta n_r = 0 \qquad [\text{multiplier } \beta]$$

$$\therefore \sum_r \left[\ln\left(\frac{g_r - n_r}{n_r}\right) - \alpha - \beta\varepsilon_r\right]\delta n_r = 0 \quad (*)$$

[Go to Math. Aside on Lagrange multipliers]

Following the arguments of the method of Lagrange multipliers,

$$\ln\left(\frac{g_r - n_r}{n_r}\right) - \alpha - \beta\varepsilon_r = 0$$

$$\Rightarrow n_r = g_r \cdot \frac{1}{e^{\alpha}e^{\beta\varepsilon_r} + 1}$$

$$\Rightarrow \boxed{\frac{n_r}{g_r} = \frac{1}{e^{\alpha}e^{\beta\varepsilon_r} + 1}}$$

Math. Aside: Standard Arguments of Lagrange Multipliers

We arrived at:

$$\sum_r \left[\ln\left(\frac{g_r - n_r}{n_r}\right) - \alpha - \beta\varepsilon_r\right]\delta n_r = 0 \qquad (M0)$$

1/. It is tempting to jump to the conclusion that

$$\ln\left(\frac{g_r - n_r}{n_r}\right) - \alpha - \beta\varepsilon_r = 0 \text{ for all cells } r, \qquad (M1)$$

But don't jump too fast!

Eqs.(M1) are true if δn_r (different r) are independent of each other. Are they?

2/. Recall: Two constraints

$$\sum_r n_r = N \Rightarrow \sum_r \delta n_r = 0 \Rightarrow \delta n_1 + \delta n_2 + \delta n_3 + \cdots = 0 \qquad (M2)$$

Eq.(M2) says δn_r's are related. They are not independent!

For example, we can express

$$\underbrace{\delta n_1 + \delta n_2 = -\delta n_3 - \delta n_4 - \cdots}_{\delta n_1,\ \delta n_2 \text{ expressed in terms of other } \delta n_r\text{'s}} \qquad (M2')$$

$$\sum_r \varepsilon_r n_r = E \Rightarrow \sum_r \varepsilon_r \delta n_r = 0$$

$$\Rightarrow \varepsilon_1 \delta n_1 + \varepsilon_2 \delta n_2 + \varepsilon_3 \delta n_3 + \varepsilon_4 \delta n_4 + \cdots = 0 \quad (M3)$$

Eq. (M3) says δn_r's <u>are related</u>, thus <u>not independent</u>!

For example, we can express

$$\varepsilon_1 \delta n_1 + \varepsilon_2 \delta n_2 = -\varepsilon_3 \delta n_3 - \varepsilon_4 \delta n_4 - \cdots \quad (M3')$$

3/. Each constraint gives a relation among δn_r's similar to Eq. (M2') and Eq. (M3')

Now, with <u>two constraints</u>, Eq. (M2') & Eq. (M3') imply <u>two δn's are not independent</u> of the other δn's.

<u>E.g.</u> Solving Eq. (M2') & Eq. (M3') for δn_1 and δn_2 in terms of $\delta n_3, \delta n_4, \cdots$.

4/. Thus, we may take $\{\delta n_3, \delta n_4, \cdots\}$ to be <u>independent variables</u>. From Eq. (M0), we have

$$\ln\left(\frac{g_r - n_r}{n_r}\right) - \alpha - \beta\varepsilon_r = 0 \quad \text{for } r = 3, 4, \cdots \quad (M4)$$

because $\delta n_3, \delta n_4, \cdots$ are independent.

5/. How about the remaining two terms in Eq. (M0)?

$$\underbrace{\left[\ln\left(\frac{g_1 - n_1}{n_1}\right) - \alpha - \beta\varepsilon_1\right]}\delta n_1 + \underbrace{\left[\ln\left(\frac{g_2 - n_2}{n_2}\right) - \alpha - \beta\varepsilon_2\right]}\delta n_2 = 0$$

We can choose α and β (the two Lagrange multipliers) to <u>make</u> these two pre-factors zero!

Thus,

$$\left.\begin{aligned} \ln\left(\frac{g_1 - n_1}{n_1}\right) - \alpha - \beta\varepsilon_1 &= 0 \\ \ln\left(\frac{g_2 - n_2}{n_2}\right) - \alpha - \beta\varepsilon_2 &= 0 \end{aligned}\right\} \quad (M5)$$

by use of Lagrange multipliers α and β

6/. Putting Eqs. (M4) and (M5) together, we have

$$\boxed{\ln\left(\frac{g_r - n_r}{n_r}\right) - \alpha - \beta\varepsilon_r = 0 \quad \text{for all } r \quad (r = 1, 2, 3, 4, \cdots)} \quad (M6)$$

which are the <u>equations (M1)</u> that we wanted to jump into!
[this is a set of equations]

7/. See, α and β are introduced to handle the constraints, i.e., they can be fixed by the constraints.

Done! Return to (*) on p. VII-10. See Appendix for Recipe.

After going through the derivation, we have

$$\frac{n_i}{g_i} = f_i = \frac{1}{e^{\alpha} e^{\beta \varepsilon_i} + 1}$$

Formally, α is determined by $\sum_i n_i = N$

β is determined by $\sum_i n_i \varepsilon_i = E$

[After making contact with thermodynamics, it can be shown that $\beta = \frac{1}{kT}$, $\alpha = -\frac{\mu}{kT}$]

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

$$= \underbrace{g_i}_{\substack{\#\text{ states} \\ \text{with energy } \varepsilon_i}} \underbrace{\left(\frac{1}{e^{(\varepsilon_i - \mu)/kT} + 1} \right)}_{\#\text{ particles per state of energy } \varepsilon_i}$$

$\therefore$ general and useful

does not depend on confining potential

(depends on the confining potential, e.g. box size, harmonic trap, etc)

Taking ε_i as continuous:

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

- Fermi-Dirac distribution function

[governs the electrons in a metal, the neutrons in a neutron star, etc.]

fermions

Key concept: Physical meaning of $f_{FD}(\varepsilon)$

$$f_{FD}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \quad \text{Fermi-Dirac "distribution"}$$

was obtained as $\frac{n_i}{g_i}$ for the cell with single-particle states of energy ε.

Key concept →

$$\boxed{\text{Thus, it is \underline{the number of fermion per single-particle state at the energy } \varepsilon}.}$$

$$\underset{\substack{\#\text{ fermions} \\ \text{at energy } \varepsilon_i}}{n_i} = \underbrace{g_i}_{\substack{\#\text{ single-particle} \\ \text{state at energy } \varepsilon_i}} \underbrace{\left(\frac{1}{e^{\frac{(\varepsilon_i - \mu)}{kT}} + 1} \right)}_{f_{FD}(\varepsilon_i)}$$

[could be large, could be zero, i.e. no s.p. state at ε_i]

Since $f_{FD}(\varepsilon)$ is less than OR equal to 1, it is often referred to as "the probability" of finding a fermion at a state of energy ε. But this interpretation is true only for fermions. Use it with great care!

D. The most probable distribution

– Bosons and the Bose-Einstein distribution

- Same problem as for fermions
- Bosons : No restriction on number of particles in each single-particle state

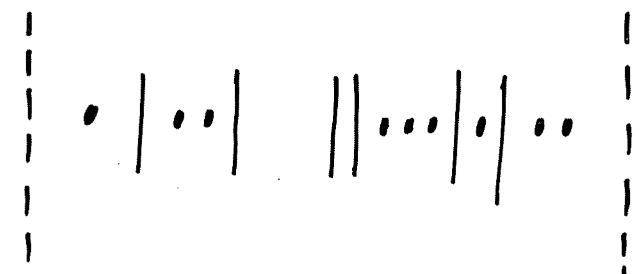
Consider :

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

$$\begin{array}{llll} & \downarrow & \downarrow & & \downarrow \\ \text{cell/group} & \varepsilon_1, & \varepsilon_2, & \cdots, & \varepsilon_i, \cdots \\ \text{\# states in cell} & g_1, & g_2, & \cdots, & g_i, \cdots \end{array}$$

Q: Consider group/cell i. What is the number of ways to distribute n_i identical particles into the g_i states, with no restriction on the occupancy of each state?

Consider $(g_i - 1)$ lines and n_i balls. Count the ways that these $n_i + (g_i - 1)$ objects can be arranged.



$(g_i - 1)$ lines divide the n_i balls into g_i partitions

Number of ways to distribute† the particles in cell i

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

The same argument works for every cell of states.

– Given a distribution $\{n_i\}$, the number of microstates

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

Bose-Einstein

product is over all the cells/groups i

– Total number of particle N

$$\therefore \sum_i n_i = N$$

Total energy E

$$\therefore \sum_i n_i \varepsilon_i = E$$

constraints

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† This is the same as how many ways $(n_i + g_i - 1)$ symbols can be arranged into n_i balls and $(g_i - 1)$ lines.

The mathematical problem of finding the Bose-Einstein distribution amounts to finding $\{n_i\}$ that maximizes $\ln W_{BE}$ subjected to the constraints

$$\sum_i n_i = N \ , \ \sum_i n_i \varepsilon_i = E$$

$$\ln W_{BE} = \ln \prod_i \frac{(g_i+n_i)!}{g_i!\, n_i!}$$

$$= \sum_i \left[\ln(g_i+n_i)! - \ln g_i! - \ln n_i!\right]$$

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

$$\delta \ln W_{BE} = 0 \Rightarrow \sum_i \ln\left(\frac{g_i+n_i}{n_i}\right)\delta n_i = 0 \qquad \text{(Ex.)}$$

<u>Constraints</u>: $\sum_i n_i = N = \text{constant} \Rightarrow \sum_i \delta n_i = 0$

$\sum_i \varepsilon_i n_i = E = \text{constant} \Rightarrow \sum_i \varepsilon_i \delta n_i = 0$

Introduce two multiplers, we have

$$\sum_i \left(\ln\left(\frac{g_i+n_i}{n_i}\right) - \alpha - \beta\varepsilon_i\right)\delta n_i = 0$$

The argument behind the method of Lagrange multiplers allows us to write:

$$\ln\frac{g_i+n_i}{n_i} - \alpha - \beta\varepsilon_i = 0$$

$$\Rightarrow \frac{n_i}{g_i} = \frac{1}{e^{\alpha}e^{\beta\varepsilon_i} - 1} \equiv f_i$$

equilibrium occupation per state of energy ε_i

Formally, α is fixed by $\sum_i n_i = N$

β is fixed by $\sum_i n_i\varepsilon_i = E$

[After making contact with thermodynamics, $\beta = \frac{1}{kT}$, $\alpha = -\frac{\mu}{kT}$]

$$n_i = g_i \left(\underbrace{\frac{1}{e^{(\varepsilon_i-\mu)/kT} - 1}}_{\#\text{ particles per state of energy } \varepsilon_i}\right)$$

general and useful

states with energy ε_i (depends on confining potential)

Taking ε_i as continuous:

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

- Bose-Einstein distribution function

[governs liquid ^{4}He, gas of ultracold atoms]

Key concepts: Physical Meaning of $f_{BE}(\varepsilon)$

$$f_{BE}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}-1} \qquad \text{Bose-Einstein "distribution"}$$

was obtained as $\frac{n_i}{g_i}$ for the cell with single-particle states of energy ε.

Key concept

$\boxed{\text{Thus, it is the number of bosons per single-particle state at the energy } \varepsilon.}$

This number can be bigger than 1 for some states
[Don't interpret it as a probability]

$\boxed{\text{This number} \geq 0 \text{ for all single-particle state}}$

($\because$ it is "number of bosons", can't have negative number of bosons)

The reason for Bose-Einstein condensation in Bose gas.