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Applications of the Grand Ensemble: Fermi-Dirac and Bose-Einstein statistics

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Directory

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1. Introduction

We have seen that an ideal gas is a gas of noninteracting molecules in the limit of low concentration. We have previously determined whether or not a gas could be treated as ideal by considering the quantum concentration (related to the de Broglie wavelength.) We will now refine this definition by considering thermal averages of the number of particles occupying orbitals. An *orbital* is a state of Schrödinger's equation for one particle. (The term is widely used in chemistry, less widely in physics, we'll use it as it useful) We will call the thermal average occupancy the distribution function $f(\varepsilon, T, \mu)$ where ε is the energy of the orbital.

From your studies of quantum mechanics, you should recall the importance of the orbital approach. The essence of the method is that if interparticle interactions are weak, and we have N particles, then we can approximate the N particle quantum state by assigning the particles to orbitals with each orbital being a solution of a one-particle Schrödinger equation. There are normally an infinite number of orbital available for occupancy. If there are no interactions between particle, the orbital model solution of the N-particle problem is exact.

2. Fermions and Bosons

All particles are either fermions or bosons. Particles with integer spins are bosons and are described by Bose-Einstein statistics. Particles with half-integer spins are fermions and obey Fermi-Dirac statistics. In composite particles, the spins combine so that the resulting combination is a fermion or a boson. As example ^{3}He is a fermion ^{4}He is a boson. The allowed occupancies for each of these species are different. An orbital can be occupied by any integral number of bosons of the same type (including zero). An orbital can be occupied by at most one fermion of the same species. We will examine each of these possibilities in turn.

2.1. Fermions and Fermi-Dirac Statistics

To find the Fermi-Dirac distribution function we consider a system consisting of a single orbital. The system is placed in thermal and diffusive contact with a reservoir. (If this bothers you consider the fact that we have always taken our system as the piece we are interested in and assigned everything else to the reservoir. This is just what we are doing here. The real system may contain a large number of particles, we are simply assigning their associated oribitals to the reservoir.) Our task is to evaluate the grand partition function $\mathcal{Z}$. So we need to evaluate

$$\mathcal{Z} = \sum_{N,r} \mathrm{e}^{\beta(N\mu - E_{Nr})}$$

for all states and occupancies of the orbital.

For fermions, the only allowed values of N are 0 and 1, all other occupancies are ruled out by the Paul exclusion principle. We will let the energy of the orbital be ε if the orbital is occupied and and 0 it is unoccupied. We can evaluate the sum simply, as

$$\mathcal{Z} = 1 + \mathrm{e}^{\beta(\mu-\varepsilon)}$$

The term 1 results from $N = 0$ and $\varepsilon = 0$, the other term results from $N = 1$ and $E_{Nr} = \varepsilon$.

Using

$$p_{Nr} = \frac{\mathrm{e}^{\beta(\mu N - E_{Nr})}}{\mathcal{Z}}$$

the average thermal occupancy of the orbital is given by

$$\langle N \rangle = \sum_{N,r} N p_{Nr}.$$

In this case then, we can write

$$\begin{aligned} \langle N(\varepsilon) \rangle &= \frac{\mathrm{e}^{\beta(\mu-\varepsilon)}}{1 + \mathrm{e}^{\beta(\mu-\varepsilon)}} \\ &= \frac{1}{1 + \mathrm{e}^{-\beta(\mu-\varepsilon)}} \end{aligned}$$

$$= \frac{1}{e^{\beta(\varepsilon-\mu)}+1}.$$

Now let the average occupancy of the orbital with energy ε be denoted as $\langle f(\varepsilon)\rangle$, i.e.

$$f(\varepsilon) = \langle N(\varepsilon)\rangle,$$

and we finally write

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

this is the Fermi-Dirac distribution function. This equation gives the average number of fermions in an orbital of energy ε. The value of f lies between 0 and 1.

In solid state physics, the chemical potential μ is often called the *Fermi level*. Chemical potential usually depends on temperature. We call the chemical potential at $T = 0$ the *Fermi energy*. That is

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

At $T = 0$ all orbitals with energies less than the Fermi energy are filled (that is they each contain a fermion). All orbital with energies above the Fermi energy are unoccupied. An orbital whose energy is equal to the chemical potential will be half full. This is easy to see as

$$f(\varepsilon = \mu) = \frac{1}{1+1}.$$

Orbitals with lower energy will be more than half full, orbitals with higher energy are less than half full.

We will sometimes write Fermi-Dirac distribution as

$$\langle N_i \rangle = \frac{1}{\mathrm{e}^{\beta(\varepsilon_i - \mu)} + 1},$$

then we can use

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

to relate N to μ for a given T.

2.2. Bosons and the Bose-Einstein Distribution

Bosons are essentially different from fermions as there is no limitation on the the occupancy of an orbital. We want to find the distribution function for bosons as we did for fermions. This time consider a system of noninteracting bosons in thermal and diffusive contact with a reservoir. Let ε be the energy of an orbital when it is occupied by one boson. Thus, when the occupancy is N, the energy will be $n\varepsilon$. As before, we treat one orbital as the system, the rest as part of the reservoir. The number of particles in the single orbital is arbitrary. Our task is again to evaluate

$$\mathcal{Z} = \sum_{N,r} e^{\beta(N\mu - E_{Nr})}$$

for all states and occupancies of the orbital. This time we write

$$\begin{aligned} \mathcal{Z} &= 1 + e^{\beta(\mu-\varepsilon)} + e^{2\beta(\mu-\varepsilon)} + e^{3\beta(\mu-\varepsilon)} + \ldots \\ &= 1 + e^{\beta(\mu-\varepsilon)} + \left(e^{\beta(\mu-\varepsilon)}\right)^2 + \left(e^{\beta(\mu-\varepsilon)}\right)^3 + \ldots . \end{aligned}$$

We can rewrite this in compact form as

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta N(\mu-\varepsilon)} = \sum_{N=0}^{\infty} [e^{\beta(\mu-\varepsilon)}]^N$$

The upper limit on N should be the number of particles in the combined system and reservoir. Since the reservoir can be as large as we like, we will let the sum run to∞ to enable the series to be conveniently summed.

If we let $x = \mathrm{e}^{\beta(\mu-\varepsilon)}$, then we have a geometric series.

$$\mathcal{Z} = \sum_{N=0}^{\infty} x^N = \frac{1}{1-x} = \frac{1}{1-\mathrm{e}^{\beta(\mu-\varepsilon)}}.$$

This summation is possible provided that $\mathrm{e}^{\beta(\mu-\varepsilon)} < 1$. This will be true in all applications since if it were not the number of bosons in the system would not be bounded.

Now that we have the grand partition function, we can determine the average occupancy. Thus the average occupancy of an orbital is

$$\langle N \rangle = \sum_{N,r} N p_{Nr}$$

Since we are taking care of the sum over states by writing $N\varepsilon$, we can replace this by a sum over N. Thus, we write

$$\langle N\rangle = \sum_N N p_N = 0\cdot p_0 + 1\cdot p_1 + 2\cdot p_2 + \ldots .$$

Thus we need to evaluate

$$\langle N\rangle = \sum_N N \frac{\mathrm{e}^{N\beta(\mu-\varepsilon)}}{\mathcal{Z}} = \sum_N N \frac{\mathrm{e}^{-N\beta(\varepsilon-\mu)}}{\mathcal{Z}}.$$

To evaluate this let $x = \beta(\varepsilon-\mu)$, then we can write

$$\langle N\rangle = \sum_N N \frac{\mathrm{e}^{-Nx}}{\mathcal{Z}}.$$

We can see that this can be easily rewritten [1] as

$$\langle N\rangle = -\frac{1}{\mathcal{Z}}\sum_N \frac{\partial}{\partial x}\mathrm{e}^{-Nx} = -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial x}$$

Now we can evaluate this expression

$$\begin{aligned}\langle N\rangle &= -(1-\mathrm{e}^{-x})\frac{\partial}{\partial x}(1-\mathrm{e}^{-x})^{-1}\\ &= (1-\mathrm{e}^{-x}(1-\mathrm{e}^{-x})^{-2}(\mathrm{e}^{-x})\\ &= \frac{\mathrm{e}^{-x}}{1-\mathrm{e}^{-x}}\end{aligned}$$

[1] To get this result, I have gone back to an intermediate expression for the grand partition function and written it as

$$\begin{aligned}\mathcal{Z} &= 1+\mathrm{e}^{-\beta(\varepsilon-\mu)}+\left(\mathrm{e}^{-\beta(\varepsilon-\mu)}\right)^2+\left(\mathrm{e}^{-\beta(\varepsilon-\mu)}\right)^3+\ldots\\ &= 1+\mathrm{e}^{-x}+\mathrm{e}^{-2x}+\mathrm{e}^{-3x}+\ldots.\end{aligned}$$

$$
\begin{aligned}
&= \frac{1}{\mathrm{e}^{x} - 1} \\
\langle N \rangle &= \frac{1}{\mathrm{e}^{\beta(\varepsilon - \mu)} - 1}.
\end{aligned}
$$

This is the Bose-Einstein distribution. As we'll see the switch from $+1$ to -1 has large physical consequences.

We will sometimes write Bose-Einstein distribution as

$$
\langle N_i \rangle = \frac{1}{\mathrm{e}^{\beta(\varepsilon_i - \mu)} - 1}.
$$

3. Corrected Boltzons

Classical gases are those gases that obey Maxwell-Boltzmann statistics. In such gases $N_i \ll 1$ for all i, i.e. the mean occupancy is small for all orbitals. Under such conditions, we would expect to get similar results whether we used the Fermi-Dirac or the Bose-Einstein distribution. In fact we can write our distribution function as

$$
\langle N_i \rangle = \frac{1}{\mathrm{e}^{\beta(\varepsilon_i - \mu)} \pm 1, 0}.
$$

Where
$+1 \Rightarrow$ Fermi-Dirac
$-1 \Rightarrow$ Bose-Einstein
$0 \Rightarrow$ Maxwell-Boltzmann

In this expression we observe that $\langle N_i \rangle \ll 1$ for all i if $\mathrm{e}^{\beta(\varepsilon_i - \mu)} \gg 1$. Then we have

$$\langle N_i \rangle = \mathrm{e}^{-\beta(\varepsilon_i - \mu)} = \mathrm{e}^{\beta(\mu - \varepsilon_i)}$$

Why does this work? If $\langle N_i \rangle \ll 1$ for all i, it doesn't matter how we weigh states for $\langle N_i \rangle \geq 2$, none of them are occupied. In the classical regime all three distributions are equal. The terminology *corrected boltzons* takes note of the fact that to calculate partition functions we write

$$Z = \frac{Z_1^N}{N!}.$$