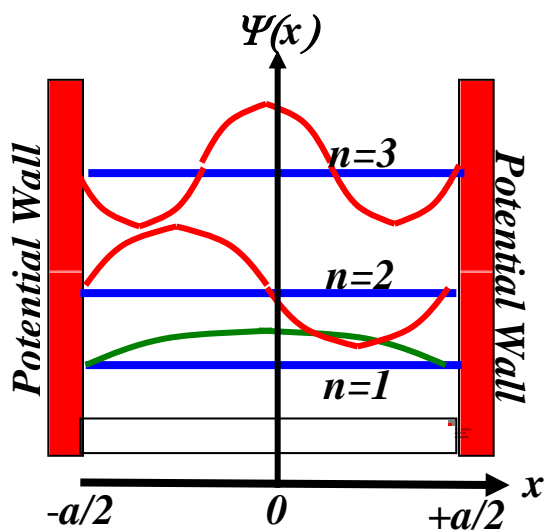## The Fermi Gas Model
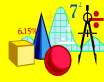
The Fermi-gas model represents a surprisingly successful attempt to capture the quantal nature of subatomic particles within an *N*-particle approach based on the ideas of a quasi-ideal quantal gas of **Fermions (particles with non-integer spin)**. The particles are supposed to be interaction-free with respect to one another, but are contained within the walls of a container or in a holding field. This model generalizes the well-known **particle-in-a-box model** to three dimensions. As shown in the sketch for a one-dimensional box of width **a**, the system is confined by two vertical potential walls at $x = \pm a/2$ with a flat bottom at $V = 0$ between the two walls. The walls are assumed to be infinitely high,

$$V(x) = \begin{cases} 0 & -\dfrac{a}{2} < x < +\dfrac{a}{2} \\[2mm] \infty & |x| \ge \dfrac{a}{2} \end{cases} \qquad (1)$$

Therefore, the wave functions of any particle in the box must disappear at the boundaries of $x = \pm a/2$. Therefore, the stationary single-particle states correspond to wave functions whose half-wave length ($\lambda_n/2$) fits an integer number (*n*) of times into the length **a** of the box

$$n \cdot \frac{\lambda_n}{2} = a \qquad n = 1, 2, \ldots \ldots \tag{2}$$

Furthermore, since the potential is symmetric with respect to reflection at the origin, $V(-x) = V(+x)$, the wave functions must have a ***well-defined parity***. They must be either even functions of the spatial coordinate x or odd functions, specifically, one has to require

$$\Psi_n(-x) = (-1)^n \cdot \Psi_n(+x) \tag{3}$$

As already indicated on the sketch, these requirements are fulfilled by the ***sin*** and ***cos*** functions,

$$\begin{aligned}
\Psi_n(x) &= A_n \cos(k_n \cdot x) \quad \textit{for } n = odd \\
\Psi_n(x) &= A_n \sin(k_n \cdot x) \quad \textit{for } n = even
\end{aligned} \tag{4}$$
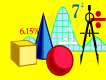
with the quantized wave vectors (π divided by Equ. 2)

$$k_n = n \cdot \frac{\pi}{a} \tag{5}$$

The particle-in-a-box momenta p are related to the wave vector as

$$p_n = \hbar \cdot k_n = n\sqrt{2m\varepsilon} \tag{6}$$

where m is the mass of the particle in the box. Consequently, the energies of the different stationary states are

$$\varepsilon_n = \frac{\hbar^2}{2m} \cdot k_n^2 = \frac{\hbar^2}{2m} \cdot \left(n \cdot \frac{\pi}{a}\right)^2 = \frac{\hbar^2 \pi^2}{2ma^2} \cdot n^2 \tag{7}$$

The energy spectrum is, hence, discrete, as expected for a bound system. The energies of the levels increase in distance from the ground state (**n=1**) quadratically.

However, because of the inverse relation between the energy levels ε_i and the length **a**, these energies become smaller with increasing dimension of the box. In the limit of a very large box, $a \to \infty$, both the energies ε_i and momenta k_i become continuous variables. Then, one has essentially a free gas without any walls. Therefore, this limit represents the classical ideal gas.

The above 1-dimensional model can be trivially expanded to three spatial dimensions, *x, y,* and *z*. Assuming that these different degrees are independent, i.e., that the motion is decoupled, one can copy the above derivation and obtains for the wave functions in 3 dimensions a product of individual 1-dimensional wave functions,

$$\Psi_{n_x n_y n_z}(x, y, z) = \Psi_{n_x}(x) \cdot \Psi_{n_y}(y) \cdot \Psi_{n_z}(z) \tag{8}$$

The states are now numbered by triplets $\{n_x, n_y, n_z\}$ of natural numbers, each one describing the excitation along one degree of freedom. Accordingly, the momenta are now vectors with components given by Equ. 6 and energies, which are the sums of three terms of the form of Equ. 7. If the three-dimensional box is a cube with three equal sides **a**, one can write for the sum of a 3-D level

$$\varepsilon_{n_x n_y n_z} = \frac{\hbar^2}{2m} \cdot \left(k_{n_x}^2 + k_{n_y}^2 + k_{n_z}^2 \right) = \frac{\hbar^2 \pi^2}{2ma^2} \cdot \left(n_x^2 + n_y^2 + n_z^2 \right) \tag{9}$$

The momentum (phase) space is characterized by the triplet $\{n_x, n_y, n_z\}$ of quantum numbers just like a regular vector in ordinary space is characterized by three coordinates $\{x,y,z\}$. One has to keep
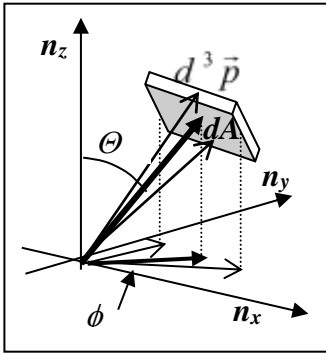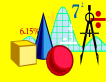
in mind, however, that only natural numbers are allowed for each quantum number. Therefore, only the space $\{n_x > 1, n_y > 1, n_z > 1\}$ is physical, i.e., only one of the 8 octants of the entire mathematical space, excluding the origin.

The most natural coordinate system is the polar system, since the total energy and the total momentum are of interest in the present context. Hence, one deals with volume elements $d^3\vec{p}$ such as pictured in the sketch above, where the square of the distance from the origin is written as

$$\rho^2 = n_x^2 + n_y^2 + n_z^2 = p^2 \cdot \left(\frac{a}{\pi\hbar}\right)^2 \tag{10}$$

It is of interest to know the number of single-particle states in a volume element, which is equal to the number of different triplets $\{n_x, n_y, n_z\}$ that can be formed of the natural numbers $n_i = 1, 2, \dots$. Each state can be thought to lie on one of the corners of a unit cube, a cube of side length $\Delta n_x = \Delta n_y = \Delta n_z = 1$. Then, the number of single-particle states Ω inside a sphere of radius ρ is exactly equal to the volume of the sphere, and its differential is given by

$$d\Omega = \frac{1}{8} \cdot 4\pi\rho^2 d\rho = \frac{1}{2} \cdot \pi\rho^2 d\rho \tag{11}$$

Inserting Equ. 10 into 11, one obtains for the differential number of single-particle states for a given momentum p,
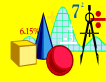
$$d\Omega(p) = \frac{1}{2} \cdot \pi \rho^2 d\rho = \frac{1}{2}\left(\frac{a}{\pi\hbar}\right)^3 \cdot \pi p^2 dp = \frac{a^3}{2\pi^2\hbar^3} p^2 dp \qquad (12)$$
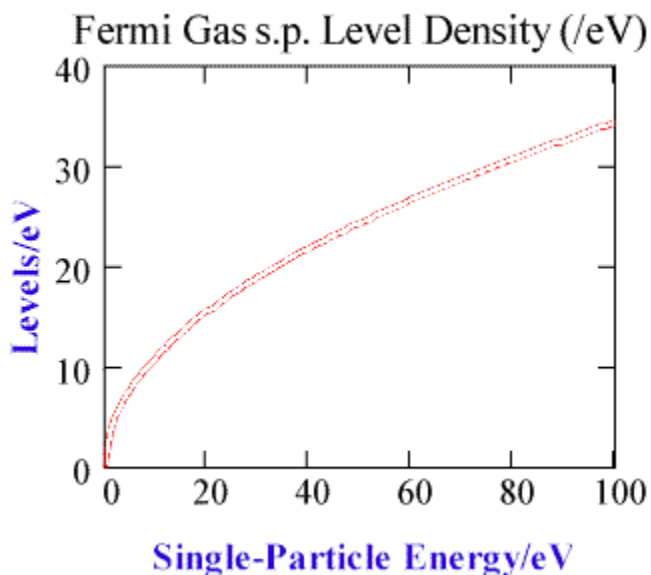
Hence, the number of single-particle states in a shell in momentum space is proportional (1/8th times) to the volume of that shell. This must be so, because the particle momentum is proportional to the its quantum number *n*.

The number of single-particle states for a given energy ε is now also easy to calculate. Since $p^2 = 2m\varepsilon$ and, therefore,

$$dp^2 = 2pdp = 2md\varepsilon \qquad (13)$$

Equ. 12 can be transformed into

$$d\Omega(\varepsilon) = f(\varepsilon)d\varepsilon = \frac{a^3}{2\pi^2\hbar^3} p^2 dp = \frac{\left(\sqrt{m}a\right)^3}{\sqrt{2}\pi^2\hbar^3}\sqrt{\varepsilon}d\varepsilon \qquad (14)$$

Fermi Gas s.p. Level Density (/eV)

In the figure, the density function $f(\varepsilon)$ for single particles is depicted for electrons in a three-dimensional box of volume $a^3 = 1\text{Å}^3$. Plotted is the number of energy levels vs. the energy in units of *eV*.

If electrons have high enough energies, they are allowed energetically to fill all states up to a highest level,
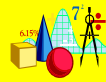
the Fermi energy ε_F. This is also the case for the ground state (lowest energy, $T=0$) of the N-electron gas. Since an electron has a spin of 1/2, two electrons (spin up and spin down) could fit into any given level. Then, the integral over the density $f(\varepsilon)$ up to $\varepsilon = \varepsilon_F$ has to equal *1/2 N*, where N is the number of electrons that have to be placed into the single-particle level scheme :

$$\frac{N}{2} = \int_0^{\varepsilon_F} d\varepsilon \, f(\varepsilon) = \frac{\left(\sqrt{ma}\right)^3}{\sqrt{2}\pi^2\hbar^3} \int_0^{\varepsilon_F} d\varepsilon \sqrt{\varepsilon} = \frac{\left(\sqrt{ma}\right)^3}{\sqrt{2}\pi^2\hbar^3} \frac{2}{3} \varepsilon_F^{\frac{3}{2}}$$

(15)
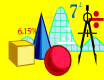
This can be solved for the Fermi energy ε_F:

$$\varepsilon_F^{-\frac{3}{2}} = \frac{\left(\sqrt{ma}\right)^3}{\sqrt{2}\pi^2\hbar^3} \frac{2 \cdot 2}{3N} = \frac{\sqrt{8}\left(\sqrt{ma}\right)^3}{3N\pi^2\hbar^3}$$

(16)

and

$$\varepsilon_F = \frac{3^{\frac{2}{3}} N^{\frac{2}{3}} \pi^{\frac{4}{3}}\hbar^2}{2m(a)^2} = \frac{3^{\frac{2}{3}} \pi^{\frac{4}{3}}\hbar^2}{2m} \cdot \left(\frac{N}{a^3}\right)^{\frac{2}{3}}$$

(17)

Realizing that the last factor on the right of Equ. 17 is equal to a power of the particle density ($\rho_N = N/a^3$), one arrives at the important result that the Fermi energy is the higher, the higher the spatial density of the particles under consideration,

$$\varepsilon_F \propto \rho_N^{\frac{2}{3}}$$

(18)

As an example, Cu has one free electron per atom in the conduction band. Hence, the spatial electron density of copper is $\rho_N \approx 8\cdot 10^{22}\, cm^{-3}$. Equation 17 the predicts a Fermi energy of $\varepsilon_F = 7\ eV$.

The level density function $f(\varepsilon)$ of Equ. 14 was derived above under the assumption that the system was isolated from its surroundings. However, the surroundings can influence the electronic energy distribution. For example, it is shown elsewhere that, if the electronic system is held at the constant temperature of a heat bath of temperature T, then the energy distribution of the electrons becomes equal to

$$f(\varepsilon) \propto \sqrt{\varepsilon} \cdot e^{-\frac{\varepsilon}{kT}} \tag{19}$$

This is a very familiar result. It is comforting that the treatment of the quantal electron system leads to an energy distribution consistent with the Boltzmann distribution.

The above discussion pertained to the energy spectrum and the number of states available to any single quantal particle in a box. Now, consider N particles together in the same gas, each having the same opportunity to occupy a given energy level (neglecting the Pauli exclusion principle, for the time being). Then, according to Equ. V.81, the total number of N-particle states is the product of N identical factors, Ω, each representing the single-particle states available to any one of the N particles. The number of states can be evaluated as before for a single particle, except that there are $3N$, instead of 3, coordinates. In addition, the available energy U is the sum of all individual energies,
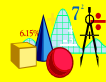
$$U = \sum_{n=1}^{N} \varepsilon_n \qquad (V.20)$$

For a single particle, the energy ε was distributed randomly over *3* independent degrees of freedom. Now, the problem consists in distributing the total energy *U* over *3N* degrees of freedom. Therefore, the number of states (or level density, or degeneracy) is approximately given by

$$\Omega_N(U) \approx \frac{\sqrt{2}^N \left(\sqrt{m}\right)^{3N}}{\left(3\pi^2 \hbar^3\right)^N} V^N U^{3N/2} \propto V^N U^{3N/2} \qquad (21)$$

Here, $V = a^3$ stands for the volume of the gas (not the potential!). The qualification "approximately" refers to the neglect of the Pauli Principle disallowing certain combinations and the fact that $N \pi 1$ has been assumed.

The above expression is an over-estimation for the quantal gas, because of the indistinguishability of the particles. Any renumbering of the sequence {*1, 2, 3, 4,.....,N*} refers to the same quantal state. There are *N!* possible permutations of these numbers. Therefore, a better approximation of the number of states of the *N*-particle system is given by dividing the expression of Equ. V.20 by (see Stirling's Formula)

$$N! \approx \left(N/e\right)^N \qquad (22)$$

equivalent to

$$\ln N! \approx N(\ln N - 1) \qquad (22a)$$
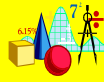
Finally, one obtains an expression for the number of N-particle states for indistinguishable particles (Bosons or Fermions):

$$\ln\Omega(U,V,N) \approx \ln\left(\frac{\Omega_N}{N!}\right) \approx \frac{3}{2}N\ln\frac{U}{N} + N\ln\frac{V}{N} + N\cdot const.$$

(23)

or

$$\Omega(U,V,N) \approx \left(\frac{\sqrt{2m^3}}{3\pi^2\hbar^3}\right)^N \cdot \left(\frac{U}{N}\right)^{3N/2} \cdot \left(\frac{V}{N}\right)^N$$
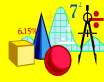
(24)

where the constant factor is generally not important in the use of these equations. Hence, the *number of states per particle is proportional to the volume per particle (V/N) and depends on the available energy per particle as (U/N)³/².*

Equation V.23 is proportional to the macroscopic entropy, which can be written as

$$S = k\ln\Omega(U,V,N) \approx Nk\left(\frac{3}{2}\ln\frac{U}{N} + \ln\frac{V}{N} + const\right).$$

(25)

Occupation Number Distribution of a Fermi Gas

So far, only the ***number*** of single-particle levels for a quantal gas of indistinguishable particles (Fermions or Bosons) has been considered. For a macroscopic volume, this number is very large, much larger than the number of particles in a mole. This raises the question as to how the particles are distributed over the various levels. These

energy configurations are the (energy projections of the) ***microstates*** of the *N*-particle system. On general grounds, one can postulate already, that the largest entropy is associated with the most random distribution of the particles over the available single-particle levels. This distribution is calculated below.

Let the index *i* number the single-particle levels, ε_i their energies and g_i their degeneracies (number of states at each energy level ε_i). Considering the quantal *N*-particle system as isolated, the following conservation laws (***constraints***) have to be valid,

$$\sum_i n_i = N \tag{26}$$

i.e., particle number conservation and

$$\sum_i n_i \varepsilon_i = U \tag{27}$$

i.e., energy conservation.

The number of *N*-particle configurations, the total degeneracy Ω, is given by the number of ways the numbers n_i of particles per level *i* can be distributed over the g_i substates of the respective level. For one level *i,* there are

$$\varpi_i = \frac{g_i!}{n_i!(g_i - n_i)} \tag{28}$$

ways to distribute n_i particles over the g_i states of the level. For many levels, the numbers of particles occupying them are zero, $n_i = 0$. In any case, the total degeneracy is given by the product of expressions of the type of Equ. 28 for every level,
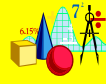
$$\Omega = \prod_i \varpi_i = \prod_i \frac{g_i!}{n_i!(g_i - n_i)} \tag{29}$$

The most probable configurations correspond to maximum entropy, i.e., the maximum degeneracy Ω. This maximum is deduced from the constrained variational condition,

$$\delta\left\{\ln\Omega - \alpha\sum_i n_i - \beta\sum_i n_i\varepsilon_i\right\} = 0 \tag{30}$$

Here, the logarithm of Ω has been chosen for convenience. The constraints, Equs. (26) and (27), have been included with the *La-grange multipliers* α and β. Applying the variation yields

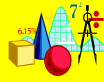$$\delta\ln\Omega - \sum_i\left\{\alpha - \beta\varepsilon_i\right\}\delta n_i = 0 \tag{31}$$

Evaluating the first terms is simple for large degeneracies, when the *Stirling formula*

$$\ln(n!) \approx n\ln n - n \tag{32}$$

can be used, i.e., for large numbers $n_i\pi 1$. Then, one obtains

$$\ln\Omega = \ln\prod_i\frac{g_i!}{n_i!(g_i - n_i)} =$$
$$= \sum_i\left\{g_i(\ln g_i - 1) - n_i(\ln n_i - 1) - (g_i - n_i)[\ln(g_i - n_i) - 1]\right\} = \tag{33}$$
$$= \sum_i\left[n_i\ln(\frac{g_i}{n_i} - 1) - g_i\ln(1 - \frac{n_i}{g_i})\right]$$

Inserting this result into Equ. 31 gives

$$\sum_i \left[\ln\left(\frac{g_i}{n_i} - 1 \right) - \alpha - \beta\varepsilon_i \right] \cdot \delta n_i = 0 \tag{34}$$

for the set $\{n_i\}$ maximizing the degeneracy Ω with the two constraints of particle and energy conservation. Now, since the variations δn_i are arbitrary, each term in the sum of Equ. 34 has to vanish, i.e., for every i

$$\left[\ln\left(\frac{g_i}{n_i} - 1 \right) - \alpha - \beta\varepsilon_i \right] \cdot \delta n_i = 0 \tag{35}$$

This is equivalent to

$$\frac{g_i}{n_i} = 1 + e^{\alpha + \beta\varepsilon_i} \tag{36}$$

and

$$\langle n_i \rangle = \left. \frac{n_i}{g_i} \right|_{\max\Omega} = \frac{1}{1 + e^{\alpha + \beta\varepsilon_i}} \tag{37}$$

This is the average number of particles per state such that the total degeneracy Ω is maximized. For all practical purposes, $\langle n_i \rangle$ is the average occupation of single-particle states of a Fermi gas. The simplifications made limit the application of this formula to large single-particle level degeneracies and large particle numbers. The parameters α and β have to be determined in an independent consideration. Anticipating the results of such a consideration for a grand-canonical situation,

$$\alpha = -\frac{\mu}{k_B T} \qquad \beta = \frac{1}{k_B T} \tag{38}$$
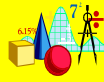
these parameters are determined by the chemical potential μ and the temperature T. For ***Fermions***

$$\langle n_i \rangle = \frac{1}{1 + e^{-\frac{\mu - \varepsilon_i}{k_B T}}} \tag{39}$$

For ***Bosons***, a similar consideration yields

$$\langle n_i \rangle = \frac{1}{e^{-\frac{\mu - \varepsilon_i}{k_B T}} - 1} \tag{39}$$