

# FERMI-DIRAC and BOSE-EINSTEIN Distribution Functions derived from Classic Thermodynamics

G. Job

Job-Stiftung, c/o Institut für Physikalische Chemie, Universität Hamburg, Bundesstr. 45, 20146 Hamburg, Germany



## Introduction

Both, the FERMI-DIRAC (abr. as FD) and BOSE-EINSTEIN (abr. as BE) distribution functions are commonly regarded as important results from quantum statistics, whereas the BOLTZMANN (abr. as BO) distribution function is an outcome of statistical mechanics already. Actually, it is possible to obtain all these functions easily on the basis of classic thermodynamics by using the chemical potential as the main tool.

## Concept of a substance

Key element of the following discussion is the concept of a *chemical substance*: An "elementary" substance may be defined as a set of identical particles. A "real" substance represents a mixture of such elementary components.

The indistinguishability of the particles within an elementary substance is an inherent feature of the chemical potential. Let us consider a proton  $H^+$  in a diluted aqueous solution. The chemical potential  $\mu_{H^+}$  of the protons is given by the equation

$$\mu_{H^+} = \mu_{H^+}^{\circ} + R T \ln \frac{c_{H^+}}{c^{\circ}} \quad (1)$$

a small circle ( $^{\circ}$ ) attached to a symbol labels standard values and  $c_{H^+}$  is the proton concentration in the solution. If it would be possible to differentiate protons into  $N$  groups ( $H_1^+$  and  $c_{H_1^+} = \frac{1}{N} c_{H^+}$ ), the chemical potentials of these protons would be

$$\mu_{H_1^+} = \mu_{H_1^+}^{\circ} + R T \ln \frac{c_{H_1^+}}{c^{\circ}} = \mu_{H^+}^{\circ} + R T \ln \frac{c_{H^+}}{N \cdot c^{\circ}} .$$

Since all  $H_1^+$  are protons by definition, the chemical potential of a proton  $\mu_{H_1^+}$  in each of these  $N$  subsets has to be the same as  $\mu_{H^+}$  to maintain the original chemical properties of the solution.

$$\mu_{H_1^+} = \mu_{H^+}^{\circ} + R T \ln \frac{c_{H^+}}{N \cdot c^{\circ}} = \mu_{H^+}^{\circ} + R T \ln \frac{c_{H^+}}{c^{\circ}} = \mu_{H^+} \quad (2)$$

This equation is only true for  $N = 1$ . Therefore, the framework of the chemical potential does not allow us to separate the particles of a substance into different groups and in reverse, the particles of a substance are indistinguishable in the light of the chemical potential.

## BOLTZMANN statistics

An atomistic view on a gas B reveals that the molecules are in different energetic states  $i$ . Next, we treat the collection of all molecules in the same energetic state as a substance  $B(i)$ . The chemical potential  $\mu_i$  of  $B(i)$  may be expressed as

$$\mu_i = \mu_i^{\circ} + R T \ln \frac{c_i}{c^{\circ}} = \mu_0^{\circ} + \frac{\epsilon_i}{\tau} + R T \ln \frac{c_i}{c^{\circ}} \quad \text{with} \quad \mu_i^{\circ} = \mu_0^{\circ} + \frac{\epsilon_i}{\tau}$$

( $\mu_i^{\circ}$  is the standard potential of  $B(i)$ ,  $\epsilon_i$  the energy of  $B(i)$ ,  $c_i$  the concentration of  $B(i)$  and  $\tau = N_A^{-1}$ ). The chemical potential of the substance made from molecules in their ground state ( $\epsilon_{i=0} = 0$ ) simplifies as follows:

$$\mu_0 = \mu_0^{\circ} + R T \ln \frac{c_0}{c^{\circ}}$$

This separation of the gas into several substances  $B(i)$  is in agreement with the previous conclusion on the inseparability of a substance, since the gas molecules differ in the energetic state, which is reflected in the varying values of  $\mu_i^{\circ}$ .

Chemical equilibrium requires all  $\mu_i$  to be same and by combining the equations for  $\mu_0$  and  $\mu_i$  regarding  $R = k/\tau$  we obtain

$$\mu_0^{\circ} + \frac{\epsilon_i}{\tau} + R T \ln \frac{c_i}{c^{\circ}} = \mu_0^{\circ} + R T \ln \frac{c_0}{c^{\circ}} \rightarrow c_i = c_0 \exp\left(\frac{-\epsilon_i}{k T}\right)$$

## FERMI-DIRAC statistics

We take a pictorial view at the electron orbitals for analysis of the FD distribution function. A spin-orbital is regarded as a place, which can be occupied by a single electron B. Next we focus on a set of  $N$  equivalent places, which all have the same energy if occupied. These places are depicted by a small rectangle ( $\square$ ) in the following text or more generalized as  $\overline{iB}$  ( $i = 0, 1$ ). Thus, the occupation of an orbital by an electron can be transferred into a more chemical language with the following equation:



The chemical potential of an orbital  $\overline{iB}$  is given in the generalized form ( $i = 0, 1$ ):

$$\mu(\overline{iB}) = \mu^{\circ}(\overline{iB}) + R T \ln \theta_i \quad \text{and} \quad \mu^{\circ}(\overline{iB}) = \frac{i \epsilon}{\tau} \quad i = 0, 1$$

( $\theta_i = N_i/N$  is the degree of occupancy for an  $i$ -type vacancy,  $\epsilon$  the energy of the singly occupied place).

The chemical potentials on both sides of equation (3) have to be equal in the state of equilibrium.

$$\mu^{\circ}(\square) + R T \ln \theta_0 + i \mu(B) = \mu^{\circ}(\overline{iB}) + R T \ln \theta_i \quad \mu^{\circ}(\square) = 0, \mu(B) \equiv \mu$$

$$R T \ln \theta_0 + i \mu = \frac{i \epsilon}{\tau} + R T \ln \theta_i$$

## FERMI-DIRAC statistics (continued)

Solving the last equation for  $\theta_i$  yields for any value of  $i$

$$\theta_i = \theta_0 \exp\left(\frac{\mu\tau - \epsilon}{kT}\right)^i = \theta_0 q^i \quad (4)$$

Equation 4 is transformed into two independent ones in two steps. First, the left and the right side of the equation are summed for all values of  $i$  and second, both sides of equation 4 are multiplied with  $i$  prior to the summation.

$$\text{step 1: } \theta_0(1 + q) = \theta_0 + \theta_1 = 1 \rightarrow \theta_0 = (1 + q)^{-1}$$

$$\text{step 2: } \theta_0 q = \theta_1 = \theta$$

The combination of both equations yields the FD distribution function.

$$\theta = (q^{-1} + 1)^{-1} \rightarrow \theta = \frac{1}{e^{\frac{\epsilon - \mu\tau}{kT}} + 1}$$

## BOSE-EINSTEIN statistics

Unlike fermions, many bosons can occupy the same state / vacancy ( $\overline{iB}$   $i = 0, 1, 2, \dots$ ) and the evaluation of equation 4 yields two slightly more complicated equations.

$$\text{step 1: } \theta_0(1 + q + q^2 + q^3 + \dots) = \frac{\theta_0}{1 - q} = \theta_0 + \theta_1 + \theta_2 + \theta_3 + \dots = 1 \rightarrow \theta_0 = 1 - q$$

$$\text{step 2: } \theta_0 q(1 + 2q + 3q^2 + \dots) = \frac{\theta_0 q}{(1 - q)^2} = \theta_1 + 2\theta_2 + 3\theta_3 + \dots = \theta$$

The sums have been replaced using the properties of a geometric series:

$$\sum_{i=0}^{\infty} q^i = \frac{1}{1 - q} \quad \sum_{i=0}^{\infty} (i + 1) \cdot q^i = \frac{1}{(1 - q)^2} \quad q < 1$$

The combination of both equations yields the BOSE-EINSTEIN distribution function.

$$\theta = \frac{q}{1 - q} = \frac{1}{q^{-1} - 1} \rightarrow \theta = \frac{1}{e^{\frac{\epsilon - \mu\tau}{kT}} - 1}$$

## Comparison

As the exponential term in the denominator becomes much larger than 1, both the FD and the BE distribution function turn into the BO distribution function.

$$e^{\frac{\epsilon - \mu\tau}{kT}} \gg 1 \rightarrow \frac{1}{e^{\frac{\epsilon - \mu\tau}{kT}} - 1} \approx \frac{1}{e^{\frac{\epsilon - \mu\tau}{kT}} + 1} \approx \frac{1}{e^{\frac{\epsilon - \mu\tau}{kT}}} = e^{\frac{\mu\tau - \epsilon}{kT}} = \theta$$

The figures below demonstrate how these distribution functions turn into each other as the exponential term becomes large. This is always the case, if  $\mu\tau$  is much smaller than the  $\epsilon$  or in other words the chemical potential  $\mu$  of the particle smaller than the excitation energy and the occupation of the higher energy levels therefore sparse.

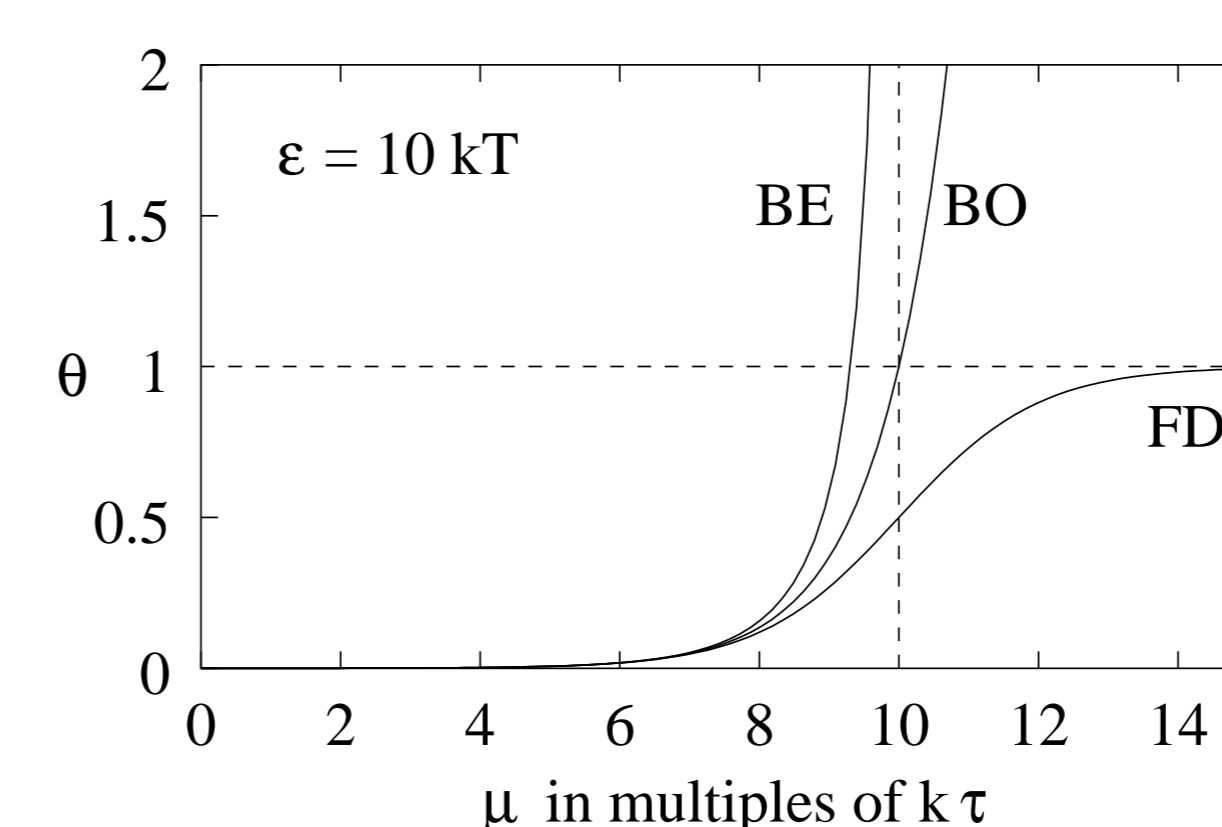


Fig. 1  $\theta$  as a function of  $\mu$

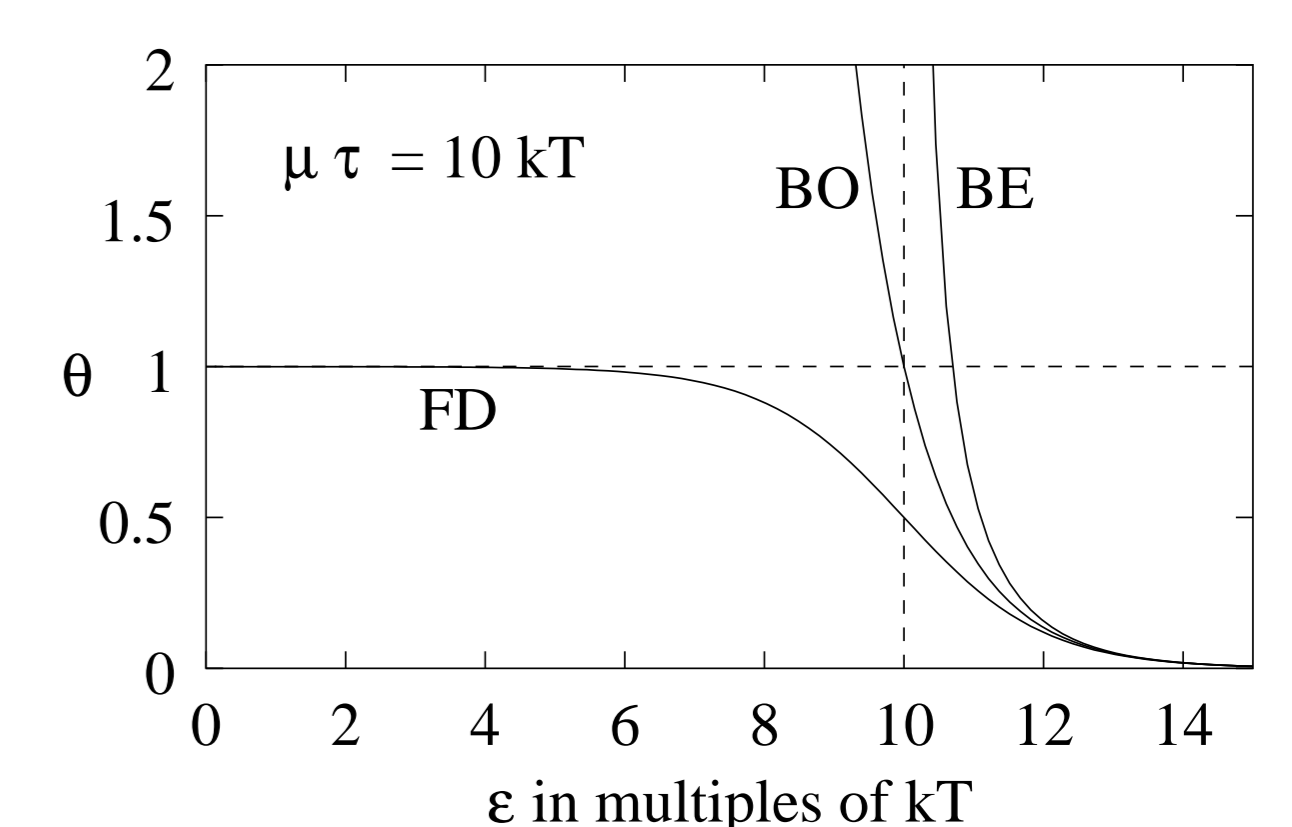


Fig. 2  $\theta$  as a function of  $\epsilon$

## Summary

I hoped to show two important aspects of phenomenological thermodynamics on this poster:

1. The chemical concept of a substance can be easily extended to suit physical problems.
2. Both the FERMI-DIRAC and the BOSE-EINSTEIN distribution can be obtained from phenomenological thermodynamics exploiting the properties of the chemical potential.
3. The *chemical* BOLTZMANN distribution function is just a border-line case of both the FD and the BE functions.

If you have further questions please contact the author at [Georg.Job@Job-Stiftung.de](mailto:Georg.Job@Job-Stiftung.de) or visit our web-page <http://www.job-stiftung.de>.