

Some important results of Statistical Mechanics

Ionization Equilibrium - Saha's Equation

Consider the ionization/recombination reaction for an atom A :



The Law of Mass Action for this reaction is,

$$\frac{n_e n_i}{n_a} = \frac{q_e q_i}{q_a} \quad \left(q = \frac{Q}{V} \right) \quad (2)$$

When calculating the various partition functions, it is very important to measure all energies from the same reference. For this particular case, suppose we arbitrarily assign zero energy to an atom at rest and to an ion at rest. Since the energy needed to produce an electron-ion pair is eV_i , we then have to assign the energy eV_i to an electron at rest, or $eV_i + \epsilon_i^R$. The translational partition function for an electron,

$$Q_e^{tr.} = \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} V$$

was derived based on the set ϵ_i^R for the free electron in a box. Since $Q = \sum_i g_i e^{-\frac{\epsilon_i}{kT}}$, we now have,

$$Q_e^{tr.} = \sum_i g_i e^{-\frac{eV_i + \epsilon_i^R}{kT}} = \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} V e^{-\frac{eV_i}{kT}} \quad (3)$$

Including now the spin degeneracy $g = 2$ of a free electron,

$$q_e = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\frac{eV_i}{kT}} \quad (4)$$

Similarly, for ions and atoms, including their electronic excitation degeneracy g_i, g_a ,

$$q_i = g_i \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \quad (5)$$

$$q_a = g_a \left(\frac{2\pi m_a kT}{h^2} \right)^{3/2} \quad (6)$$

and since $m_i \simeq m_a$, Equation (1) yields,

$$\frac{n_e n_i}{n_a} = 2 \frac{g_i}{g_a} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\frac{eV_i}{kT}} \quad (7)$$

which is called the Saha equation for ionization equilibrium.

As developed, the equation applies to ionization of an atom. Molecules and molecular ions have other degrees of freedom (vibration, rotation), and the equation needs to be modified

accordingly. But the modifications are formally very simple: replace g_i, g_a by the respective Internal Partition Functions:

$$\begin{aligned} Q_i^{int} &= Q_i^{exc} Q_i^{vib} Q_i^{rot} \dots \\ Q_m^{int} &:= Q_m^{exc} Q_m^{vib} Q_m^{rot} \dots \quad (m \text{ for molecule}) \end{aligned} \quad (8)$$

and then,

$$\frac{n_e n_i}{n_m} = 2 \frac{Q_i^{int}}{Q_m^{int}} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\frac{eV_i}{kT}} \quad (9)$$

In MKS units,

$$\frac{n_e n_i}{n_m} = 2 \frac{Q_i^{int}}{Q_m^{int}} \times 4.84 \times 10^{21} T^{3/2} e^{-\frac{eV_i}{kT}} \quad (10)$$

The dominant T dependence is in $e^{-\frac{eV_i}{kT}} = e^{-\frac{V_i}{T(eV)}}$. For moderately low temperatures (up to a few eV), this factor is extremely sensitive:

$$\frac{d \ln(e^{-V_i/T})}{d \ln T} = \frac{V_i}{T} \gg 1$$

In quasi-neutral plasma $n_i = n_e$, and Saha relates n_e to n_a . The full equilibrium composition requires an extra condition, typically the pressure,

$$P = (n_e + n_i + n_a)kT = (2n_e + n_a)kT$$

Useful properties for selected atoms:

Element	$M(g/md)$	V_i (V)	E_{12} (V)(1st exc.)	g_0^{atom}	g_0^{ion}	ξ_1 (Outer shell electrons)
H	1.008	13.6	10.2	2	1	1
He	4.003	24.6	19.8	1	2	2
Li	6.94	5.39	1.85	2	1	1
N	14.01	14.6	2.38	4	~ 9	3
O	16	13.6	1.97	~ 9	4	4
Ne	20.18	21.6	16.6	1	~ 6	6
Na	23.00	5.14	2.10	2	1	1
A	39.94	15.8	11.5	1	~ 6	6
K	39.10	4.34	1.61	2	1	1
Xe	131.3	12.1	8.32	1	4	6
Cs	132.9	3.89	1.39	2	1	1
Hg	200.6	10.4	4.67	1	2	2

Free electrons in metals

As we saw already, electrons obey Fermi-Dirac statistics:

$$N_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1} \quad \text{where} \quad \alpha = -\frac{\mu}{kT} \quad \text{and} \quad \beta = \frac{1}{kT}$$

We assume, to first order that electrons do not interact among themselves, so only translational degrees of freedom will be considered.

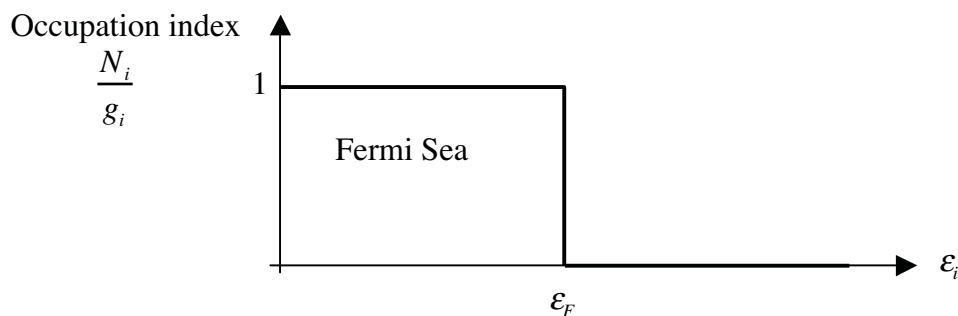
Let us analyze the case of very low temperature, in the limit $T \rightarrow 0$, and define the “Fermi Energy” as $\mu = \varepsilon_F$, so we have,

$$N_i = \frac{g_i}{e^{\frac{\varepsilon_i - \varepsilon_F}{kT}} + 1}$$

The exponential part of this expression becomes extremely large or very small whenever $\varepsilon_i \neq \varepsilon_F$, so we identify two regions of interest depending on the energy with respect to the Fermi level:

1. When $\varepsilon_i < \varepsilon_F$ then $N_i = g_i$ Since there can only be one particle in each state (electrons obey the exclusion principle), all states are occupied. We say the electron gas is “degenerate”.
2. When $\varepsilon_i > \varepsilon_F$ then $N_i = 0$ All states are empty.

This situation can be illustrated with the following diagram:



Even at $T = 0$ there are particles with energies larger than zero ($\varepsilon_i < \varepsilon_F$) contrary to the classical description of an ideal gas that has zero energy for zero temperature.

What is the Fermi Energy?

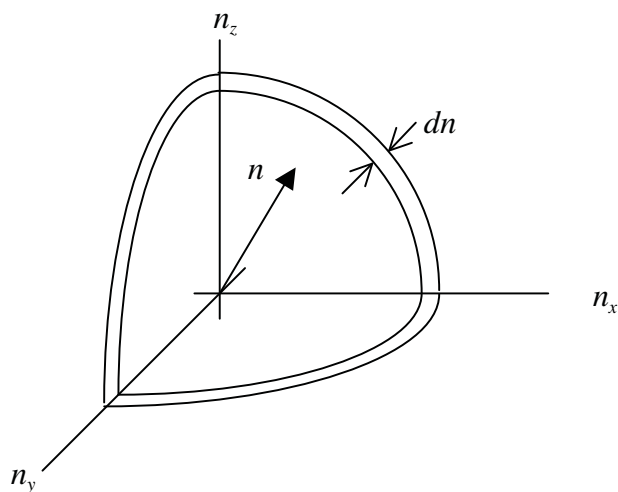
We know that all particles are contained in the states with energies lower than ε_F , and that there is only one particle per state. Assuming that levels are closely spaced between each other, so the summation can be replaced with an integral, the total number of particles becomes,

$$N = \int_0^{\varepsilon_F} dg$$

After solving Schrödinger's equation for a free particle in a box with volume $V = L_x L_y L_z = L^3$ we find that the quantum number n and the energy are related by,

$$n = \frac{L}{\pi} \sqrt{\frac{2m\varepsilon}{\hbar^2}} \quad \text{where} \quad n^2 = n_x^2 + n_y^2 + n_z^2$$

Earlier we saw that the degeneracy is the number of quantum states that share the same energy level. In this case we see that several combinations of the three numbers n_x , n_y , and n_z will yield a particular n . In fact (see figure), every point over the spherical surface in the n -space (in the positive octant where the domain of the n 's coincide, since $n_i > 0$ for $i = x, y, z$) will have the same energy.



The elementary volume in this space will then be the elementary part of the degeneracy,

$$dg = 2 \frac{4\pi n^2 dn}{8}$$

where the “2” comes from the spin of electrons (“up” or “down”), while the “8” is there since we are only interested in the octant where the n 's exist.

Combining the last two expressions we see that,

$$dg = \frac{\partial g}{\partial \varepsilon} d\varepsilon = g_\varepsilon d\varepsilon = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} d\varepsilon$$

which can be integrated directly,

$$\int_0^{\varepsilon_F} dg = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{3/2} = N$$

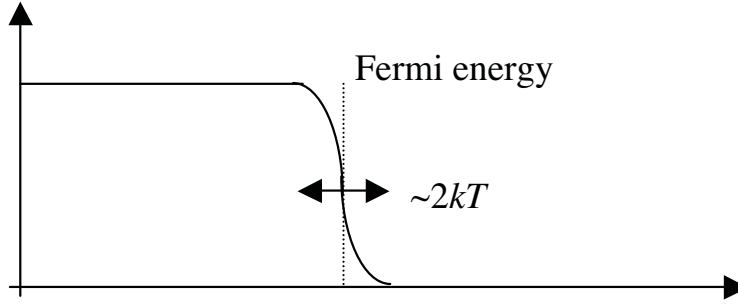
Finally we solve for the Fermi energy,

$$\varepsilon_F = \left(3\pi^2 \frac{N}{V} \right)^{2/3} \frac{\hbar^2}{2m}$$

Example: For Cu,

$$\frac{N}{V} = \frac{\# \text{ atoms}}{\text{Vol}} = \frac{\# \text{ electrons}}{\text{Vol}} = \frac{N_A}{w} \rho = \frac{6.02 \times 10^{26} \text{ kmol}^{-1}}{63.5 \text{ kg/kmol}} 8940 \text{ kg/m}^3 = 8.5 \times 10^{28} \text{ m}^{-3}$$

For this example, the Fermi energy results in $\varepsilon_F = 7.04 \text{ eV} \approx 80,000^\circ\text{K}$.



This means that T does not need to be very small (for instance, room temperature, at 300K) for the electron gas to be very degenerate. In general, at temperatures larger than zero, the particle distribution is modified just slightly, and will look similar to the figure above.

Of course one could argue that not all particles in the system have the Fermi energy, perhaps many of them will have energies significantly smaller. To resolve this issue we can calculate the mean energy per particle $\bar{\varepsilon} = E_0/N$, where E_0 is the total energy at zero temperature, which can be found by direct integration,

$$E_0 = \int_0^{\varepsilon_F} \varepsilon dN = \int_0^{\varepsilon_F} \varepsilon dg$$

Using previous expressions, written in terms of the Fermi energy,

$$E_0 = \frac{3}{2} N \varepsilon_F^{-3/2} \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon = \frac{3}{5} N \varepsilon_F$$

Then, the mean energy is,

$$\bar{\varepsilon} = \frac{E_0}{N} = \frac{3}{5} \varepsilon_F$$

This value is not too far from the Fermi energy (just 3/5 of it). This means that most particles have large energies even at zero temperature.

This situation can be better understood with a diagram. First we note that (for closely spaced energy levels) the F.D. distribution can be written as (when $T = 0$),

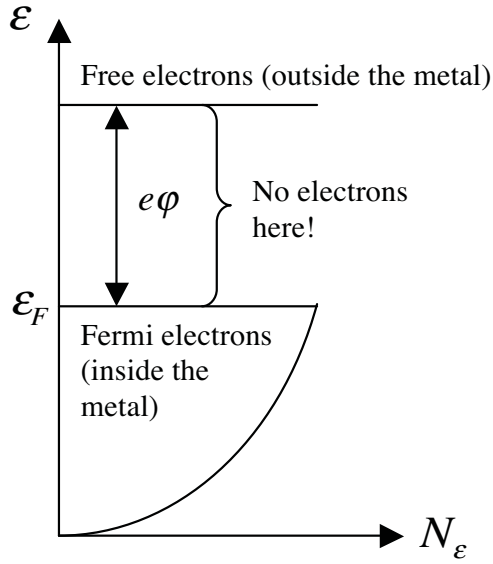
$$dN = \frac{\partial N}{\partial \varepsilon} d\varepsilon = N_\varepsilon d\varepsilon = g_\varepsilon d\varepsilon \quad \text{therefore} \quad N_\varepsilon = g_\varepsilon$$

Where N_ε is the number of particles per unit energy.

It is clear that the electron population grows with the square root of the energy up to the Fermi level, where it suddenly goes to zero.

Now, we consider also the existence of free electrons outside the metal, these particles may come from the material surface after being extracted from it.

We define $e\phi$ as the work required to extract an electron from the metal surface at the Fermi level (the work function).



Those electrons outside of the metal can be described by the classical approximation of a diluted gas, and therefore their chemical potential and partition function (for translational and spin degrees of freedom) are given by,

$$\mu_{ext} = -kT \ln \frac{Q}{N}$$

and,

$$Q = Q^s Q^{tr} = 2 \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V$$

We note that these expressions are written at the zero energy level of the free electrons outside of the metal. In other words, free electrons (energetically speaking) are located at an energy

$\mu_{ext} + \epsilon_F + e\phi$ with respect to the zero energy level in the Fermi system. To make the analysis consistent, we shift the energy levels of the electrons outside of the metal to match the Fermi level, this is simply done by making $\mu_{ext} = -e\phi$. In this way, the equations above can be used to write,

$$e\phi = kT \ln \left[2 \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \frac{1}{n_e^*} \right] \quad \text{with} \quad n_e^* = \frac{N}{V}$$

where n_e^* is the free electron density.

The flux of electrons (number of particles that cross an arbitrary surface, per unit time, per unit area) is given by,

$$\Gamma_e = \frac{n_e^* \bar{c}_e}{4} \quad \text{with} \quad \bar{c}_e = \sqrt{\frac{8kT}{\pi m_e}}$$

It is important to realize this is the flux of electrons coming from outside of the metal. In equilibrium, an equal flux must be leaving the metal.

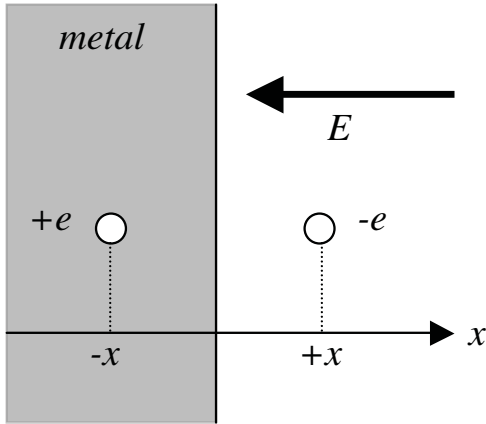
The (bi-directional) electron current density is then given by,

$$j_e = e\Gamma_e = \frac{4\pi e m_e}{h^3} (kT)^2 e^{-\frac{e\phi}{kT}} = 120 \times 10^4 T^2 e^{-\frac{e\phi}{kT}} \text{ Cm}^{-2}$$

and if electrons are withdrawn from the outside, only the emission part remains. This is known as the Richardson-Dushman thermionic emission law.

Thermionic emission enhanced with a normally applied electric field

To increase the extraction rate from the metal surface, we could apply an electric field E normal to it. To quantify this situation we compute the work W (potential energy) of the extracted electron assuming that the only force that binds it to the surface is that of its image charge inside the material.



This energy is formed by two parts: that required to bring the particle from infinity to a position x from the metal surface under the image force plus the one that arises from applying the electric field,

$$W = \int_{\infty}^x F dx + eEx \quad \text{with} \quad F = \frac{-e^2}{4\pi\epsilon_0(2x)^2}$$

therefore,

$$W = \frac{e^2}{16\pi\epsilon_0 x} + eEx$$

In terms of the potential, we have,

$$\phi_E = -\frac{W}{e} = -\frac{e}{16\pi\epsilon_0 x} - Ex$$

We take the derivative of this potential and set it to zero to find the position x_m where ϕ_E is maximum,

$$x_m = \sqrt{\frac{e}{16\pi\epsilon_0 E}}$$

The net effect of E is to decrease the potential barrier by,

$$\phi_{E,max} = -\sqrt{\frac{eE}{4\pi\epsilon_0}}$$

thus modifying Richardson's law which we rewrite here as,

$$j_e = e\Gamma_e = \frac{4\pi em_e}{h^3} (kT)^2 e^{-\frac{e}{kT}(\phi - \sqrt{\frac{eE}{4\pi\epsilon_0}})}$$

Black Body radiation

We now turn to Bose-Einstein statistics since photons do not obey Pauli's exclusion principle. Furthermore, the Lagrange multiplier α identified with the conservation of the total number of particles in a system will vanish here, since photons are not conserved in number. Energy on the other hand, is conserved. For example, a photon with energy $2h\nu$ can be absorbed by the material surface while two photons with energy $h\nu$ can be emitted. If the energy levels are closely spaced, then we can write the B.E. distribution as,

$$dN = \frac{dg}{e^{\frac{h\nu}{kT}} - 1} \quad \text{or} \quad \frac{\partial N}{\partial \nu} d\nu = \frac{1}{e^{\frac{h\nu}{kT}} - 1} \frac{\partial g}{\partial \nu} d\nu \quad \text{or} \quad N_\nu d\nu = \frac{g_\nu d\nu}{e^{\frac{h\nu}{kT}} - 1}$$

where N_ν and g_ν are the number of particles and degeneracies per unit frequency, respectively. The wave equation solution for photons in a "box" of sides L_x , L_y and L_z is proportional to $(\sin k_x x)(\sin k_y y)(\sin k_z z)$. The solution vanishes at $x, y, z = 0$, but also must vanish at every boundary, so we require (consider all sides of the box of length L),

$$\begin{aligned} k_x L_x &= n_x \pi & L_x &= L_y = L_z = L \\ k_y L_y &= n_y \pi & \text{and since } k^2 &= k_x^2 + k_y^2 + k_z^2 & \text{we have that } kL &= n\pi \\ k_z L_z &= n_z \pi & n^2 &= n_x^2 + n_y^2 + n_z^2 \end{aligned}$$

As with the analysis of free electrons in metals, the degeneracy of this system is related to the number of ways in which the quantum numbers that form n can be arranged to give the same energy. So we have once more $dg = 2(4\pi n^2 dn)/8$, but this time the "2" comes from the two possible polarizations of electromagnetic waves. Now we relate n with the frequency,

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{c} \nu \quad \text{and since } k = \frac{n\pi}{L} \quad \text{then } n = \frac{2L}{c} \nu$$

In this way, the degeneracy can be written as $dg = (8\pi V/c^3)\nu^2 d\nu$ and the number of particles per unit frequency is therefore,

$$N_\nu = \frac{8\pi V}{c^3} \frac{\nu^2}{e^{\frac{h\nu}{kT}} - 1} \quad \text{and the number density (per unit frequency) is } n_\nu = \frac{N_\nu}{V}$$

With this, we can calculate Planck's Formula, which is the energy per unit volume and per unit frequency,

$$u_\nu = h\nu n_\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1}$$

which depends only on temperature, a result not predicted by classical mechanics.

The spectral emission (energy flux) is obtained from,

$$q_\nu = \frac{n_\nu c}{4} h\nu = \frac{2\pi h}{c^2} \frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1}$$

which can be integrated to obtain the overall emission,

$$q = \int_0^\infty q_\nu d\nu = \frac{2\pi h}{c^2} \int_0^\infty \frac{\nu^3 d\nu}{e^{\frac{h\nu}{kT}} - 1}$$

and by making $x = h\nu/kT$, we can write the emission as,

$$q = \frac{2\pi h}{c^2} \left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

The integral in this expression can be evaluated numerically or by expanding the exponential in power series, integrating each element and then finding to what value the new integrated series converges to. This value is $\pi^4/15$. We finally find the radiative power law,

$$\boxed{q = \sigma T^4}$$

where the Stefan-Boltzmann constant σ is given by,

$$\sigma = \frac{2\pi^5 k^4}{15c^2 h^3} = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^2}$$

The Maxwellian distribution function for velocities

From the classical approximation of a diluted gas, we already found that,

$$N_i = \frac{N}{Q} g_i e^{-\frac{\varepsilon_i}{kT}}$$

For closely spaced energy levels,

$$dN = \frac{N}{Q} e^{-\frac{\varepsilon}{kT}} dg$$

We assume only translational degrees of freedom are relevant,

$$Q = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \quad \text{and} \quad \varepsilon = \frac{\pi^2 \hbar^2}{2m} \frac{n^2}{V^{2/3}}$$

Once more, the degeneracy is given by the points on the sphere in n -space which have the same energy, so $dg = (4\pi n^2 dn)/8$, and as the energy is $\varepsilon = \frac{1}{2}mu^2$, then,

$$dg = 4\pi V \left(\frac{m}{h} \right)^3 u^2 du$$

Defining $f(u)$ as the number of particles per unit u interval and per unit volume,

$$f(u) = \frac{dN/V}{4\pi u^2 du}$$

We then find that,

$$f(u) = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mu^2}{2kT}} \quad \text{where} \quad n = \frac{N}{V}$$

A result that we had previously “discovered” through Kinetic Theory.

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16.55 Ionized Gases
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