PH-107

Quantum Physics and Applications

Elements of Statistical Physics-II

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Recap

Number of particles between *E* and *E+dE*

Depends on the product ***g(E)f(E)dE,*** which gives ***dN(E)***.

We have written the number of available energy states within the interval ***E*** and ***E+dE*** in terms of the **density of states**, ***g(E)***.

And the probability of a particle occupying an available state in the interval ***E*** and ***E+dE*** is expressed in terms of the **probability distribution function**, ***f(E)***.

***f(E)*: Dependence on Particle Characteristics**

Equilibrium Configuration

The general problem we are trying to solve is, given a system with

$$\sum_{i=1}^{\infty} N_i = N$$

$$\sum_{i=1}^{\infty} E_i N_i = E$$

What is the configuration $\{N_i\} \equiv (N_1, N_2, \ldots N_i \ldots)$ for which the multiplicity $Q(\{N_i\})$ is maximum?

For this, we have to first learn how to calculate $Q(\{N_i\})$.

Classical Particles (M-B)

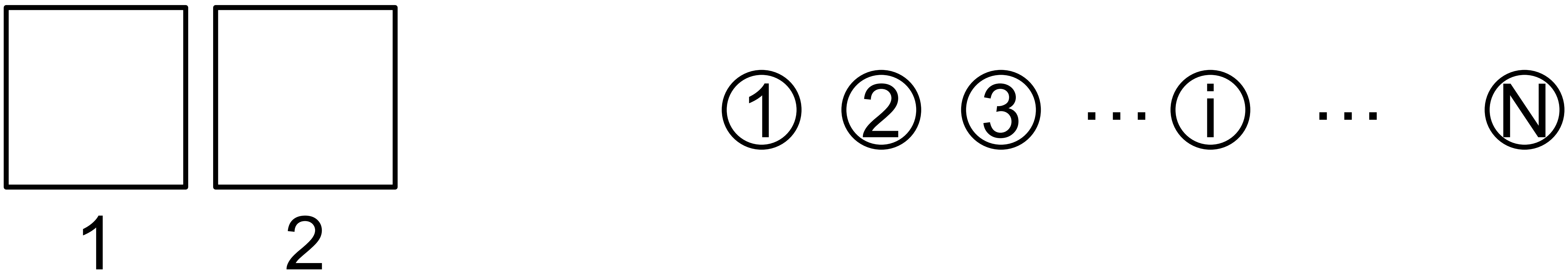
How difficult is the problem?

Let’s start by assuming that i = 2, with $g_i = 1$ for both states, and N total number of particles.

i.e., we are considering a system with two (non-degenerate) energy states (E_1 and E_2), in which N particles have to be distributed, such that $N_1+N_2 = N$ and $E_1\, N_1+E_2\, N_2 = E$

This problem is similar to distributing N **“numbered billiard balls”** in 2 **“numbered”** containers.

Classical Particles (M-B)



Let us calculate a few $Q(N_1, N_2)$ values.

What is $Q(N_1 = 0 , N_2 = N)$?

Ans: 1 (There's only one way of putting no ball in container 1 and all balls in container 2)

What is $Q(N_1 = 1 , N_2 = N\text{-}1)$?

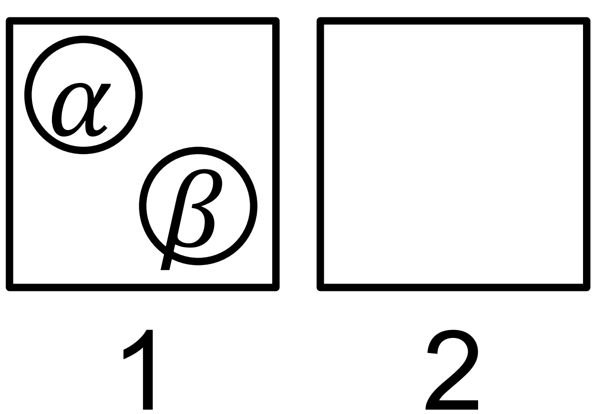
Ans: N (There are N ways of putting 1 ball in container 1 and the rest N-1 in container 2)

Classical Particles (M-B)

What is $Q(N_1 = 2 \,,\, N_2 = N\text{-}2\,)$?

Ans: $$\binom{N}{2} = \frac{N(N-1)}{2!}$$

(There's N choices for the 1st ball in the 1st container, and for each of them, N-1 choices for the 2nd ball in the 1st container)



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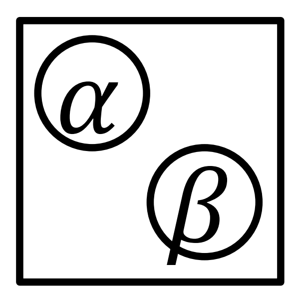
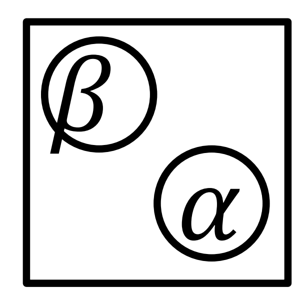
But we don't want to count 

and 

as two different cases. So, we divide by 2!

Classical Particles (M-B)

Likewise, for $Q(N_1 = 3\ ,\ N_2\ = N\text{-}3)$

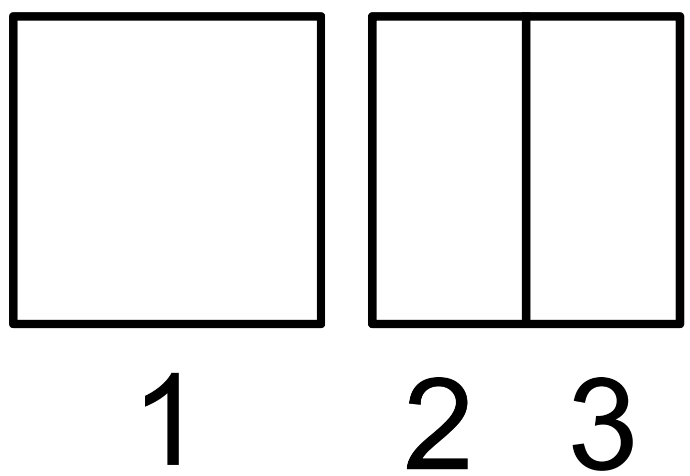
Ans: $$\binom{N}{3} = \frac{N(N-1)(N-2)}{3!}$$

So, for $Q(N_1 = N_1\ ,\ N_2\ = N\text{-}N_1)$

Ans: $$\binom{N}{N_1} = \frac{N(N-1)(N-2)....(N-N_1+1)}{N_1!} = \frac{N!}{N_1!N_2!}$$

Classical Particles (M-B)

Now we divide the 2nd container into two halves.



So that $N_2 = \nu_1 + \nu_2$

The number of ways of realizing the configuration (ν_1, ν_2) within the sub-compartments of the 2nd container is

$$Q(\nu_1, \nu_2) = \frac{N_2!}{\nu_1!\nu_2!}$$

Classical Particles (M-B)

But we could also consider this as 3 containers with N_1, ν_1, ν_2 balls,

such that

$$Q(N_1, \nu_1, \nu_2) = \frac{N!}{N_1! N_2!} \frac{N_2!}{\nu_1! \nu_2!}$$

Relabeling properly we get

$$Q(N_1, N_2, N_3) = \frac{N!}{N_1! N_2! N_3!}$$

So $$Q(N_1, N_2, ...N_i....) = Q(\{N_i\}) = \frac{N!}{\prod_i N_i!}$$

Recall that we did not consider degeneracy of the states *i*.

Classical Particles (M-B)

If we consider the state i (with energy E_i) to be g_i-fold degenerate, we need to consider a group of g_i containers (all labeled i) to distribute the N_i billiard balls.

N_i balls can be distributed in g_i copies of the container labeled i in $(g_i)^{N_i}$ ways. The first of the N_i balls can be placed in any of the g_i containers, and so can be the 2nd, 3rd, 4th, and so on…

Same holds true for distribution of N_j balls in g_j copies of the container labeled j.

Classical Particles (M-B)

So

$$Q(N_1, N_2, ...N_i....) = Q(\{N_i\}) = \frac{N!}{\prod_i N_i!} \prod_i (g_i)^{N_i}$$

So, our job now simplifies to maximizing $\displaystyle \frac{N!}{\prod_i N_i!} \prod_i (g_i)^{N_i}$

obeying the constraints $\displaystyle \sum_{i=1}^{\infty} N_i = N$ and $\displaystyle \sum_{i=1}^{\infty} E_i N_i = E$

This is done by a cumbersome mathematical technique called the method of **Lagrangean multipliers**.

Classical Particles (M-B)

It gives the condition for $Q(\{N_i\})$ to be maximized that

$$\frac{N_i}{g_i} = e^{\alpha} e^{-\beta E_i}$$

where α and β are constants to be determined.

Later, we will see that $\beta = (k_B T)^{-1}$, so that

$$N_i = g_i \; e^{\alpha} e^{-\frac{E_i}{k_B T}}$$

This equation represents the **Maxwell-Boltzmann distribution function** $f_{MB}(E_i)$.

Classical Particles (M-B)

$$\sum_{i=1}^{\infty} N_i = N \qquad \Longrightarrow \sum_{i=1}^{\infty} g_i \; e^{\alpha} e^{-\beta E_i} = N$$

$$\Longrightarrow e^{\alpha} = \frac{N}{\sum_{i=1}^{\infty} g_i \; e^{-\beta E_i}}$$

So

$$N_i = \frac{N g_i \; e^{-\beta E_i}}{\sum_{i=1}^{\infty} g_i \; e^{-\beta E_i}}$$

Or, the probability of finding the particle in state *i*

$$P_i = \frac{N_i}{N} = \frac{g_i \; e^{-\beta E_i}}{\sum_{i=1}^{\infty} g_i \; e^{-\beta E_i}}$$

Classical Particles (M-B)

With $P_i = \dfrac{N_i}{N} = \dfrac{g_i \ e^{-\beta E_i}}{\sum_{i=1}^{\infty} g_i \ e^{-\beta E_i}}$ the mean energy can be calculated as

$$\bar{E} = \sum_i P_i E_i = \frac{\sum_i g_i E_i \ e^{-\beta E_i}}{\sum_i g_i \ e^{-\beta E_i}} = \frac{1}{Z} \sum_i g_i E_i \ e^{-\beta E_i}$$

Here, $Z = \sum_i g_i \ e^{-\beta E_i}$ is called the **partition function**.

You can verify $\bar{E} = -\dfrac{\partial}{\partial \beta}(\ln Z)$

Classical Particles (M-B)

With $P_i = \dfrac{N_i}{N} = \dfrac{g_i \; e^{-\beta E_i}}{\sum_{i=1}^{\infty} g_i \; e^{-\beta E_i}}$ the mean energy can be calculated as

$$\bar{E} = \sum_i P_i E_i = \frac{\sum_i g_i E_i \; e^{-\beta E_i}}{\sum_i g_i \; e^{-\beta E_i}} = \frac{1}{Z} \sum_i g_i E_i \; e^{-\beta E_i}$$

Here, $Z = \sum_i g_i \; e^{-\beta E_i}$ is called the **partition function**.

For any other parameter

$$\bar{y} = \sum_i P_i y_i = \frac{\sum_i g_i \; y_i \; e^{-\beta E_i}}{\sum_i g_i \; e^{-\beta E_i}}$$

Maxwell-Boltzmann Distribution

Let us write $e^{\alpha} = A,$ then we can see that

$$N = \sum_{i=1}^{\infty} N_i = \sum_{i=1}^{\infty} g_i \; A \; e^{-\frac{E_i}{k_B T}}$$

In the continuum limit,

$$\sum N_i \rightarrow \int dN(E) = \int g(E) \; f_{\mathrm{MB}}(E) \; dE$$

$$f_{\mathrm{MB}}(E) = A \; e^{-\frac{E}{k_B T}}$$

with $$A = e^{\alpha} = \frac{N}{\int g(E) \; e^{-\frac{E}{k_B T}} \; dE}$$

Maxwell-Boltzmann Distribution

The energy of **point particles** of an **ideal** gas is purely translational kinetic energy, i.e. the energy of each molecule is of the form

$$E = \frac{1}{2}mv^2$$

Since the speeds of the gas particles vary continuously from 0 to ∞, the energy must also vary continuously from 0 to ∞.

Thus we can use the MB distribution to write

$$dN(E) = N(E)dE = g(E)\ A\ e^{-(\frac{1}{2}mv^2/k_BT)}\ dE$$

What is **Lagrangean multipliers** and why it is needed?

Quantum Distribution Function

Fermi-Dirac Distribution

$Q(\{N_i\})$ for Fermions

If the particles become indistinguishable (Quantum particles), the numbering of the billiard balls is gone!

In case of Fermions, the further restriction of occupancy of each state by ***only one particle*** has to be obeyed.

So, unlike for distinguishable particles where

$$Q(N_1, N_2, ...N_i....) = Q(\{N_i\}) = \frac{N!}{\prod_i N_i!}$$

For Fermions: $Q(N_1, N_2, ..., N_i..) = Q(\{N_i\}) = 1$

However, the state with energy E_i can still have degeneracy g_i

Fermi-Dirac Distribution

$Q(\{N_i\})$ for Fermions

State Index (i)	State Energy (E_i)	State Degeneracy (g_i)	State Occupancy (N_i)
1	E_1	g_1	N_1
2	E_2	g_2	N_2
$\vdots$	$\vdots$	$\vdots$	$\vdots$
i	E_i	g_i	N_i
$\vdots$	$\vdots$	$\vdots$	$\vdots$

But we need to keep in mind that for Fermions, there is a further restriction of occupancy of each state by ***only one particle***

How do we fill g_i states of energy E_i with N_i Fermions?

$$\binom{g_i}{N_i} = \frac{g_i!}{N_i!(g_i - N_i)!}$$

Fermi-Dirac Distribution

$Q(\{N_i\})$ for Fermions

This leads to

$$Q(N_1, N_2, ..., N_i...) = Q(\{N_i\}) = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}$$

Compared with distinguishable (classical) particles

$$Q(N_1, N_2, ..., N_i...) = Q(\{N_i\}) = \frac{N!}{\prod_i N_i!} \prod_i (g_i)^{N_i}$$

the multiplicity of a particular configuration of Fermions is given by

$$Q(N_1, N_2, ..., N_i...) = Q(\{N_i\}) = 1. \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}$$

Fermi-Dirac Distribution

In this case:

$$Q(N_1, N_2, ...N_i...) = Q(\{N_i\}) = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}$$

$$\frac{N_i}{g_i} = \frac{1}{1 + e^{-\alpha + \beta E_i}}$$

Writing $e^{-\alpha} = A$ and noting that $\beta = (k_B T)^{-1}$, we get

$$N_i = \frac{g_i}{1 + A\ e^{\frac{E_i}{k_B T}}}$$

Like in M-B statistics, *A* (or *e*$^{-\alpha}$) can be evaluated from $\sum_{i=1}^{\infty} N_i = N$

Fermi-Dirac Distribution

However, it is customary to write $\alpha = \beta E_F$. So that $e^{-\alpha} = e^{-E_F/k_B T}$

Fermi Energy

In terms of the Fermi energy,

$$N_i = \frac{g_i}{1 + e^{(E_i - E_F)/k_B T}}$$

Again in the continuum limit,

$$\sum_i N_i \rightarrow \int dN(E) = \int g(E) f_{\mathrm{FD}}(E) dE$$

$$f_{\mathrm{FD}}(E) = \frac{1}{1 + e^{(E - E_F)/k_B T}}$$

This is the **Fermi-Dirac distribution** function governing the equilibrium behavior of Fermions (e.g. electrons).

Fermi-Dirac Distribution

Fermi-Dirac Distribution (T=0 and T > 0)

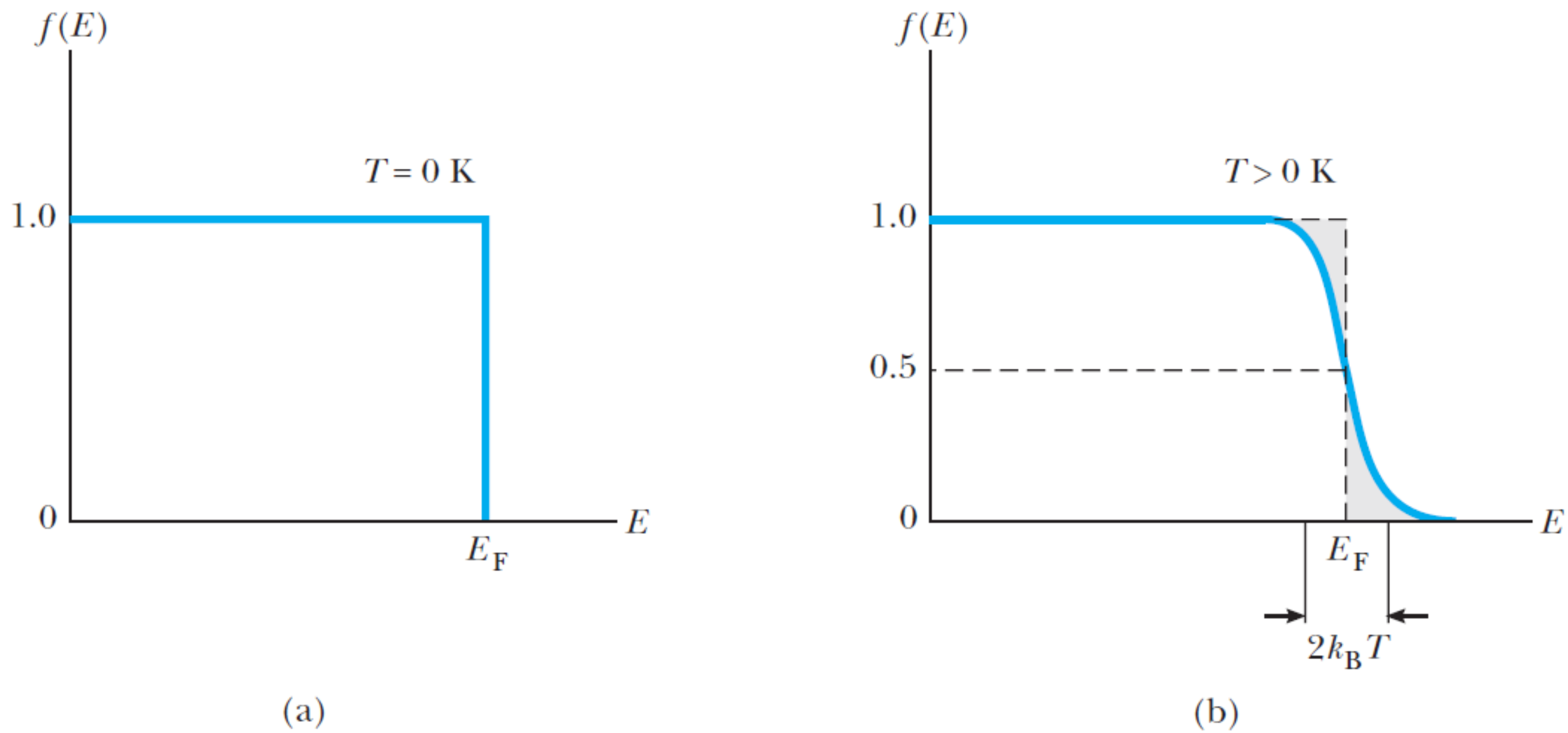


Figure 10.11 A comparison of the Fermi–Dirac distribution functions at (a) absolute zero and (b) finite temperature.

$$f_{\mathrm{FD}}(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}}$$

Bose-Einstein Distribution

$Q(\{N_i\})$ for Bosons

Bosons are indistinguishable but the restriction of occupancy of each state by *only one particle* is gone. A state *i* may be occupied by any number of particles.

$$\underbrace{\overset{1}{\text{ooooo}}\,|\,\overset{2}{\text{ooooo}}\,|\,\ldots\ldots\,|\,\overset{g_i}{\text{ooo}}}_{N_i \text{ particles (in the state with energy } E_i)}$$

In how many ways can we arrange N_i identical balls and g_i-1 partitions?

$$\binom{N_i + g_i - 1}{g_i - 1} = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

Bose-Einstein Distribution

Q({*N*ᵢ }) for Bosons

Bosons are indistinguishable but the restriction of occupancy of each state by *only one particle* is gone. A state *i* may be occupied by any number of particles.

This leads to

$$Q(N_1, N_2, ..., N_i...) = Q(\{N_i\}) = 1. \prod_i \frac{(N_i + g_i - 1)!}{N_i!((g_i - 1)!}$$

Maximization of $Q(\{N_i\})$ finally gives

$$\frac{N_i}{g_i} = \frac{1}{e^{-\alpha + \beta E_i} - 1}$$

Bose-Einstein Distribution

Again in the continuum limit,

$$\sum_i N_i \rightarrow \int N(E)dE = \int g(E)\ f_{\mathrm{BE}}(E)dE$$

$$f_{\mathrm{BE}}(E) = \frac{1}{e^{-\alpha}e^{E/k_BT} - 1} = \frac{1}{Ae^{E/k_BT} - 1}$$

This is the **Bose-Einstein** distribution function governing the equilibrium behavior of Bosons

Bose-Einstein Distribution

$$f_{\mathrm{BE}}(E) = \frac{1}{e^{-\alpha} e^{E/k_B T} - 1} = \frac{1}{A e^{E/k_B T} - 1}$$

Like in previous cases, A (or $e^{-\alpha}$) can be evaluated from $\sum_{i=1}^{\infty} N_i = N$

or in the continuum limit, from

$$N = \int g(E) \, \frac{1}{A \; e^{(E/k_B T)} - 1} dE$$

When the restriction on the number of particles is lifted (photons/ phonons), the Bose-Einstein distribution reads

$$f_{\mathrm{BE}}(E) = \frac{1}{e^{(E/k_B T)} - 1}$$

Also known as the Planckian Equilibrium Distribution

Comparison

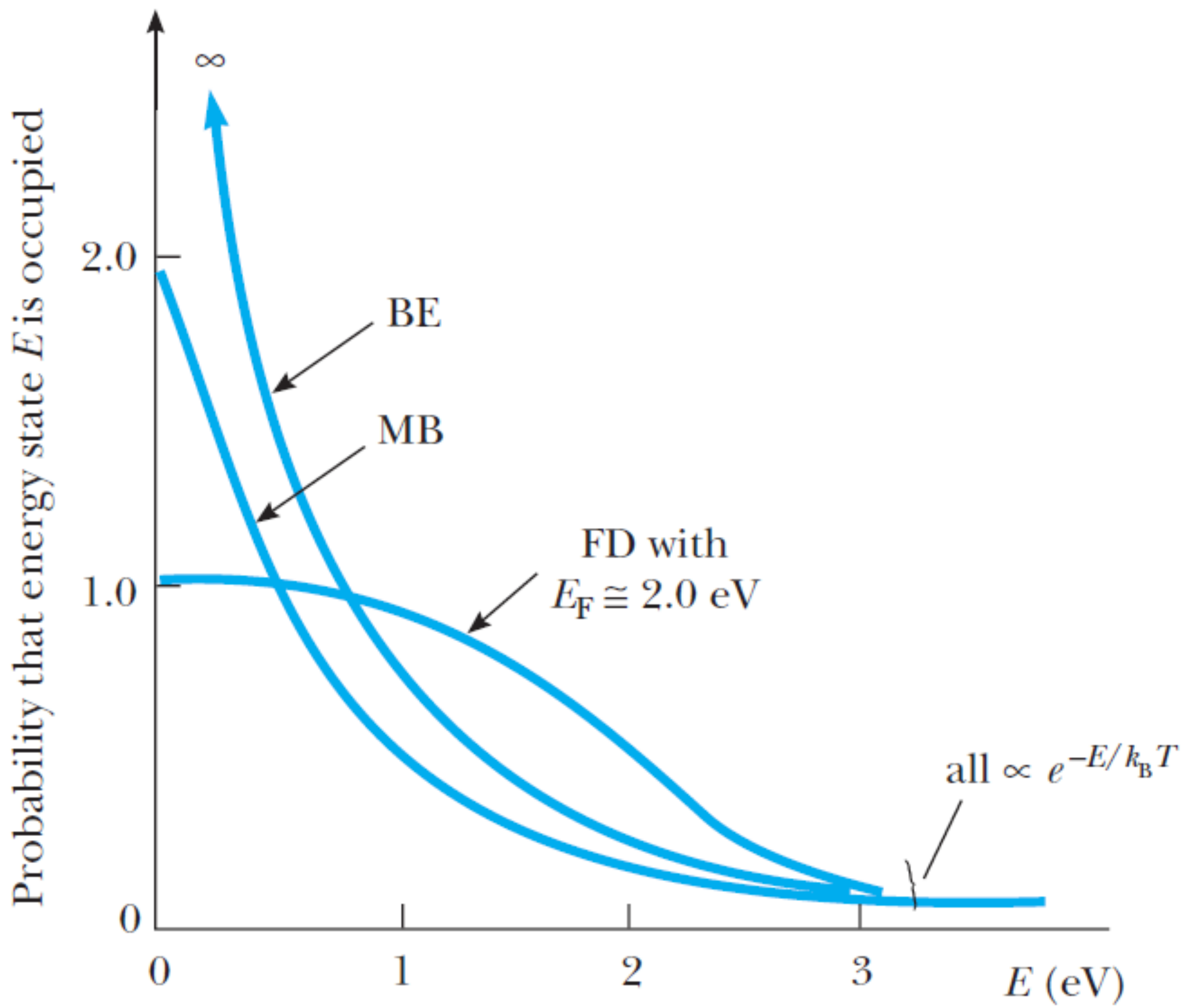


Figure 10.8 A comparison of Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distribution functions at 5000 K.

Recommended Readings

Statistical Physics, Chapter 10