Gibbs sum: distribution function

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The ideal gas is a gas of non-interacting atoms in the limit of low concentration. The thermal average occupancy is called the distribution function:

$$f = f(\varepsilon, T, \mu)$$

where ε is the energy of the orbital.

An orbital is a state of the Schrödinger equation for only one particle. If the interaction between particles are weak, the orbital model allows us to approximate an exact quantum state of the Schrödinger equation of a system of N particles in terms of an approximate quantum state that we construct by assigning the N particles to orbitals, with each orbital a solution of one particle Schrödinger equation.

The orbital model gives an exact solution of the N-particle problem only if there are no interactions between the particles. It is a fundamental result of quantum mechanics that all species of particles fall into two distinct classes, fermions and bosons. Any particle with half-integral spin is a fermion, and any particle with zero or integral spin is a boson.

((**Example**))

An atom of ^{3}He is composed of 2 electrons, 2 protons and 1 neutron – each of spin 1/2, so that ^{3}He is a fermion. An atom of ^{4}He has 2 electrons, 2 protons, and 2 neutrons, so there are even number of particles of spin 1/2, and ^{4}He is a boson.

The result of quantum theory as applied to the orbital model of non-interacting particles, appear as occupancy rules.

(1) An orbital can be occupied by any integral number of bosons of the same species, including zero.
(2) An orbital can be occupied by 0 or 1 fermion of the same species (Pauli exclusion principle).

The two different occupancy rules give rise to different Gibbs sums for each orbital.

There is a boson sum over all integral values of orbital occupancy N, and there is a fermion sum in which $N = 0$ or $N = 1$ only.

Different Gibbs sums lead to different quantum distribution functions $f = f(\varepsilon, T, \mu)$, for the thermal average occupancy.

When $f << 1$, the fermion and boson distribution functions must be similar. This limit is called the classical; regime.

((Summary))

$$\langle N \rangle = z \frac{\partial \ln Z_G}{\partial z}$$

$$Z_G(\mu, T) = \sum_{ASN} z^N \exp[-\frac{\varepsilon_s(N)}{k_B T}]$$

ASN is the abbreviation of all states of the systems for all numbers of particles

(a) Fermion: Fermi-Dirac distribution function

We consider a system composed of a single orbital that may be occupied by a fermion. The system is placed in thermal and diffusive contact with a reservoir. A real system may consist of a large number N_0 of fermions, but it is very helpful to focus on one state and call it the system. All other orbitals of the real system are thought of as the reservoir. An orbital can be occupied by zero or by one fermion. No other occupancy is allowed by the Pauli exclusion principle. The Gibbs sum is

$$\begin{aligned} Z_G &= z^0 + z\exp(-\beta\varepsilon) \\ &= 1 + z\exp(-\beta\varepsilon) \end{aligned}$$

with

$$z = \exp(\beta\mu)$$

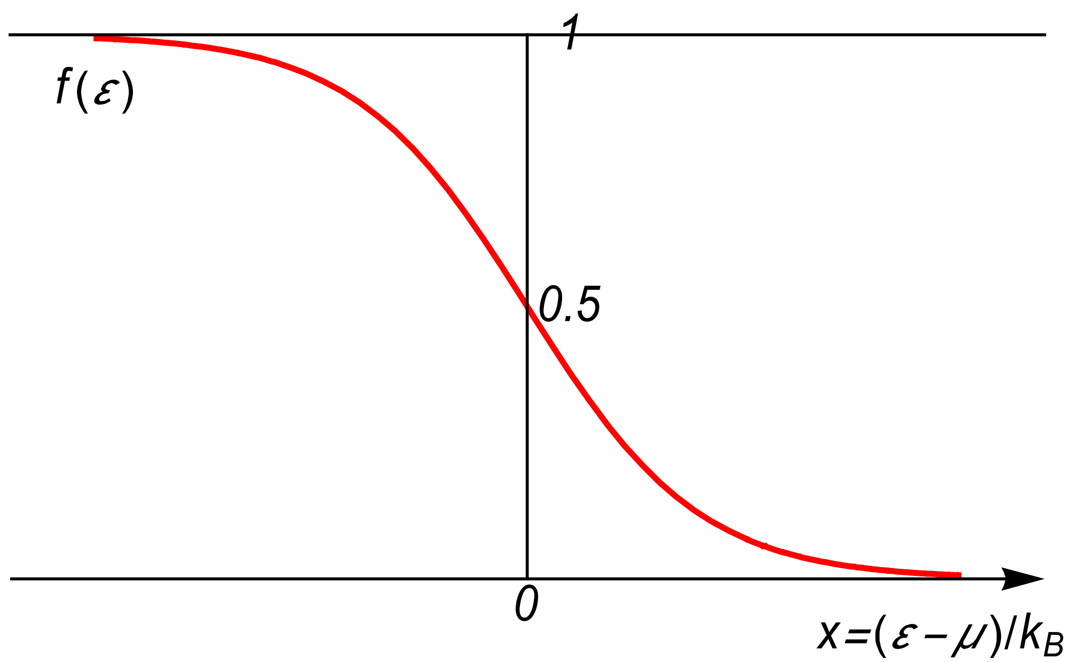
The distribution function is given by

$$
\begin{aligned}
f(\varepsilon) &= z\frac{\partial}{\partial z}\ln Z_G \\
&= z\frac{\partial}{\partial z}\ln(1+ze^{-\beta\varepsilon}) \\
&= z\frac{e^{-\beta\varepsilon}}{1+ze^{-\beta\varepsilon}} \\
&= \frac{1}{\frac{1}{z}e^{\beta\varepsilon}+1} \\
&= \frac{1}{e^{\beta(\varepsilon-\mu)}+1}
\end{aligned}
$$

We introduce for the average occupancy the conventional form $f(\varepsilon)$ that denotes the thermal average number of particles in an orbital energy ε,

$$
f(\varepsilon) = \frac{1}{\exp(\frac{\varepsilon-\mu}{k_B T})+1}
$$

This result is known as the Fermi-Dirac distribution function



The chemical potential μ is often called the Fermi level. μ depends on the temperature T.

$$\mu(T=0) = \mu(0) = \varepsilon_F$$

ε_F is called the Fermi energy.

(i) Unoccupied state

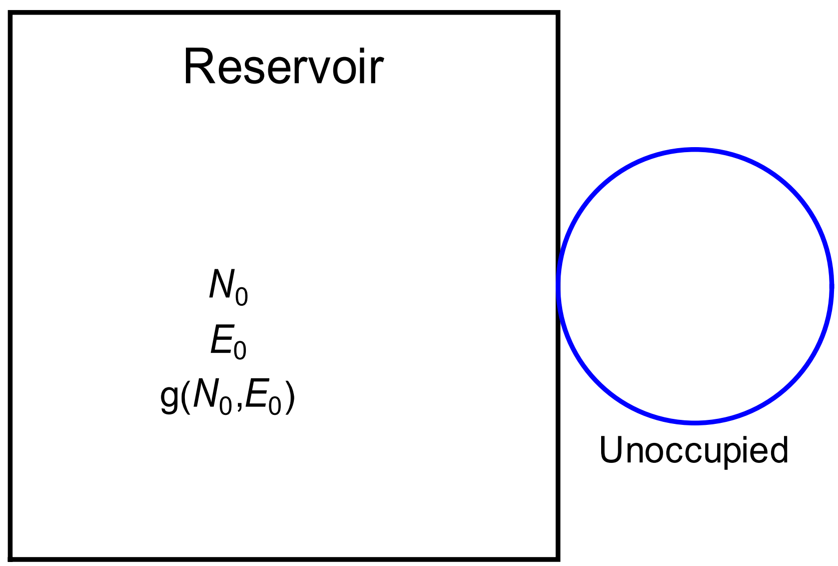


Fig. In the subsystem in the unoccupied state

0	the number of fermion
0	the energy

In the reservoir,

N_0	the number of fermions
E_0	the energy
$g(N_0, E_0)$	the number of states

The entropy is given by

$$S(N_0, E_0) = k_B \ln g(N_0, E_0)$$

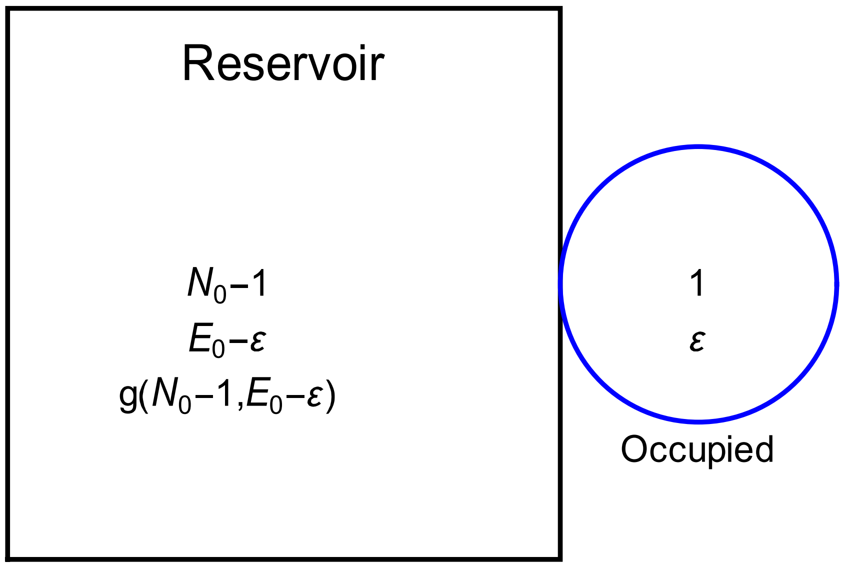
The probability is

$$P(\text{unoccupied}) \propto \exp[\frac{1}{k_B} S(N_0, E_0)]]$$

or

$$P(\text{unoccupied}) = A \ \text{=constant}$$

(ii) The occupied state



In the reservoir,

$N_0 - 1$	the number of fermions
$E_0 - \varepsilon$	the energy

In the subsystem with the occupied state;

1	the number of fermion
ε	the energy

The entropy is given by

$$S(N_0-1,\ E_0-\varepsilon)=k_B\ \ln \mathrm{g}(N_0-1,\ E_0-\varepsilon)$$
$$=S(N_0,E_0)-\frac{\partial S(N_0,E_0)}{\partial N_0}-\frac{\partial S(N_0,E_0)}{\partial E_0}\varepsilon$$
$$=S(N_0,E_0)+\frac{\mu-\varepsilon}{T}$$

The probability is

$$P(\text{occupied})\propto \exp[\frac{1}{k_B}S(N_0-1,\ E_0-\varepsilon)]$$
$$=\exp[\frac{1}{k_B}S(N_0,E_0)]\exp(\frac{\mu-\varepsilon}{k_BT})$$

or

$$P(\text{occupied})=A\exp(\frac{\mu-\varepsilon}{k_BT})=Ae^{\beta(\mu-\varepsilon)}$$

Since $P(\text{occupied})+P(\text{unoccupied})=1$, we have

$$P(\text{occupied})=\frac{Ae^{\beta(\mu-\varepsilon)}}{A+Ae^{\beta(\mu-\varepsilon)}}=\frac{1}{e^{\beta(\varepsilon-\mu)}+1}=f(\varepsilon,\mu)$$

$$P(\text{unoccupied})=1-f(\varepsilon,\mu)$$

(iii) Gibbs sum

The Gibbs sum is given by

$$Z_G(\varepsilon)=\sum_{N=0}^{1}z^N\exp(-\beta N\varepsilon)$$
$$=1+ze^{-\beta\varepsilon}$$

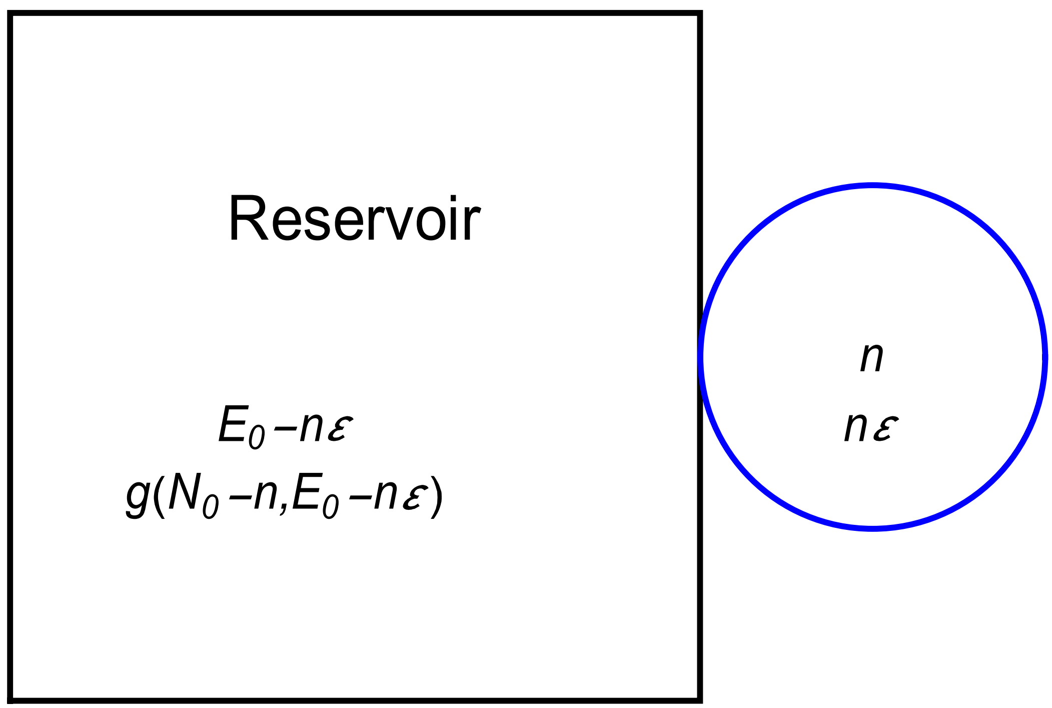
Then we have

$$
\begin{aligned}
n(\varepsilon) &= z\frac{\partial}{\partial z}\ln Z_G(\varepsilon) \\
&= \frac{ze^{-\beta\varepsilon}}{1+ze^{-\beta\varepsilon}} \\
&= \frac{1}{\frac{1}{z}e^{\beta\varepsilon}+1} \\
&= \frac{1}{e^{\beta(\varepsilon-\mu)}+1}
\end{aligned}
$$

This result is known as the Bose-Einstein distribution function

2. Boson: Bose-Einstein distribution function

We consider the distribution function for a system of non-interacting bosons in thermal and diffusive contact with a reservoir. We assume the bosons are all of the same species. Let ε denote the energy of a single state when occupied by one particle.
For 1 particle, we have energy ε. For N particles, we have energy $N\varepsilon$.



Reservior:

$N_0 - n$ bosons,

$E_0 - n\varepsilon$: energy

$g(N_0 - n, E_0 - n\varepsilon)$

Entropy:

$$S(N_0 - n, E_0 - n\varepsilon) = k_B \ln g(N_0 - n, E_0 - n\varepsilon)$$
$$= S(N_0, E_0) - n\frac{\partial S(N_0, E_0)}{\partial N_0} - n\frac{\partial S(N_0, E_0)}{\partial E_0}\varepsilon$$
$$= S(N_0, E_0) + \frac{n(\mu - \varepsilon)}{T}$$

Note that n = 0, 1, 2, 3, …, ∞. The probability is proportional to

$$P \propto \exp[\frac{1}{k_B} S(N_0 - n,\ E_0 - n\varepsilon)]$$
$$= \exp[\frac{1}{k_B} S(N_0, E_0)] \exp[\frac{n(\mu - \varepsilon)}{k_B T}]$$

or

$$P_n = A \exp[\frac{n(\mu - \varepsilon)}{k_B T}] = Ae^{n\beta(\mu - \varepsilon)}$$

Since $\sum_{n=0}^{\infty} P_n = A \sum_{n=0}^{\infty} e^{n\beta(\mu - \varepsilon)} = 1$, we have

$$A = \frac{1}{\sum_{n=0}^{\infty} e^{n\beta(\mu - \varepsilon)}} = 1 - e^{\beta(\mu - \varepsilon)}$$

Thus we get

$$P_n = Ae^{n\beta(\mu - \varepsilon)}$$

The average number:

$$\langle n \rangle = \sum_{n=0}^{\infty} nP_n = A \sum_{n=0}^{\infty} ne^{n\beta(\mu - \varepsilon)}$$

We note that

$$\sum_{n=0}^{\infty} e^{n\beta(\mu-\varepsilon)} = \frac{1}{1-e^{\beta(\mu-\varepsilon)}}$$

We take a derivative of this equation with respect to μ,

$$\beta\sum_{n=0}^{\infty} ne^{n\beta(\mu-\varepsilon)} = \frac{\beta e^{\beta(\mu-\varepsilon)}}{[1-e^{\beta(\mu-\varepsilon)}]^2}$$

or

$$\sum_{n=0}^{\infty} ne^{n\beta(\mu-\varepsilon)} = \frac{e^{\beta(\mu-\varepsilon)}}{[1-e^{\beta(\mu-\varepsilon)}]^2}$$

Thus we get the probability

$$\langle n \rangle = \sum_{n=0}^{\infty} nP_n = \frac{1}{e^{\beta(\varepsilon-\mu)}-1} \qquad \text{(Bose-Einstein distribution function)}$$

Gibbs sum

The Gibbs sum is given by

$$\begin{aligned} Z_G &= \sum_{N=0}^{\infty} z^N \exp(-\beta N\varepsilon) \\ &= \sum_{N=0}^{\infty} [z\exp(-\beta\varepsilon)]^N \\ &= \frac{1}{1-z\exp(-\beta\varepsilon)} \end{aligned}$$

since

$$0 < z\exp(-\beta\varepsilon) < 1$$

Then the distribution function is given by

$$f(\varepsilon) = z\frac{\partial}{\partial z}\ln Z_G = \frac{1}{e^{\beta(\varepsilon-\mu)}-1}$$

This result is known as the Bose-Einstein distribution function.

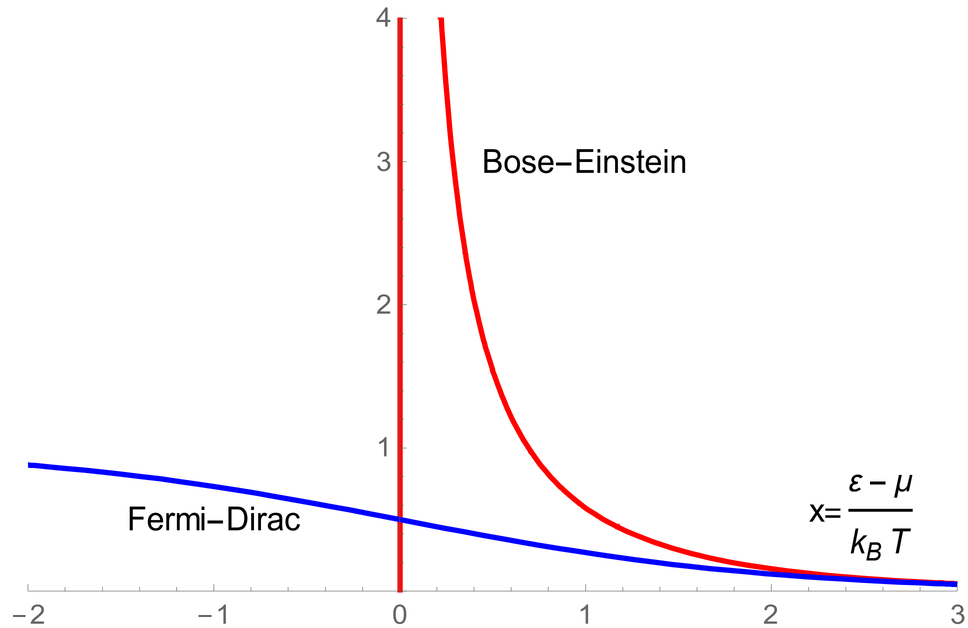


Fig. Fermi-Dirac and Bose-Einstein distribution function as a function of $x = \frac{\varepsilon-\mu}{k_B T}$. These two functions are approximately equal in the classical limit ($\varepsilon - \mu >> k_B T$).

A gas is in the classical regime when the average number of atoms in each state is much less than 1.

$f(\varepsilon) << 1 \quad \leftrightarrow \quad$ Classical limit

$f(\varepsilon) \approx 1 \quad \leftrightarrow \quad$ Quantum limit

3. Classical Limit

$f(\varepsilon)$ is the average occupancy of a state at energy ε, where ε is the energy of a state occupied by one particle,

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} \pm 1}$$

where + (FD) and – (BE)

In order that $f(\varepsilon) << 1$, we must have in this classical regime,

$$e^{\beta(\varepsilon-\mu)} >> 1$$

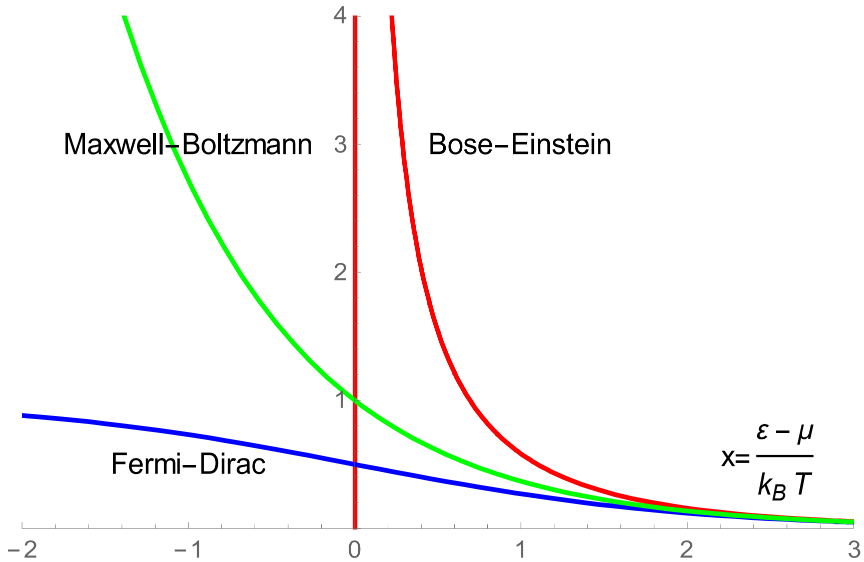
Then

$$f(\varepsilon) \approx e^{-\beta(\varepsilon-\mu)} = ze^{-\beta\varepsilon} \tag{1}$$

with

$$z = e^{\beta\mu}$$

((**Note**)) Eq.(1), although called classical, is still a result for particles described by quantum mechanics. We shall find that the expression for z or μ always involves the quantum constant $\hbar$.



REFERENCES
C. Kittel, Thermal Physics, Second Edition (W.H. Freeman and Company