Quantum Statistics

This is an article from my home page: www.olewitthansen.dk

Ole Witt-Hansen   2016

Content

Acknowledgement

The task of classical statistical mechanics is to give a theoretical foundation of the empirical laws of thermodynamics, and enable us to compute the functions of state, i.e. temperature T, pressure P, energy E and entropy S, when the mechanical constitution of the system is statistically defined.

In 1968 I attended a series of post graduate lectures given by Professor C. Møller on Statistical Mechanics at the Niels Bohr Institute in Copenhagen Denmark.
His notes in Danish were from1962, written on a typewriter, belonging to that period, and supplied with hand written formulas and drawings.

The second part of his lecture notes were dedicated to Quantum Statistics, and his presentation is at a substantial high theoretical level.
In spite of this, I still find his presentation of the subject, although on a quite stringent theoretical ground is more comprehensible than i.e. Landau and Lifshitz's classic book on Statistical mechanics.

This presentation relies heavily on the lecture notes by professor Møller. Some less important parts have been omitted, and some sections have been elaborated to strengthen the clarity. At the same time it is adapted to a more modern approach of text books in theoretical physics, without losing its original rigor.
I have translated his lectures to English, because I think that the English spoken physicist community, should benefit from Professor Møller's excellent Lectures.

August 2016   Ole Witt-Hansen

1. Gibb's ensembles in Statistical Mechanics

Previously in "Statistical Mechanics 1", we have assumed that the systems we have dealt with were subject to the laws of classical mechanics and were described by equations of motion in the Hamiltonian framework.

Analytical mechanics is characterized by describing a mechanical system in generalized coordinates usually denoted: q_1, q_2, q_3, ..., q_n. Differentiating with respect to time is indicated with a bullet above the variable e.g. $\dot{q} = dq/dt$, so that $\dot{q}_1, \dot{q}_2, \dot{q}_3, ..., \dot{q}_n$ represents the generalized velocities.

Using the Lagrange approach, the kinetic energy is written as:

$$T = T(\dot{q}_1, \dot{q}_2, \dot{q}_3, ... \dot{q}_n, q_1, q_2, q_3, ..., q_n),$$

and the potential energy:

$$U = U(q_1, q_1, q_1, ..., q_n)$$

The Lagrange function L is defined as:

(1.1) $$L = T - U$$

The Euler-Lagrange equations of motion are

(1.2) $$\frac{\partial L}{\partial q_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} = 0$$

The generalized momentum is defined by the equation:

(1.3) $$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

The Hamilton function i.e. the energy is defined by:

(1.4) $$H = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$$

From a Legendre transformation of the Lagrangian, one may obtain the Hamiltonian Canonical Equations i.e. the equations of motion: The a's are a shorthand notation for the external parameters

(1.5) $$\frac{dq_k}{dt} = \frac{\partial H(p,q,a)}{\partial p_k} \qquad \frac{dp_k}{dt} = -\frac{\partial H(p,q,a)}{\partial q_k}$$

If D is a physical quantity of the generalized coordinates and momenta, we may write.

(1.6) $$\frac{dD}{dt} = \frac{\partial D}{\partial t} + \sum_{k=1}^{n}\left(\frac{\partial D}{\partial q_k}\dot{q}_k + \frac{\partial D}{\partial p_k}\dot{p}_k\right)$$

Furthermore if D does not explicitly depend on time, so $\dfrac{\partial D}{\partial t} = 0$, then (1.6) becomes:

(1.7)
$$\frac{dD}{dt} = \sum_{k=1}^{n}\left(\frac{\partial D}{\partial q_k}\dot{q}_k + \frac{\partial D}{\partial p_k}\dot{p}_k\right)$$

Using the Hamilton canonical equations:

$$\frac{dq_k}{dt} = \frac{\partial H(p,q,t)}{\partial p_k} \qquad \frac{dp_k}{dt} = -\frac{\partial H(p,q,t)}{\partial q_k}$$

(1.6) can be written as:

(1.8)
$$\frac{dD}{dt} = \frac{\partial D}{\partial t} + \sum_{k=1}^{n}\left(\frac{\partial D}{\partial q_k}\frac{\partial H}{\partial p_k} - \frac{\partial D}{\partial p_k}\frac{\partial H}{\partial q_k}\right) = \frac{\partial D}{\partial t} + \sum_{k=1}^{n}\{D,H\}_k$$

Where the Poisson parenthesis $\{D,H\}_k$ is defined by

$$\{D,H\}_k = \frac{\partial D}{\partial q_k}\frac{\partial H}{\partial p_k} - \frac{\partial D}{\partial p_k}\frac{\partial H}{\partial q_k}$$

If F is a physical expression that does not explicitly depend on time i.e. $\dfrac{\partial F}{\partial t} = 0$, then F is an integral to the equations of motion, if the Poisson parenthesis vanish:

(1.9)
$$\frac{dF}{dt} = 0 \quad \Leftrightarrow \quad \{H,F\} = 0 \quad \Leftrightarrow \quad \frac{\partial F}{\partial q_k}\frac{\partial H}{\partial p_k} - \frac{\partial F}{\partial p_k}\frac{\partial H}{\partial q_k} = 0$$

Specifically, if $F = q_k$ or $F = p_k$, then according to (1.8)

(1.10)
$$\dot{q}_k = \frac{dq_k}{dt} = \{q_k,H\} = \frac{\partial q_k}{\partial q_k}\frac{\partial H}{\partial p_k} - \frac{\partial q_k}{\partial p_k}\frac{\partial H}{\partial q_k} = \frac{\partial H}{\partial p_k}$$

(1.11)
$$\dot{p}_k = \frac{dp_k}{dt} = \{p_k,H\} = \frac{\partial p_k}{\partial q_k}\frac{\partial H}{\partial p_k} - \frac{\partial p_k}{\partial p_k}\frac{\partial H}{\partial q_k} = -\frac{\partial H}{\partial q_k}$$

We shall use this formulation in the generalization of Classical Statistical Mechanics to Quantum Statistic.

Specifically if $P(p,q,t)$ is the probability density in phase space, then according to Liouvilles theorem:

(1.12)
$$\frac{dP}{dt} = 0 \quad \Leftrightarrow \quad \frac{\partial P}{\partial t} + \sum_{k=1}^{n}\left(\frac{\partial P}{\partial q_k}\frac{\partial H}{\partial p_k} - \frac{\partial P}{\partial p_k}\frac{\partial H}{\partial q_k}\right) = 0$$

The mean value of a physical variable $F(p,q)$ is:

(1.13)
$$\overline{F}(p,q) = \int\int F(p,q)P(p,q,t)dpdq$$

Where the probability density is normalized to 1.

$$\int\int P(p,q,t)dpdq = 1$$

2. Gibb's ensembles in Quantum Statistics

Before we introduce quantum mechanical systems, we shall present the two different views of the dynamics of quantum mechanical systems.
In the Heisenberg Picture the dynamical variables are Hermitian time dependent operators. Their variation with time are in principle the same as for classical systems, with the "only" difference that the Poisson parenthesis are substituted by commutators between operators.

(2.1)
$$\dot{q}_k = \frac{1}{i\hbar}[q_k, H] = \frac{1}{i\hbar}(q_k H - Hq_k)$$

(2.2)
$$\dot{p}_k = \frac{1}{i\hbar}[p_k, H] = \frac{1}{i\hbar}(p_k H - Hp_k)$$

In the Schrödinger Picture, on the other hand, the dynamical variables are time independent operators, which act on a time dependent state, the complex wave function $\psi(x,y,z,t)$.
The changes in the wave function $\psi(x,y,z,t)$, is given by the Schrödinger equation:

(2.3)
$$i\hbar\frac{\partial \psi}{\partial t} = H\psi$$

The probability, that a particle is found within a volume $dV = dxdydz$ at a time t is given by $|\psi|^2$ the absolute square of the complex wave function ψ.

The momentum p is calculated by the operator: $i\hbar\frac{\partial}{\partial x}$.

If the Hamilton function is: $H = \frac{\vec{p}^2}{2m} + U(\vec{x})$, where U denotes the potential, the Schrödinger equation takes the more familiar form:

(2.4)
$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(\vec{x})\psi = i\hbar\frac{\partial \psi}{\partial t}$$

∇^2 is the Laplace operator: $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

There is, however, an essential difference between the classical mechanical systems, and the quantum mechanical systems, namely for the latter, one always have to operate with ensembles, even if the system is in a certain state. The mean of a certain operator acting on the ensemble is given by the scalar product.

(2.5) $< L >= \psi \cdot L\psi = \int \psi L\psi dV$

For thermodynamic systems, however, a state is practically never a pure state, but rather a so called mixture of states, which is described by the density operator $\rho(p,q,t)$.

In the following, we shall adapt to the Schrödinger representation, where ρ is a hermitian operator with eigenvalues in the interval from 0 to 1 only. The mean value of a physical quantity $L(p,q)$, in an ensemble, corresponding to the mixture of states in question, is given by the formula:

(2.6) $< L >= tr\{L\rho\} = tr\{\rho L\}$

Where tr means trace, that is, the sum of diagonal elements in a matrix representation.
In an arbitrary representation, the trace of an operator is defined as the sum of the diagonal elements ξ of the matrix, which represents the operator in this representation. Formally:

(2.7) $tr\{A\} = \sum_{\xi'} < \xi'| A | \xi'>$

The summation may be replaced by integration. The trace is independent of the representation ξ.

The formula (2.7) is written with the quantum mechanical notation, invented by P.A.M Dirac, where the state $<\psi|$ is called a "*bra vector* ", and the state $|\psi>$ is called a "*ket vector*". The *ket* vectors are the dual vector space to the *bra* vectors.
Thus $< \psi | A | \psi >$ is the expected value of the operator A, when acting on the state ψ.
Specifically for the density ρ:

(2.8) $tr\{\rho\} = \sum_{\xi'} < \xi'| \rho | \xi'> = 1$

In the ξ -representation (2.5) becomes:

(2.9) $< L >= tr\{L\rho\} = \sum_{\xi'} \sum_{\xi''} < \xi'| \rho | \xi''> < \xi''| \rho | \xi'>$

The case of a pure state ψ expanded on the complete set $| \xi >$, where $\rho = |\psi><\psi|$:

(2.10) $< \xi'| \rho | \xi''>= \psi(\xi')\psi *(\xi'')$

In this case (2.8) is the same as (2.5).

ρ is an idempotent operator i.e. $\rho^2 = \rho$, because: $\rho = |\psi><\psi|$ follows $\rho^2 = |\psi><\psi|\cdot|\psi><\psi| = |\psi><\psi|$

In general the density operator is time dependent (also in the Schrödinger representation), so it satisfies the differential equation:

(2.11) $\dfrac{\partial \rho}{\partial t} + \dfrac{1}{i\hbar}[\rho, H] = 0$

Which is the quantum mechanical analog to Liouville's theorem: The probability density in the development of a system in phase space does not change with time. In other words, the density operator, which characterizes the quantum mechanical ensemble plays the same role as the probability density function $P(p,q,t)$ in the classical statistical mechanics[1].

From (2.6) and (2.11) follows the time derivative of a physical quantity $L(p,q)$.

(2.12)
$$\frac{d}{dt} < L >= tr\{L\frac{\partial\rho}{\partial t}\} = \frac{1}{i\hbar}tr\{L[H,\rho]\}$$
$$= \frac{1}{i\hbar}tr\{(LH-HL)\rho\} =< [L,H] >$$

In generally (2.12) is non zero. Only if L is an integral to the equations of motion, i.e. when L commutates with H: $[L,H] = 0$, then L is a constant of motion.

There are, however, ensembles in which the mean of arbitrary physical quantity L is constant in time, namely when ρ commutates with H.

(2.13)
$$[\rho,H]=0 \quad \Rightarrow \quad \frac{\partial\rho}{\partial t}=0$$

In that case the ensemble is in statistical equilibrium. It occurs for example, when $\rho(p,q,t)$ is a function f of the Hamilton operator alone. That is, when the ensemble is in statistical equilibrium.

(2.14)
$$\rho = f(H,a,T)$$

3. Canonical ensembles of quantum mechanical systems

To establish the mixture of states which describe a quantum mechanical system with a certain temperature we may proceed exactly, as we did for classical systems[1], when we replace the probability density function P, by the density matrix (operator) ρ.
For a system composed of two independent parts with density operators ρ_1 and ρ_2, the density matrix for the composed system is simply:

(3.1)
$$\rho_{1+2} = \rho_1\rho_2 = \rho_2\rho_1$$

Leading as described in detail in[1] to an exponential dependence of ρ on H, and further to the canonical density matrix.

(3.2)
$$\rho = e^{\frac{\psi(a,\theta)-H(p,q,a)}{\theta}} \qquad where \qquad \theta = kT$$

$\psi(a,\theta)$ is a real function, defined by the equation: $tr\,\rho = 1$, or by the equation:

---

[1] Ole Witt-Hansen: Statistical Mechanics 1

$$(3.3) \qquad e^{-\frac{\psi(a,\theta)}{\theta}} = tr\left\{ e^{-\frac{H(a)}{\theta}} \right\}$$

The mean value of an arbitrary physical quantity in the canonical ensemble is now, according to (3.3) and (2.9).

$$(3.4) \qquad <L> = tr\{L\rho\} = tr\left\{ Le^{\frac{\psi-H}{\theta}} \right\} = e^{\frac{\psi}{\theta}} tr\left\{ Le^{-\frac{H}{\theta}} \right\}$$

And according to (3.3)

$$(3.5) \qquad <L> = \frac{tr\left\{ Le^{-\frac{H}{\theta}} \right\}}{tr\left\{ e^{-\frac{H}{\theta}} \right\}}$$

We introduce the "density exponent" η by:

$$(3.6) \qquad \eta = \ln\rho = \frac{\psi - H}{\theta}$$

As it is the case in Statistical Mechanics 1, we can now identify ψ, $<H>$ and $-k<\eta>$ (where k is Boltzmann's constant) with the *free energy*, the *internal energy*, and the *entropy* respectively, since the relations between these quantities are exactly the same as the relations derived in the classical statistical mechanics. As a consequence we also have:

$$(3.7) \qquad d\psi = <\eta> d\theta - \sum_{l=1}^{m} <A_l> da_l$$

Where $\theta = kT$, a_l are the external parameters, A_l are the generalized forces, and

$$(3.8) \qquad <\eta> = \frac{\psi - <H>}{\theta} \qquad \Leftrightarrow \qquad \psi = <H> + \theta<\eta>.$$

From (3.7) we get immediately:

$$(3.9) \qquad <\eta> = \frac{\partial\psi}{\partial\theta} \qquad <A_l> = -\frac{\partial\psi}{\partial a_l} \qquad <H> = \psi - \theta\frac{\partial\psi}{\partial\theta}$$

In much the same manner, as we did in the classical statistical mechanics, we can obtain expressions for the fluctuations e.g.

$$(3.10) \qquad \sigma^2(H) = <(H - <H>)^2> = -\theta^3\frac{\partial^2\psi}{\partial\theta^2} = \theta^2\frac{\partial<H>}{\partial\theta}$$

This and similar formulas are the same as for classical systems, but $\psi(\theta,a)$ are generally different from the corresponding classical systems.

For example the equipartion principle i.e. that the mean kinetic energy for a an atomic particle in thermodynamic equilibrium is equal to $\frac{1}{2}kT$ for each degree of freedom is not in general valid for quantum mechanical systems.

Let us accordingly choose a representation of the quantum mechanical system , where the complete set of observable $\{\xi\}$ is a set of quantities $\{\alpha\}$, which are integrals to the equations of motion, that is, commutates with the Hamilton operator.

(3.11)
$$[\{\alpha\},H]=0$$

In the $\{\alpha\}$ representation both H and $\rho=e^{\frac{\psi(a,\theta)-H(p,q,a)}{\theta}}$ are on diagonal form, with the eigenvalues

H' and $\rho'=e^{\frac{\psi-H'}{\theta}}$, represented by diagonal matrices.

We shall assume, that H and the $\{\alpha\}$ have only discrete eigenvalues, which is met for practically all thermodynamic systems. So we can numerate the eigenvalues for H and the $\{\alpha\}$, as:

$$E_1(a), E_2(a), E_3(a),....., E_i(a),...... \quad\quad and \quad\quad \alpha_1',\alpha_2',\alpha_3',....,\alpha_i',...$$

We have made explicit the energy dependence of the external parameters (a) (e.g. position of a piston in a container) . In the α representation, the variables $\{\alpha\}$, H and ρ are given, by the matrices:

$$<i\,|\,\alpha\,|\,k>=(\alpha)_{ik}=(\alpha'_i)\delta_{ik}$$
(3.12)
$$<i\,|\,H\,|\,k>=H_{ik}=E_i\delta_{ik}$$
$$<i\,|\,\rho\,|\,k>=\rho_{ik}=e^{\frac{\psi-E_i(a)}{\theta}}\delta_{ik}$$

While any other physical quantity, will be given by: $<i\,|\,L\,|\,k>=L_{ij}$.
The trace of an arbitrary matrix A is: $tr\{A\}=\sum A_{ii}$.
So in the matrix representation (3.3):

$$e^{-\frac{\psi(a,\theta)}{\theta}}=tr\left\{e^{-\frac{H(a)}{\theta}}\right\}$$

becomes:

(3.13)
$$e^{-\frac{\psi}{\theta}}=\sum_i e^{-\frac{E_i(a)}{\theta}}=Z(a,\theta)$$

where Z usually is called the sum of states. The free energy $\psi(\theta, a)$ can therefore be calculated from Z, since:

(3.14)
$$\psi = -\theta \ln \left(\sum_i e^{-\frac{E_i(a)}{\theta}} \right) = -\theta \ln Z$$

The thermodynamic quantities: Free energy (F) , Potential energy (U), Entropy (S) etc, are obtained from (3.8) and the fluctuations can likewise be calculated from (3.9).

For a system in thermodynamic equilibrium at a certain temperature T, the probability p_i of finding the system in a certain stationary state $| i >$ is according to (3.12).

(3.15)
$$p_i = e^{\frac{\psi - E_i}{kT}}$$

Which is named the Boltzmann factor. According to (3.5) the mean value of an arbitrary physical quantity L, which has a diagonal form in this representation, can be written as:

(3.16)
$$< L >= \frac{\sum_i L_i e^{-\frac{E_i}{\theta}}}{\sum_i e^{-\frac{E_i}{\theta}}} = \frac{\sum_i L_i e^{-\frac{E_i}{\theta}}}{Z}$$

4. An ideal gas consisting of non identical particles

We shall first consider a single particle with mass m in a box with the sides a, b and c. From the elementary quantum mechanic we know that the stationary states are characterized by three positive numbers (n_1, n_2, n_3) and the corresponding energies are.

(4.1)
$$E_{n_1,n_1,n_1} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \qquad (n_1, n_2, n_3) = 1,2,3\ldots$$

From (3.13) we then get for the free energy for this system:

(4.2)
$$e^{-\frac{\psi}{\theta}} = \left(\sum_{n_1=1}^{\infty} e^{-\frac{\hbar^2 \pi^2 n_1^2}{2ma^2\theta}} \right) \left(\sum_{n_2=1}^{\infty} e^{-\frac{\hbar^2 \pi^2 n_2^2}{2mb^2\theta}} \right) \left(\sum_{n_3=1}^{\infty} e^{-\frac{\hbar^2 \pi^2 n_3^2}{2mc^2\theta}} \right) = Z(a,\theta)$$

To evaluate the sum of states, we have to evaluate a sum:

(4.3)
$$\sum_{n=1}^{\infty} e^{-\frac{\hbar^2 \pi^2 n^2}{2ml^2\theta}}$$

Introducing the variable $x = \frac{\hbar \pi}{l} n$, where $l = a,b,c$, and considering n as a continuous variable, so that $dx = \frac{\hbar \pi}{l} dn$ the sum can be transformed into an integral:

$$\frac{l}{\hbar\pi}\int_0^\infty e^{-\frac{x^2}{2m\theta}}dx$$

and using the fact that $\displaystyle\int_0^\infty e^{-t^2}dt = \frac{\sqrt{\pi}}{2}$ we find:

(4.4) $$\sum_{n=1}^\infty e^{-\frac{\hbar^2\pi^2 n^2}{2ml^2\theta}} = \frac{l}{\hbar\pi}\int_0^\infty e^{-\frac{x^2}{2m\theta}}dx = \frac{l\sqrt{2m\pi\theta}}{2\pi\hbar} = \frac{l\sqrt{2m\pi\theta}}{h}$$

From which we from (4.2) get the expression for the free energy ψ.

(4.5) $$e^{-\frac{\psi}{\theta}} = \frac{abc(\sqrt{2m\pi\theta})^3}{h^3} = \frac{V(2m\pi\theta)^{\frac{3}{2}}}{h^3}$$

If we consider a system of N particles with no mutual interaction, the total energy is the sum of the energies of the individual particle, but since the energy appears as an exponent of the exponential function, we shall multiply the results for a single particle to get the expression (4.5) for the free energy.

(4.6) $$Z(a,\theta) = e^{-\frac{\psi}{\theta}} = \frac{V^N(2\pi\theta)^{\frac{3N}{2}}(m_1 m_2 m_3 \cdots m_N)^{\frac{3}{2}}}{h^{3N}}$$

From

(3.7) $$d\psi = <\eta> d\theta - \sum_{l=1}^m < A_l > da_l$$

(3.9) $$<\eta> = \frac{\partial\psi}{\partial\theta} \qquad < A_l > = -\frac{\partial\psi}{\partial a_l} \qquad <H> = \psi - \theta\frac{\partial\psi}{\partial\theta}$$

(3.8) $$\psi = <H> + \theta<\eta>$$

(3.14) $$\psi = -\theta\ln\left(\sum_i e^{-\frac{E_i(a)}{\theta}}\right) = -\theta\ln Z$$

and (4.6) it follows:

(4.7) $$\psi = -\theta N \ln V - \tfrac{3N}{2}\theta\ln(2\pi\theta) - \tfrac{3}{2}\theta((m_1 m_2 m_3 \cdots m_N) + 3N\ln(h)$$

$$\frac{\partial\psi}{\partial\theta} = -N\ln V - \tfrac{3N}{2}\ln(2\pi\theta) - \tfrac{3N}{2} - \tfrac{3}{2}((m_1 m_2 m_3 \cdots m_N)$$

$$\theta\frac{\partial\psi}{\partial\theta} = -\theta N\ln V - \tfrac{3N}{2}\theta\ln(2\pi\theta) - \tfrac{3N}{2}\theta - \tfrac{3}{2}\theta((m_1 m_2 m_3 \cdots m_N)$$

The total energy appears in the familiar form

(4.7) $\qquad < H >= \psi - \theta \dfrac{\partial \psi}{\partial \theta} = \frac{3N}{2}\theta = \frac{3N}{2}kT$

If we put the volume $V = a \cdot D$, where D is the cross section of the container, and a is the position of the piston, we have for the generalize force $F = <A_l>$.

(4.8) $\qquad F =< A_l >= -\dfrac{\partial \psi}{\partial a} = \theta N \dfrac{\partial}{\partial a}\ln(aD) = \dfrac{\theta N}{a} = \dfrac{\theta N D}{V}$

From which we get the pressure:

(4.9) $\qquad P = \dfrac{F}{D} = \dfrac{\theta N}{V} = \dfrac{NkT}{V}$

Being the (classical) equation of state for ideal gasses.

The derivation of (4.5), (4.7) and (4.9) relies on the assumption that all the masses of the particles are different, that they do not interact, and also that:

(4.10) $\qquad \dfrac{\hbar^2 \pi^2}{2ml^2\theta} << 1 \quad or \quad T >> \dfrac{\hbar^2 \pi^2}{2ml^2 k}.$

We define $T_0 \equiv \dfrac{\hbar^2 \pi^2}{2ml^2 k}$. When l is about 0.01 m, and even if we insert m as the mass of the electron, then T_0 becomes of the order 10^{-10} degrees, our approximation is very good indeed.

Under the conditions stated above, quantum mechanics give the same results as above, but for identical particles, however, there appear some typical quantum mechanical effects for example for an electron gas in metals. Also Maxwell's distributions of velocities

(4.11) $\qquad P(v) = \dfrac{4}{\sqrt{\pi}}\left(\dfrac{m}{2kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$

Where $P(v)dv$ is the probability of finding a particle with a velocity in the interval $[v, v + dv]$, in a system in thermodynamic equilibrium, is still valid within the quantum mechanical framework described above. There may, however, be a minor difference in the fluctuations.

5. The linear harmonic oscillator. Solid crystal materials

From elementary quantum mechanics, we are familiar with the stationary states of the harmonic oscillator are characterized by an integral number n, having the values $n = 0, 1, 2, 3,\ldots$ with the corresponding eigenvalues:

(5.1) $\qquad E_n = (n+\tfrac{1}{2})\hbar v \quad$ Where $\quad v = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$

The constant k is the "elastic constant" from Hooke's law: $F = kx$, and m is the mass of the particle. The sum of states Z becomes in this case:

$$(5.2) \qquad Z = e^{-\frac{h\nu}{2\theta}} \sum_{n=1}^{\infty} (e^{-\frac{h\nu}{\theta}})^n$$

This represents an infinite geometric series with a quotient $x = e^{-\frac{h\nu}{\theta}}$, where $x < 1$.

$$(5.3) \qquad Z = \frac{e^{-\frac{h\nu}{2\theta}}}{1 - e^{-\frac{h\nu}{\theta}}}$$

$$(5.4) \qquad \ln Z = -\frac{h\nu}{2\theta} - \ln(1 - e^{-\frac{h\nu}{\theta}}) \qquad \text{and} \qquad \psi = -\theta \ln Z$$

From (4.7)

$$<H> = \psi - \theta \frac{\partial \psi}{\partial \theta} = -\theta \ln Z + \theta \ln Z + \theta^2 \frac{\partial \ln Z}{\partial \theta} = \theta^2 \frac{\partial \ln Z}{\partial \theta}$$

$$(5.5) \qquad <H> = \theta^2 \frac{\partial \ln Z}{\partial \theta} \qquad \Rightarrow \qquad <H> = \frac{h\nu}{2} + \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

The first term i (5.5) is the so called zero point energy. It is independent of the temperature, and since the internal energy only is defined apart from a constant, we may use the following expression for the energy of a harmonic oscillator in thermodynamic equilibrium.

$$(5.6) \qquad E = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} = kTP(\frac{h\nu}{kT})$$

Where $P(x) = \frac{x}{e^x - 1}$ is called the Planck factor. Only for high temperatures, where $x \to 0$ (or the classical limit $\hbar \to 0$), we have $P(x) \to 1$, and the expression (5.6) passes into the expression for a classical harmonic oscillator.

We obtain the first important use of (5.6), when we consider that a massive crystalline material consisting of N atoms (or ions). In the first approximation, it can be treated as $3N$ independent but identical harmonic oscillators with the same frequency ν. To find the energy, we simply add the energies from the $3N$ oscillators.

$$(5.7) \qquad E = 3NkTP(\frac{h\nu}{kT}) = 3NkT\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

By differentiation with respect to T, we get the heat coefficient for constant volume c_V.

(5.8) $c_V = 3NkT\, E(\dfrac{h\nu}{kT})$ where $E(x) = \dfrac{\frac{1}{2}x^2}{\cosh x - 1}$

Which qualitatively corresponds with the experience.

The formulas (5.7) and (5.8) were first derived by Einstein in a famous paper, and they were one of the first steps to support Planck's original quantum hypothesis. In the further development done by Debye, Karman and Born, the real frequencies were inserted, and the results became also quantitative in correspondence with experimental data.

6. Planck's law for black body radiation

Above we calculated the energy of a quantum harmonic oscillator as:

(6.1) $E = \dfrac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$

We shall now look at the energy distribution of radiation of a system consisting of atoms in thermodynamic equilibrium, meaning that it does not emit or receive radiation or other forms of energy. The radiation emitted from such a body has been given a somewhat misleading name (e.g. when applied to the sun), namely: Black Body Radiation.

We assume that the body consists of harmonic oscillators, each having a frequency ν, and emitting electromagnetic radiation with an energy given by (6.1).

The only thing we need to know is therefore the density $\rho(\nu)$ of oscillators with frequency ν.
To establish this, we look at a one dimensional stationary wave confined by a length L.
Below is illustrated the familiar modes:

p = 1:   a = $\frac{\lambda}{2}$ p = 2:   a = $2\cdot\frac{\lambda}{2}$ p = 3:   a = $3\cdot\frac{\lambda}{2}$
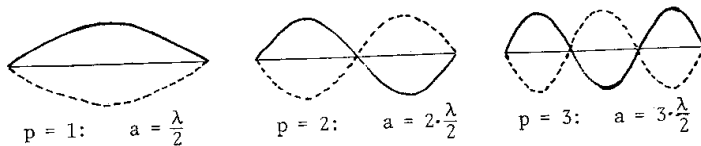
The relation between the length L of the confinement and the individual modes is seen to be:

(6.2) $\lambda = \dfrac{2L}{n}$, $n = 1,2,3....$

We are, however interested in finding the number of waves with a certain frequency, so we

introduce the number of wave per length as $\kappa = \dfrac{2}{\lambda} = \dfrac{n}{L}$ $\Leftrightarrow$ $n = L\kappa$ $\Rightarrow$ $dn = L d\kappa$.

In a box with 3 dimensions, we have: $dn_x dn_y dn_z = L^3 d\kappa_x d\kappa_y d\kappa_z$.

When we are dealing with electromagnetic radiation, we have however two possibilities for polarisations, that we must take into account by adding a factor 2.

(6.3) $dn_x dn_y dn_z = 2L^3 d\kappa_x d\kappa_y d\kappa_z$

Introducing polar coordinates for the wave number, where we in ordinary space have:

$dV = 4\pi r^2 dr$ (Area of a sphere time its thickness dr), we get, since $\kappa = \dfrac{2}{\lambda} = \dfrac{2v}{c}$

(6.4) $$\rho(v)dv = 2L^3 4\pi \kappa^2 d\kappa = V\frac{8\pi v^2}{c^3}dv$$

The density per unit volume is therefore:

$$\rho_V(v) = \frac{\rho(v)}{V}dv = \frac{8\pi v^2}{c^3}dv$$

Multiplying this result with (6.1), the energy of one oscillator, we get Planck's famous formula for the intensity distribution of the black body radiation, that is, the distribution of electromagnetic radiation for a body in thermodynamic equilibrium.

(6.5) $$I(v)dv = \frac{8\pi h v^3}{c^3(e^{\frac{hv}{kT}} - 1)}dv$$

In the limit of high temperatures or in the limit where $\hbar \to 0$, we may expand $e^{\frac{hv}{kT}} - 1 \approx \dfrac{hv}{kT}$, and

Planck's formula becomes:

(6.6) $$I(v)dv = \frac{8\pi h v^3}{c^3 \dfrac{hv}{kT}}dv = \frac{8\pi v^2}{c^3}kTdv$$

This is the Rayleigh –Jeans formula, derived from Maxwell's equations. The Rayleigh –Jeans formula was one of the most serious obstacles to the classical description of electromagnetism, since the density of radiation goes to infinity as the square of the frequency, the so called "ultraviolet catastrophe". This led Planck to introduce the idea of quantization of energy, obtaining his famous formula for the energy of a photon: $E = hv$.

The total energy radiated can then be calculated as:

(6.7) $$\int_0^\infty I(v)dv = \int_0^\infty \frac{8\pi h v^3}{c^3(e^{\frac{hv}{kT}} - 1)}dv$$

Making the substitution: $x = \dfrac{hv}{kT} \Rightarrow v = \dfrac{kT}{h}x \Rightarrow dv = \dfrac{kT}{h}dx$

The integral is transformed into:

(6.8) $$\int_0^\infty I(v)dv = \frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3}{(e^x - 1)}dx$$

The integral has no analytic solution expressed by standard functions, but it is a numerical value. The essential content of (6.8) is, however, that the total intensity emitted per unit area is proportional to T^4. This is known as Stefan-Boltzmann's law.

(6.9) $$I = I(T) = \sigma T^4 \qquad \text{where} \quad \sigma = 5.67 \, 10^{-8} \, W/(m^2 K^4)$$

One may also derive Wiens law of displacement, which concerns the displacement of the frequency v_{max}, which is the frequency having the largest intensity I_{max}.
To do so we differentiate

(6.10) $$I(v)dv = \frac{8\pi h v^3}{c^3(e^{\frac{hv}{kT}} - 1)} dv$$

With respect to v and put $I'(v) = 0$. However the result is much easier to comprehend, if we use the variable $x = \dfrac{hv}{kT}$, and express the v dependence with x.

(6.11) $$I(x) = \frac{8\pi k^3 T^3}{c^3 h^2} \frac{x^3}{e^x - 1}$$

If we calculate $I'(x)$ (but we don't), $I'(x) = 0$ turns out to be a transcendent equation, but in any case the solution x_{max} will be a real number. So we will have:

(6.12) $$x_{max} = \frac{h v_{max}}{kT} = r \quad \Rightarrow \quad v_{max} = \frac{kT}{h} r$$
$$v_{max} = \kappa T$$

This is Wiens law of displacement. The frequency, which has the highest intensity grows linearly with the temperature.

Often this relation is written using the wavelength instead of frequency: $\lambda = \dfrac{c}{T}$.

We obtain the free energy of the black body radiation by summing over all oscillators, omitting the zero point energy $\frac{hv}{2}$ in each term.

(6.11) $$\psi = -\theta \sum_i \ln Z_i \qquad \text{with} \quad (5.4) \quad \ln Z_i = -\frac{hv}{2\theta} - \ln(1 - e^{-\frac{hv_i}{\theta}})$$

Replacing the sum with an integral over the frequencies, as we did in (6.4) with

$$\rho(v)dv = 2L^3 4\pi \kappa^2 d\kappa = V\frac{8\pi v^2}{c^3} dv$$

gives:

(6.12) $$\psi = V\frac{8\pi\theta}{c^3} \int_0^\infty \ln(1 - e^{-\frac{hv}{\theta}}) v^2 dv$$

To evaluate the integral we use the same substitution as we have done several times previously:

$$x = \frac{h\nu}{kT} \quad \Rightarrow \quad \nu = \frac{kT}{h}x \quad \Rightarrow \quad d\nu = \frac{kT}{h}dx$$

To transform the integral into:

(6.13)
$$\int_0^\infty \ln(1 - e^{-\frac{h\nu}{\theta}})\nu^2 d\nu = \left(\frac{kT}{h}\right)^3 \int_0^\infty x^2 \ln(1 - e^{-x})dx$$

The integral is then rewritten using a partial integration

(6.14)
$$\int_0^\infty x^2 \ln(1 - e^{-x})dx = \int_0^\infty \ln(1 - e^{-x})d\frac{x^3}{3} = \left[\ln(1 - e^{-x})\frac{x^3}{3}\right]_0^\infty - \frac{1}{3}\int_0^\infty \frac{x^3 e^{-x}}{(1 - e^{-x})}dx$$

The first term vanishes when inserting both the upper and lower limit

(6.15)
$$\int_0^\infty x^2 \ln(1 - e^{-x})dx = -\frac{1}{3}\int_0^\infty \frac{x^3}{(e^x - 1)}dx$$

When we remember (6.8) Stefan-Boltzmann's law.

(6.16)
$$\int_0^\infty I(\nu)d\nu = \frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3}{(e^x - 1)}dx = \sigma T^4 \quad \text{where } \sigma = 5.67\,10^{-8}\,W/(m^2 K^4)$$

We finally find for (6.12), using the constant $\left(\frac{kT}{h}\right)^3$ from (6.13) :

(6.17)
$$\psi = V\frac{8\pi\theta}{c^3}\int_0^\infty \ln(1 - e^{-\frac{h\nu}{\theta}})\nu^2 d\nu = -V\frac{8\pi k^4}{3c^3}\int_0^\infty \frac{x^3}{(e^x - 1)}dx = -\frac{V}{3}\sigma T^4$$

For the radiation pressure we find:

(6.18)
$$P = -\frac{\partial\psi}{\partial V} = \tfrac{1}{3}\sigma T^4 = \tfrac{1}{3}E$$

Finally we can obtain the entropy density $s = \frac{S}{V}$ from $S = -k <\eta> = -k\frac{\partial\psi}{\partial\theta} = -\frac{\partial\psi}{\partial T} = \tfrac{4}{3}V\sigma T^3$, so

(6.19)
$$s = \frac{S}{V} = \tfrac{4}{3}\sigma T^3$$

7. Ideal gas of identical particles. Boltzmann-, Bose- and Fermi-particles

We shall now consider a physical system, consisting of N identical particles, which do not interact with each other. Our first task is to determine the stationary states of such a system.

If H_i is the Hamilton operator for the i'th particle, then $H_i(p_i, q_i)$ is the same function for all of the particles, and the over all Hamilton operator is:

(7.1)
$$H = \sum_{i=1}^{N} H_i(p_i, q_i)$$

Since we have assumed that the particles do not interact, or interact so weakly, so it can be neglected, the stationary states will be composed of the individual stationary states of the particles. We shall refer to the individual stationary states with an index k.

Eigenstates: $\psi_1, \psi_2, \psi_3, ... \psi_k, ...$ with eigenvalues: $E_1, E_2, E_3, ... E_k, ...$, which because of the identity of the particles are the same for all particles.

(7.2)
$$H_i(p_i, q_i)\psi_k(q_i') = E_k \psi_k(q_i')$$

The apostrophe in q_i' should remind us, that whereas p, q and H are operators the q' in the argument of the wave function is an ordinary variable.

Let us for a moment assume that even if the particles carry the same physical properties, they can in some way be distinguished. Then we can simply obtain an eigenvector for the over all system, as the product of the individual eigenvectors.

(7.3)
$$\psi^{(i)} = \psi_{k_1}(q_1')\psi_{k_2}(q_2')\psi_{k_3}(q_3')\cdots\psi_{k_N}(q_N')$$
Having the energies:
(7.4)
$$E^{(i)} = E_{k_1} + E_{k_2} + E_{k_3} + ... + E_{k_N}$$

(7.3) represents a stationary state, where particle (1) is in the state k_1, particle (2) is in the state k_2..., particle (N) is in the state k_N.
 This obviously presupposes that the particles are distinguishable.

The energies (7.4) may also be characterized in another way:
Let the numbers N_1, N_2, ... N_{k1} ... denote the number of indices (k_1, k_2, ..., k_N) in (7.3) and (7.4), which are equal to 1, 2, 3, ..., k, ... respectively, which characterizes the singular states $\psi_1, \psi_2, \psi_3, ... \psi_k, ...$. Then the energy can also be written:

(7.5)
$$E^{(i)} = \sum_k N_k E_k \qquad \text{where} \qquad N = \sum_k N_k$$

Although the energy $E^{(i)}$ is completely established by the numbers N_1, N_2, ... N_{k1}, in which the state is, are in general not unique, since multiple states may have the same energy value.

To the state (7.3) belongs namely any state $Perm(\psi^{(i)})$ that is obtained by a permutation of the variables (q_1', q_1', q_1', ... q_1',) , , having the same eigenvalue. In general $Perm(\psi^{(i)})$ is different from $\psi^{(i)}$.
Only in the case, where the permutation exchange variables belonging to the same k_i values in (7.3) , we obtain the same state. Since N_k is the number of indices in (7.3) having the value k, the

number of different states must be (according to the formula for the number of permutations of N elements, where N_1, N_2,... N_k,... elements are identical.

$$(7.6) \qquad\qquad G^{(i)} = \frac{N!}{N_1! \cdot N_2! \cdots N_k! \cdots}$$

In other words $G^{(i)}$ is the level of degeneracy of the energy level $E^{(i)}$ with respect to the particles similarity of the Hamilton operator $H^{(i)}$.
There may also be casual a degeneracy, which comes from the fact that some of the individual particle energies are identical, but that is not our concern for the present.

The description above presupposes that, although the particles have exactly the same physical properties, they are in fact distinguishable. In quantum physics such particles do not exist, but they have achieved the name *Boltzmann particles* from his treatises on statistical physics.

For truly identical particles the quantum mechanical description can not be applied to the assumption that particle (1) is in state |1>, particle (2) is in state |2> etc. and that the stationary state of the system simply is the product og the states of individual particles. But rather that the stationary state of the system may be expressed by suitable sums of products of the type (7.3).

In the quantum mechanical description of nature, there exists two kinds of identical particles.

Bose-particles:
       Where the states realized in nature are completely symmetric in the particles coordinates.

Fermi-particles:
    Where the possible states are completely anti-symmetric in the particles coordinates.

We have therefore in the two cases: $Perm_{i,j}\{\psi(q_1,...,q_i,...,q_j,...q_N)\} = \pm\psi(q_1,...,q_j,...,q_i,...q_N)$, where the plus sign applies to Bose-particles.

I elementary quantum mechanics it is shown that a symmetric or anti-symmetric state will remain symmetric or anti-symmetric independently of its interaction with other particles (or mutual by interaction), and this is the reason why we have to distinguish between Bose- and Fermi-particles.

7.1 Bose- particles

In the case of non interacting Bose-particles, the various eigenfunctions of H may be listed as:

$$(7.7) \qquad \psi^{(i)} = \sum_{perm} Perm\{\psi_{k_1}(q_1')\psi_{k_2}(q_2')\cdots\psi_{k_j}(q_j')\cdots\psi_{k_N}(q_N')\}$$

Where the summation is extended over all $N!$ permutations of the variable $(q_1',q_2',...,q_j',...q_N')$.

$\psi^{(i)}$ is obviously an eigenvector to H with energies:

$$(7.8) \qquad\qquad E^{(i)} = \sum_k N_k E_k$$

Evidently $\psi^{(i)}$ is symmetric in the variables $(q_1', q_2', ..., q_j', ... q_N')$, which also reflects the fact that the particles are indistinguishable. Thus we may no longer say that particle (j) is in the state ψ_{k_1}, but rather that there are N_{k_1} particles in that state.

So we may only conclude that there are N_1 particles in the state ψ_1, N_2 particles in the state ψ_2, and so on. By the same token, $|\psi^{(i)}(q_1', q_2', ..., q_j', ... q_N')|^2$ is the probability of finding a particle at (q_1'), another at (q_2'), and so on, but not which particle. In accordance with that, there is only one total stationary state $\psi^{(i)}$ with the energy given by (7.8), corresponding to a set of values:

$$N_1, N_2, ... N_k, ...$$

$Perm(\psi^{(i)})$ is the same state as $\psi^{(i)}$ so the degeneracy of the energy $E^{(i)}$ is $G^{(i)} = 1$.
That an energy state is degenerated means that several states belong to the same energy level.

Thus we may characterize all eigenstates $\psi^{(i)}$ by the integers N_k, where $N = \sum_k N_k$

7.2 Fermi-particles

For Fermi particles, we have instead of (7.7)

(7.9) $$\psi^{(i)} = \sum_{perm} \varepsilon_{perm} Perm\{\psi_{k_1}(q_1')\psi_{k_2}(q_2')\cdots\psi_{k_j}(q_j')\cdots\psi_{k_N}(q_N')\}$$

Where $\varepsilon_{perm} = +1$ if the permutation is even, otherwise $\varepsilon_{perm} = -1$.
Obviously (7.9) is equal to the determinant:

(7.10) $$\psi^{(i)} = \begin{vmatrix} \psi_{k_1}(q_1') & \psi_{k_1}(q_2') & ... & ... & \psi_{k_1}(q_N') \\ \psi_{k_2}(q_1') & \psi_{k_2}(q_2') & ... & ... & \psi_{k_2}(q_N') \\ -- & -- & -- & -- & -- \\ -- & -- & -- & -- & -- \\ \psi_{k_N}(q_1') & \psi_{k_N}(q_2') & ... & ... & \psi_{k_N}(q_N') \end{vmatrix}$$

From which it is clearly seen that $\psi^{(i)}$ is anti-symmetric, since a permutation of two coordinates q means permuting two columns, which changes the sign of the determinant.

As it was the case of the Bose-particles the state $\psi^{(i)}$ having the energies (7.8) is not degenerated, since a permutation of a stationary state only changes its sign, but do note generate a new state.

However Fermi-particles impose the condition on the numbers N_k that they can only have the values 0 and 1. If one of the occupation numbers N_1, N_2, ... N_k... is equal to or larger than 2, it would mean that two or more of the numbers k_1, k_2, ... k_N were equal, which again would mean that one or more of the columns in the determinant were equal, implying that $\psi^{(i)}$ is identical zero, and therefore can represent no physical state.

This expresses that Fermi-particles obey the so called **Pauli principle**, whereby a one particle state can only be occupied by one Fermi particle.

7.3 Boltzmann- ,Bose- and Fermi-particles

Besides the Bose- and Fermi-particles we shall also be concerned with the previously mentioned Boltzmann-particles. Strictly speaking Boltzmann-particles do not exist as such in nature, but at higher temperatures, as we shall see, both Bose- and Fermi-particles tend to behave like Boltzmann-particles. At higher temperature is to be understood, as above room temperature.

To treat a gas consisting of N identical particles in thermodynamic equilibrium at a certain temperature T, we must calculate the free energy ψ or the sum of states Z:

$$(7.11) \qquad\qquad Z = \sum_i e^{-\frac{E^{(i)}}{\theta}} \qquad \text{where} \qquad \psi = -\theta \ln Z,$$

and the summation is over all the energies in the total system. We have demonstrated above that for all three types of particles the energies can be written in the form:

$$(7.12) \qquad\qquad Z = \sum_{N_1, N_2, .. N_k} e^{-\frac{\sum_k N_k E_k}{\theta}} G(N_1, N_2, .. N_k)$$

Where $G(N_1, N_2, .. N_k)$ is the degree of degeneracy of the energy states $\sum_k N_k E_k$.

Boltzmann-particles: $G(N_1, N_2, ..) = \dfrac{N!}{N_1! \cdot N_2! \cdots}$

Bose-particles: $G(N_1, N_2, ..) = 1$

Fermi-particles: $G(N_1, N_2, ..) = 1$

 if all N_k are either 0 or 1, otherwise $G(N_1, N_2, ..) = 0$
With this definition, The Pauli principle is satisfied, regarding the Fermi-particles.

We shall then treat a gas, consisting of either of the three types of particles.
According to (3.16):

$$<L> = \frac{\sum_i L_i e^{-\frac{E_i}{\theta}}}{\sum_i e^{-\frac{E_i}{\theta}}} = \frac{\sum_i L_i e^{-\frac{E_i}{\theta}}}{Z}$$

and using (7.12) we find in all three cases for the mean of N_k, the average number of particles in the k'th energy level.

$$(7.13) \qquad <N_k> = \frac{1}{Z} \sum_{N_1, N_2, ..} N_k e^{-\frac{1}{\theta} \sum_{k'} N_{k'} E_{k'}} G(N_1, N_2, ...)$$

Where
$$< N_k > = -\frac{\theta}{Z}\frac{\partial Z}{\partial E_k} = -\theta\frac{\partial \ln Z}{\partial E_k}$$

To obtain the last equation, we have used the relation:

$$\frac{\partial Z}{\partial E_{k'}} = \frac{\partial}{\partial E_{k'}}\sum_{N_1,N_2,..}e^{-\frac{1}{\theta}\sum_{k'}N_k \cdot E_{k'}}G(N_1,N_2,...) = -\frac{1}{\theta}\sum_{N_1,N_2,..}N_k e^{-\frac{1}{\theta}\sum_{k'}N_k \cdot E_{k'}}G(N_1,N_2,...)$$

In a similar way we find:

(7.14)
$$< N_k^{\,2} > = \frac{1}{Z}\theta^2\frac{\partial^2 Z}{\partial E_k^{\,2}} = \theta^2\left(\frac{\partial \ln Z}{\partial E_k}\right)^2 + \theta^2\left(\frac{\partial^2 \ln Z}{\partial E_k^{\,2}}\right)$$

Which gives for the fluctuation of N_k.

(7.14)
$$\sigma^2(N_k) = < N_k^{\,2} > - < N_k >^2 = \theta^2\left(\frac{\partial^2 \ln Z}{\partial E_k^{\,2}}\right) = -\theta\frac{\partial < N_k >}{\partial E_k}$$

The bosons are the particles in nature with integral spin, like photons, alfa-particles, pi-mesons, and many others less common particles.

The Fermions are particles with half integral spin, predominantly the electron, the proton and the neutron.

As mentioned earlier, the Boltzmann particles do not exist in nature at the atomic level, but they are nevertheless of great interest, because both bosons and fermions tend to behave as Boltzmann particles, even at moderate temperatures.

8. Boltzmann particles

Let us consider N Boltzmann particles confined in a rectangular box with side lengths l_1, l_2, l_3. This is actually the situation we have already dealt with in section 4.
The single particle states are here characterized by the variables $(k) = (n_1,n_2,n_3)$, and the energy levels are given by:

(8.1)
$$E_{n_1,n_1,n_1} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_1^2}{l_1^{\,2}} + \frac{n_2^2}{l_2^{\,2}} + \frac{n_3^2}{l_3^{\,2}}\right) \qquad (n_1,\ n_2,\ n_3) = 1,2,3\ldots$$

With the formulas derived in the last section, we have the expression for the sum of states:

(8.2)
$$Z = \sum_{N_1,N_2,}\frac{N!}{N_1!N_2!\cdots}e^{-\frac{E_1}{\theta}N_1}e^{-\frac{E_2}{\theta}N_2}\cdots \qquad N = \sum_k N_k.$$

Using a generalization of binomial formula

$$(x + y)^n = \sum_{k=1}^{n} \frac{n!}{k!(n-k)!} x^k y^{n-k}$$

To the polynomial formula.

(8.3)
$$\left(\sum_k x_k\right)^N = \sum_{N_1, N_1, \ldots} \frac{N!}{N_1! N_2!} x_1^{N_1} x_2^{N_2} \cdots$$

If we put $x_k = e^{-\frac{E_k}{\theta}}$ we can see, that (8.2) is actually equal to $\left(\sum_k e^{-\frac{E_k}{\theta}}\right)^N$, so we have (not

surprisingly) that for Boltzmann particles $Z = z^N$, where $z = \sum_k e^{-\frac{E_k}{\theta}}$ is the sum of states

for a single particle. The expression can be further partitioned as the product of three sums of states, one for each degree of freedom.

If we approximate the sums by integrals the derived result above becomes identical to what we obtained earlier in (4.4) for an ideal gas.

From (7.13) $<N_k> = -\theta \frac{\partial \ln Z}{\partial E_k}$ and if we recall that $Z = z^N$, we find for the mean of N_k.

(8.4)
$$<N_k> = -\theta \frac{\partial \ln z^N}{\partial E_k} = -\frac{\theta N}{z} \frac{\partial z}{\partial E_k} = \frac{N}{z} e^{-\frac{E_k}{\theta}}$$

$$<H> = \theta^2 \frac{\partial \ln Z}{\partial \theta} = \theta^2 \frac{\partial \ln z^N}{\partial \theta}$$

From (5.5)
$$= \frac{N\theta^2}{z} \frac{\partial z}{\partial \theta} = \frac{N\theta^2}{z} \frac{\partial}{\partial \theta} \sum_k e^{-\frac{E_k}{\theta}}$$

$$= \frac{N}{z} \sum_k E_k e^{-\frac{E_k}{\theta}}$$

Hold together with (8.4) $<N_k> = \frac{N}{z} e^{-\frac{E_k}{\theta}}$ we find:

(8.5)
$$<H> = \sum_k <N_k> E_k$$

And in accordance with (7.8) $E^{(i)} = \sum_k N_k E_k$.

9. Bose-particles

For bosons the sum of states is according to (7.12)

(9.1)
$$Z = \sum_{N_1, N_2, \ldots N_k} e^{-\frac{\sum_k N_k E_k}{\theta}} \qquad \text{where} \qquad N = \sum_k N_k$$

This bond, however, makes the sum difficult (actually impossible) to evaluate. If N is sufficiently large, however, we may approximate it with a weighted mean of mixture of states, where N_k can have values from 0 to infinity. So we replace each term (k) with:

$$z_k = \sum_{N_k=0}^{\infty} e^{-\frac{N_k E_k}{\theta} - \lambda N_k}$$

For the total sum of state we then get:

(9.2)
$$Z = \sum_{N_1,N_2...=0}^{\infty} e^{-\frac{1}{\theta}\sum_k N_k E_k - \lambda N_k}$$

The accuracy of this approximation depends of course on the choice of λ.
Such a weighted mixture of ensembles was already considered by Gibb's regarding classical systems as a "grand ensemble". In a grand ensemble, the relative probability of finding a certain set of occupation numbers is.

(9.3)
$$P(N_1, N_2,...) = e^{-\frac{1}{\theta}\sum_k N_k E_k - \lambda N_k}$$

The mean and fluctuation of N_k is obtained as in (7.13) and (7.14).

$$<N_k> = -\frac{\theta}{Z}\frac{\partial Z}{\partial E_k} = -\theta\frac{\partial \ln Z}{\partial E_k} \quad \text{and} \quad <N_k^2> = \frac{1}{Z}\theta^2\frac{\partial^2 Z}{\partial E_k^2} = \theta^2\left(\frac{\partial \ln Z}{\partial E_k}\right)^2 + \theta^2\left(\frac{\partial^2 \ln Z}{\partial E_k^2}\right)$$

(9.4)
$$<N> = \sum_k <N_k> = \frac{1}{Z}\sum_{N_1,N_2,...} N e^{-\frac{1}{\theta}\sum_k N_k E_k - \lambda N} =$$
$$= -\frac{1}{Z}\frac{\partial Z}{\partial \lambda} = -\frac{\partial \ln Z}{\partial \lambda}$$

And furthermore

(9.5)
$$<N^2> = \frac{1}{Z}\frac{\partial^2 Z}{\partial \lambda} = \left(\frac{\partial \ln Z}{\partial \lambda}\right)^2 + \left(\frac{\partial^2 \ln Z}{\partial \lambda^2}\right)$$

(9.6)
$$\sigma^2(N) = <N^2> - <N>^2 = \frac{\partial^2 \ln Z}{\partial \lambda^2} = -\frac{\partial <N>}{\partial \lambda}$$

As the summation over each of the variables (N_1, N_1, ...) are independent of each other, the sum of states Z is simply the product of all individual sum of states.

$$(9.7) \qquad Z = \prod_k \left(\sum_{N_k = 0}^{\infty} \left(e^{-\frac{E_k}{\theta} - \lambda} \right)^{N_k} \right)$$

$$= \prod_k \frac{1}{1 - e^{-\frac{E_k}{\theta} - \lambda}}$$

Where we have used the formula for an infinite geometric series:

$$\sum_{k=0}^{\infty} x^k = \frac{1}{1 - x} \quad \text{with } x = e^{-\frac{E_k}{\theta} - \lambda}.$$

$$(9.8) \qquad \ln Z = -\sum_k \ln\left(1 - e^{-\frac{E_k}{\theta} - \lambda} \right)$$

For the mean of N, we get from (9.4).

$$(9.9) \qquad <N> = -\frac{\partial \ln Z}{\partial \lambda} = \sum_k \frac{e^{-\frac{E_k}{\theta} - \lambda}}{1 - e^{-\frac{E_k}{\theta} - \lambda}} = \sum_k \frac{1}{e^{\frac{E_k}{\theta} + \lambda} - 1}$$

And for the variance:

$$(9.10) \qquad \sigma^2(N) = <N^2> - <N>^2 = \frac{\partial^2 \ln Z}{\partial \lambda^2} = -\frac{\partial <N>}{\partial \lambda} = \sum_k \frac{e^{\frac{E_k}{\theta} + \lambda}}{(e^{\frac{E_k}{\theta} + \lambda} - 1)^2} =$$

And from (7.13) it follows in a similar manner.

$$(9.11) \qquad <N_k> = -\theta \frac{\partial \ln Z}{\partial E_k} = \frac{1}{e^{\frac{E_k}{\theta} + \lambda} - 1}$$

Finally we get from (7.14)

$$\sigma^2(N_k) = <N_k^2> - <N_k>^2 = \theta^2 \left(\frac{\partial^2 \ln Z}{\partial E_k^2} \right) = -\theta \frac{\partial <N_k>}{\partial E_k}$$

$$(9.12) \qquad \sigma^2(N_k) = \frac{e^{\frac{E_k}{\theta} + \lambda}}{(e^{\frac{E_k}{\theta} + \lambda} - 1)^2}$$

$$\sigma^2(N_k) = \frac{1}{e^{\frac{E_k}{\theta} + \lambda} - 1} (1 + \frac{1}{e^{\frac{E_k}{\theta} + \lambda} - 1}) = <N_k> (1 + <N_k>) = <N_k> + <N_k>^2$$

Which comply with (9.10), since the variables N_k are statistically independent.

$$(9.14) \qquad \sigma^2(N) = \sum_k \sigma^2(N_k) = \sum_k (<N_k> + <N_k>^2) = <N> + \sum_k <N_k>^2,$$

Finally we find for the Hamilton function (The energy).

$$< H >= \theta^2 \frac{\partial \ln Z}{\partial \theta} = -\theta^2 \sum_k \frac{e^{-\frac{E_k}{\theta}-\lambda}}{1-e^{-\frac{E_k}{\theta}-\lambda}} \frac{E_k}{\theta^2}$$

(9.15)

$$< H >= \sum_k \frac{E_k}{e^{\frac{E_k}{\theta}+\lambda} -1}$$

Which shows that

(9.16)
$$< H >= \sum_k < N_k > E_k$$

We may then realize that when the total mean $<N>$ is a very large number N_0, the fluctuations of N around $<N>$ will in general be very small compared to $<N>$, and consequently the calculations applied using the "grand ensemble", will practically be identical to the original ensemble, when we identify $<N>$ with N_0.
To show that this is in fact the case, we notice that

$$<N_k> = \frac{1}{e^{\frac{E_k}{\theta}+\lambda} -1} \text{ is practically equal to } \frac{1}{e^\lambda -1}, \text{ as long as } E_k << \theta \text{ that is } E_k << kT .$$

(In the opposite case the particles will behave like Boltzmann particles.)

If n is the number of single particle states k for which $E_k << kT$, then we have that the sum of all $<N_k>$ is of the order of $<N> = N_0$ equal to

(9.17)
$$n < N_k >= \frac{n}{e^\lambda -1} = N_0$$

Implicating that

(9.18)
$$< N_k >\cong \begin{cases} \dfrac{N_0}{n} & for \quad E_k < kT \\ 0 & for \quad E_k > kT \end{cases}$$

From (9.14) we have:

(9.19)
$$\sigma^2(N) =< N > + \sum_k < N_k >^2 = N_0 + n\left(\frac{N_0}{n}\right)^2$$

Since we have assumed that $<N>=N_0$, we find:

(9.20)
$$\frac{\sigma^2(N)}{< N >^2} = \frac{1}{N_0} + \frac{1}{n}$$

In general both N_0 and n will be extremely high numbers. To illustrate this, we consider a cube with side length l containing the particles. According to (8.1) the energy levels are characterized by three numbers $(k) = (n_1, n_2, n_3)$, and the energy levels are given by (8.1).

(9.21)
$$E_{n_1, n_1, n_1} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{l_1^2} + \frac{n_2^2}{l_2^2} + \frac{n_3^2}{l_3^2} \right)$$

If we put $l_1 = l_2 = l_3 = l$, we find: $E_{n_1, n_1, n_1} = \frac{\hbar^2 \pi^2}{2ml^2} \left(n_1^2 + n_2^2 + n_3^2 \right)$.

Then solving $E_k < kT$ from (9.18) Results in:

(9.22)
$$\left(n_1^2 + n_2^2 + n_3^2 \right) < \frac{2ml^2}{\hbar^2 \pi^2} kT$$

We are interested in finding the number of positive integers (n_1, n_2, n_3) which satisfy this relation.

In a (n_1, n_2, n_3) space $n_1^2 + n_2^2 + n_3^2 < R^2$ with $R^2 = \frac{2ml^2}{\hbar^2 \pi^2} kT$ is the volume of a sphere equal to

$\frac{4}{3} \pi R^3$. However we should only count the volume of the octant, where (n_1, n_2, n_3) are positive integers. So the number of states n can therefore be estimated to:

(9.22)
$$n \approx \frac{1}{8} \frac{4\pi}{3} \left(\frac{2ml^2}{\hbar^2 \pi^2} kT \right)^{\frac{3}{2}} \propto \left(\frac{T}{T_0} \right)^{\frac{3}{2}}$$

Where T_0 is the in (4.10) defined $T_0 \equiv \frac{\hbar^2 \pi^2}{2ml^2 k}$.

For alfa-particles in a volume of 1 cm^3 $T_0 = 10^{-13}$ K. So even for low temperatures the number n is extremely large. For $T = \frac{1}{10} K$, a calculation shows that $. n \cong 10^{18}$.

In other words for a boson gas having a large number of particles (9.7)

$$Z = \prod_k \frac{1}{1 - e^{\frac{E_k}{\theta} - \lambda}}$$

is a very good approximation to the sum of states (9.1):

$$Z = \sum_{N_1, N_2, .. N_k} e^{-\frac{\sum_k N_k E_k}{\theta}},$$

as well as for the mean number of particles in the single particle state (9.9):

$$< N_k > = \frac{1}{e^{\frac{E_k + \lambda}{\theta}} - 1}$$

This in contrast to (8.4) $<N_k> = \dfrac{N}{z} e^{-\frac{E_k}{\theta}}$, which is valid for Boltzmann Particles.

For a gas of bosons the average number of particles with a velocity between v and $v + dv$ the "Maxwell's distribution of velocities" becomes:

(9.23)
$$n(v)dv = \frac{C}{e^{\frac{mv^2}{2kT}+\lambda} - 1} v^2 dv$$

The most important application of this, is Planck's black body radiation of a boson gas, where the particles can be perceived as having an energy $E_k = hv$, and with a number of states k, corresponding to a frequency between v and dv, of which the density is given by (6.4):

(9.24)
$$\rho(v)dv = V\frac{8\pi v^2}{c^3} dv$$

By summation of

$$<N_k> = \frac{1}{e^{\frac{E_k+\lambda}{\theta}} - 1}$$

over states k within this interval, we find for the average number of with energy hv and $hv +hdv$.

(9.24)
$$n(v)dv = \frac{1}{e^{\frac{hv}{kT}} - 1} V\frac{8\pi v^2}{c^3} dv$$

The mean energy of the photons having frequency between v and dv is then:

(9.25)
$$\frac{hv}{e^{\frac{hv}{kT}} - 1} V\frac{8\pi v^2}{c^3} dv$$

In accordance with Planck'a formula (6.5).

Also the expression for the mean energy comply with that of Boltzmann particles, if we perceive the black body radiation consisting of a boson gas of a grand ensemble with $\lambda = 0$. This means that the total number of photons is not fixed, but rather depends on the temperature and the volume. From (9.24) we get the total average number of photons per unit volume.

(9.25)
$$<N> = \frac{8\pi}{c^3} \int_0^\infty \frac{v^2}{e^{\frac{hv}{kT}} - 1} dv$$

Making the same substitution $x = \dfrac{hv}{kT}$ as we did in (6.8) the integral is transformed into:

$$(9.26) \qquad\qquad < N >= 8\pi \left(\frac{kT}{hc} \right)^3 \int_0^\infty \frac{x^2 dx}{e^x - 1}$$

So the total number of photons per unit volume grows in proportion with the third power of the temperature.

In a similar manner we find from (9.10)

$$\sigma^2(N) = \sum_k \frac{e^{\frac{E_k}{\theta} + \lambda}}{(e^{\frac{E_k}{\theta} + \lambda} - 1)^2}$$

with $\lambda = 0$.

$$(9.27) \qquad\qquad \sigma^2(N) = 8\pi \left(\frac{kT}{hc} \right)^3 \int_0^\infty \frac{x^2 e^x dx}{(e^x - 1)^2}$$

Which is vanishing small compared to $<N>^2$ from (9.26).

On the other hand, if we consider a system of Bose particles with a fixed large number of photons N_0, the value of λ is determined by (9.9)

$$(9.28) \qquad\qquad N_0 = \sum_k \frac{1}{e^{\frac{E_k}{\theta} + \lambda} - 1}$$

The solution to this equation is considered to be solved with respect to $\lambda = \lambda (N_0, \theta)$ to get ln Z, and thus finding the free energy as a function of $\theta = kT$. For large values of λ, the formula (9.9)

$$< N_k >= \frac{1}{e^{\frac{E_k}{\theta} + \lambda} - 1}$$

turns into the corresponding formula for Boltzmann particles:

$$< N_k >= \frac{N}{z} e^{-\frac{E_k}{\theta}},$$

since for large λ:

$$< N >= \sum_k \frac{1}{e^{\frac{E_k}{\theta} + \lambda} - 1} \cong \sum_k \frac{1}{e^{\frac{E_k}{\theta} + \lambda}} = e^{-\lambda} \sum_k e^{-\frac{E_k}{\theta}} = \frac{N}{z} \sum_k e^{-\frac{E_k}{\theta}}$$

For a gas under common conditions this occurs already at normal temperatures.

10. Fermi particles

For Fermi particles the sum of states is again by the expression (9.1)

$$(10.1) \qquad Z = \sum_{N_1,N_2,..N_k} e^{-\frac{\sum_k N_k E_k}{\theta}} \qquad \text{where} \qquad N = \sum_k N_k$$

With the condition that all N_k are either 0 or 1. To do the summation we replace the ensemble with that of a canonical grand ensemble belonging to the sum of states, which relives us from the band imposed on N_k. We then find:

$$(10.2) \qquad Z = \prod_k \left(\sum_{N_k = 0}^{1} e^{-(\frac{E_k}{\theta}+\lambda)N_k} \right) = \prod_k \left(1 + e^{-(\frac{E_k}{\theta}+\lambda)} \right)$$

$$(10.3) \qquad \ln Z = \sum_k \ln(1 + e^{-(\frac{E_k}{\theta}+\lambda)})$$

For the mean and the fluctuations of N, we get as before.

$$(10.4) \qquad < N >= \frac{\partial}{\partial \lambda} \ln Z = \sum_k \frac{1}{1 + e^{\frac{E_k}{\theta}+\lambda}}$$

$$(10.5) \qquad \sigma^2(N) = -\frac{\partial < N >}{\partial \lambda} = \sum_k \frac{e^{\frac{E_k}{\theta}+\lambda}}{(1 + e^{\frac{E_k}{\theta}+\lambda})^2}$$

Analogously to what we found for bosons. Furthermore we get for Fermi particles, according to (7.13) and (7.14)

$$(10.6) \qquad < N_k >= -\theta \frac{\partial \ln Z}{\partial E_k} = \frac{1}{1 + e^{\frac{E_k}{\theta}+\lambda}}$$

$$(10.7) \qquad \sigma^2(N_k) = -\theta \frac{\partial < N_k >}{\partial E_k} = \frac{e^{\frac{E_k}{\theta}+\lambda}}{(1 + e^{\frac{E_k}{\theta}+\lambda})^2}$$

Which can also be written:

$$\sigma^2(N_k) =< N_k > (1- < N_k >)$$

$$(10.8) \qquad \sigma^2(N) = \sum_k \sigma^2(N_k) = \sum_k < N_k > (1- < N_k >)$$

(10.9)
$$\sigma^2(N) = \sum_k < N_k > (1- < N_k >) < \sum_k < N_k >= N$$

Consequently
$$\frac{\sigma(N)}{<N>} < \frac{1}{\sqrt{N}}$$

This shows that the fluctuations of N can be neglected. As long as N is a large number i.e. comparable to Avogadro's number. It is therefore completely safe to replace the original canonical ensemble with a fixed total number N_0 with a grand ensemble where the mean <N> is equal to N_0.

As we found in (10.3)

$$\ln Z = \sum_k \ln(1 + e^{-(\frac{E_k}{\theta}+\lambda)})$$

(10.10)
$$<H> = \theta^2 \frac{\partial \ln Z}{\partial \theta} = -\theta^2 \sum_k \frac{e^{-\frac{E_k}{\theta}-\lambda}}{1+e^{-\frac{E_k}{\theta}-\lambda}} \frac{E_k}{\theta^2}$$

$$<H> = \sum_k \frac{E_k}{e^{\frac{E_k}{\theta}+\lambda}+1} = \sum_k < N_k > E_k$$

Also the Fermi distribution passes into the Boltzmann distribution for large values of N. For a given large total number N_0, the parameter λ is determined by the equation

(10.11)
$$N_0 = \sum_k \frac{1}{e^{\frac{E_k}{\theta}+\lambda}+1}$$

This equation is considered to be solved with respect to $\lambda = \lambda(N_0,\theta)$ to get ln Z, and thus finding the free energy as a function of $\theta = kT$. For large values of λ, the formula (10.6)

(10.12)
$$<N_k> = -\theta \frac{\partial \ln Z}{\partial E_k} = \frac{1}{1+e^{\frac{E_k}{\theta}+\lambda}}$$

turns into the corresponding formula for Boltzmann particles:

(10.13)
$$<N_k> = \frac{N}{z} e^{-\frac{E_k}{\theta}},$$

since for large λ:

$$<N> = \sum_k \frac{1}{e^{\frac{E_k}{\theta}+\lambda}+1} \cong \sum_k \frac{1}{e^{\frac{E_k}{\theta}+\lambda}} = e^{-\lambda} \sum_k e^{-\frac{E_k}{\theta}} = \frac{N}{z} \sum_k e^{-\frac{E_k}{\theta}}$$

On the other hand, near the absolute zero, only the lowest energy levels are occupied. According to the Pauli principle, this means that all N_k from $k = 1$ to $k = N_0$ are 1, while $N_k = 0$ for $k > N_0$. If we put $E_{N_0} = E_0$, the equation (10.12) will for $\theta \to 0$ have the form:

(10.14)
$$< N_k >= \frac{1}{1 + e^{\frac{(E_k - E_0)}{\theta}}}$$

Which allegedly for $\theta \to 0$ has the property of being 1 for $E_k < E_0$, and being 0 for $E_k > E_0$. In other words for $T \to 0$ we must have

(10.15)
$$\lambda = -\frac{E_0}{\theta}$$

In the following section, we shall investigate more closely the energy distribution in an electron gas in the energy area in between.

11. An electron gas

The most important application of Fermi particles, is an electron gas of non relativistic electrons, which we assume are contained in a rectangular box with sides l_1, l_2, l_3. Then the energy levels are determined by (8.1)

(11.1)
$$E_{n_1, n_1, n_1} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{l_1^2} + \frac{n_2^2}{l_2^2} + \frac{n_3^2}{l_3^2} \right) \qquad (n_1, n_2, n_3) = 1,2,3\ldots$$

Where each state is to be counted twice, because of the electron spin. Writing (11.1) in terms of the momenta.

(11.2)
$$E_{n_1, n_1, n_1} = \frac{1}{2m} (p_1^2 + p_2^2 + p_3^2) = \frac{p^2}{2m}$$

(11.3)
$$p_k(n_k) = \frac{h}{2l_k} n_k \qquad k = 1,2,3 \quad n_k = 1, 2,3\ldots$$

We can assume, that the momenta p_k are practically continuous variables having values from zero to infinity. The number of states lying between p_k and $p_k + dp_k$ are

(11.4)
$$2 dn_1 dn_2 dn_3 = 2 \frac{8 l_1 l_2 l_3}{h^3} dp_1 dp_2 dp_3$$

In polar coordinates: $dp_1 dp_2 dp_3 = 4\pi p^2 dp$. Assuming that the components of $\vec{p}$ only takes positive values, we have only one octant of the sphere, we get for the number of states between p and $p + dp$.

(11.5)
$$\rho(p) dp = 2 \frac{8V}{h^3} \frac{4\pi}{8} p^2 dp \qquad \Rightarrow \qquad \rho(p) = \frac{8\pi V}{h^3} p^2$$

The energies for these states are $E_i = E(p) = \frac{p^2}{2m}$. According to (10.12):

$$< N_k >= \frac{1}{1+e^{\frac{E_k}{\theta}+\lambda}}$$

The number of electrons with a momentum between p and $p + dp$ is therefore:

(11.6)
$$n(p)dp = \frac{\rho(p)dp}{1+e^{\frac{E_k}{\theta}+\lambda}}$$

If all sums are converted to integrals then for example the equation that fixes λ for a given N_0 becomes.

(11.7)
$$\int n(p)dp = \int_0^\infty \frac{\rho(p)dp}{1+e^{\frac{E_k}{\theta}+\lambda}} = N_0$$

And for the sum of states we have from (10.3) $\ln Z = \sum_k \ln(1+e^{-(\frac{E_k}{\theta}+\lambda)})$

(11.8)
$$\ln Z = \int_0^\infty \rho(p)\ln(1+e^{\frac{E_k}{\theta}+\lambda})dp$$

And for the energies

(11.9)
$$E =< H >= \theta^2 \frac{\partial \ln Z}{\partial \theta} = \int_0^\infty \frac{\rho(p)E(p)dp}{1+e^{\frac{E_k}{\theta}+\lambda}} = \int_0^\infty n(p)E(p)dp$$

For the pressure we get

(11.10)
$$P = \theta \frac{\partial \ln Z}{\partial V} = \frac{8\pi\theta}{h^3} \int_0^\infty p^2 \ln(1+e^{-\frac{E(p)}{\theta}-\lambda})dp$$

Doing a partial integration

(11.11)
$$P = \frac{8\pi\theta}{h^3}\left[\tfrac{1}{3}p^3 \ln(1+e^{-\frac{E(p)}{\theta}-\lambda})\right]_0^\infty - \int_0^\infty \tfrac{1}{3}p^3 \frac{e^{-\frac{E(p)}{\theta}-\lambda}}{(1+e^{-\frac{E(p)}{\theta}-\lambda})}(-\frac{p}{m\theta})dp$$

The contributions from the upper and lower limits are both 0, and the integral can be rewritten after some elementary transformations.

(11.12)
$$P = \frac{2V}{3}\int_0^\infty \frac{\rho(p)E(p)}{1+e^{-\frac{E(p)}{\theta}-\lambda}}dp = \frac{2}{3}\frac{<H>}{V} = \tfrac{2}{3}u$$

Where $u = <H>/V$ the energy density in the electron gas.
To establish the energy and pressure as a function of θ and volume V for a fixed total number N_0, we shall imagine that (11.7) is solved with respect to λ, so that we have:

(11.13) $\lambda = \lambda(\theta, V, N_0)$

This expression is then to be inserted into the right side of (11.9) and (11.12). Introducing the variable x, by

(11.14) $x = \dfrac{E(p)}{\theta} = \dfrac{p^2}{2m\theta}$

As a new integration variable in (11.8) and (11.9) these equations can be written as.

(11.15) $N_0 = \dfrac{8\pi V}{h^3} m\sqrt{2m}\theta^{\frac{3}{2}} \varsigma(\lambda, \tfrac{1}{2})$

(11.16) $E = \dfrac{8\pi V}{h^3} m\sqrt{2m}\theta^{\frac{5}{2}} \varsigma(\lambda, \tfrac{3}{2})$

Where the function $\varsigma(\lambda, \mu)$ is defined by

(11.17) $\varsigma(\lambda, \mu) = \int\limits_0^\infty \dfrac{x^\mu dx}{e^{x+\lambda} + 1}$

From (11.12), (11.15) and (11.16) we furthermore get.

(11.18) $H = N_0 \dfrac{\varsigma(\lambda, \frac{3}{2})}{\varsigma(\lambda, \frac{1}{2})}$ and $P = \dfrac{2}{3} \dfrac{N_0}{V} \theta \dfrac{\varsigma(\lambda, \frac{3}{2})}{\varsigma(\lambda, \frac{1}{2})}$

These expressions are exact, and they are valid for all temperatures. In the domain of very large temperatures and near the absolute zero, on can establish some approximate expressions.
For large temperatures $\lambda \gg 1$,, we get from (10.13)

$$n(p)dp = \dfrac{N_0 e^{-\frac{E(p)}{\theta}}}{z(\theta, V)} \rho(p)dp$$

(11.19) $$z(\theta, V) = \int\limits_0^\infty \rho(p) e^{-\frac{E(p)}{\theta}} dp = \dfrac{2V}{h^3}(2\pi m\theta)^{\frac{3}{2}}$$

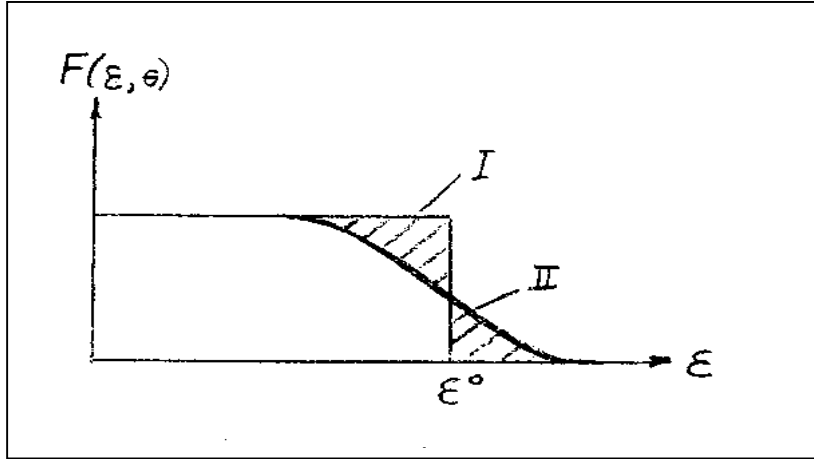$$<H> = \int\limits_0^\infty \rho(p)E(p) \dfrac{N_0 e^{-\frac{E(p)}{\theta}}}{z} dp = \dfrac{3N_0}{2}\theta$$

So for the energy we arrive at the same expression as for the Boltzmann particles.
Near the absolute zero, that is, for $\theta \to 0$, we have according to (10.14) and (10.15)

(11.20) $n_0(p) = \dfrac{1}{V}\rho(p)F(E, 0)$

(11.21) $$F(E,\theta) = \frac{1}{e^{(E(p)-E_0)/\theta}+1} \quad , \quad \lambda = -\frac{E_0}{\theta}$$

(11.22) $$F(E,0) = \begin{cases} 1 & for & E < E_0 \\ 0 & for & E > E_0 \end{cases}$$

A graph of the function F is shown below

At the absolute zero we therefore find.

(11.23) $$N_0 = \int_0^{p_0} \rho(p)F(E,0)dp = \frac{8\pi V}{3h^3}p_0{}^3$$

(11.24) $$<H_0> = \frac{p_0^2}{2m} = \frac{1}{2m}\left(\frac{3h^3 N_0}{8\pi V}\right)^{\frac{2}{3}}$$

In the momentum space the electrons fill in the internal of a sphere with radius p_0. The energy at the surface of the sphere, (the so called Fermi sphere), is therefore E_0 and it depends according to (11.24) exclusively on the electron density $n_0 = N_0 /V$.

Energy and pressure of a Fermi gas at the absolute zero is therefore not zero, as it is in a Boltzmann gas, since we for $T = 0$ have:

(11.25) $$<H_0> = V\int n_0(p)E(p)dp = \frac{8\pi V}{h^3}\int_0^{p_0}\frac{p^4}{2m}dp = \frac{8\pi V}{h^3 2m}\frac{p_0^5}{5}$$

This can also be written

(11.26) $$<H>_0 = \frac{8\pi V}{3h^3 2m}p_0^3\frac{3}{5}\frac{p_0^2}{2m} = \frac{3}{5}N_0 E_0$$

Furthermore we get from (11.12) for the pressure at $T = 0$

(11.27)
$$P_0 = \frac{2}{3}\frac{<H>_0}{V} = \frac{2}{5}n_0 E_0$$

At the absolute zero $\lambda = -\infty$ according to (11.21). We shall now investigate the case where $\theta > 0$, but still

(11.28)
$$\Theta = kT << E_0 ,$$

Where λ has large negative values. For such values of λ, we may for the functions ς use a series expansion due to Sommerfeld, of which we shall only keep the first two terms.

(11.29)
$$\varsigma(\lambda,\mu) = \frac{(-\lambda)^{\mu+1}}{\mu+1}\left(1 + \frac{\pi^2}{6}\frac{\mu(\mu+1)}{\lambda^2} + ...\right)$$

(11.30)
$$\frac{\varsigma(\lambda,\frac{3}{2})}{\varsigma(\lambda,\frac{1}{2})} = \frac{\frac{(-\lambda)^{\frac{5}{2}}}{\frac{5}{2}}\left(1+\frac{\pi^2}{6}\frac{\frac{3}{2}\frac{5}{2}}{\lambda^2}+...\right)}{\frac{(-\lambda)^{\frac{3}{2}}}{\frac{3}{2}}\left(1+\frac{\pi^2}{6}\frac{\frac{3}{2}\frac{1}{2}}{\lambda^2}+...\right)} = \frac{3}{5}(-\lambda)\left(1+\frac{\pi^2}{2\lambda^2}+...\right)$$

So according to (11.18):

(11.31)
$$E = \tfrac{3}{5}N_0\theta(-\lambda)\left(1+\frac{\pi^2}{2\lambda^2}+...\right)$$

Where we have used the equation (11.24). We "just" need to express λ as a function of θ, V and N_0.

With the help of (11.31), the equation (11.15) $N_0 = \frac{8\pi V}{h^3}m\sqrt{2m}\theta^{\frac{3}{2}}\varsigma(\lambda,\frac{1}{2})$ can be written

(11.32)
$$\frac{N_0 h^3}{8\pi V m\sqrt{2m}\theta^{\frac{3}{2}}} = \varsigma(\lambda,\tfrac{1}{2}) = \frac{(-\lambda)^{\frac{3}{2}}}{\frac{3}{2}}\left(1+\frac{\pi^2}{6}\frac{\frac{3}{2}\frac{1}{2}}{\lambda^2}+...\right)$$

Or

(11.33)
$$\frac{(-\lambda)^{\frac{3}{2}}}{\frac{3}{2}}\left(1+\frac{\pi^2}{6}\frac{\frac{3}{2}\frac{1}{2}}{\lambda^2}+...\right) = \frac{N_0 h^3}{8\pi V m\sqrt{2m}\theta^{\frac{3}{2}}} \equiv \left(\frac{E_0}{\theta}\right)^{\frac{3}{2}}$$

Where we have used (11.24): $E_0 = \frac{p_0^2}{2m} = \frac{1}{2m}\left(\frac{3h^3 N_0}{8\pi V}\right)^{\frac{2}{3}}$

Under the condition (11.28), the right side of (11.33) is a very large number, and then it may be solved by the method of successive approximations. In the first order we get:

(11.34) $$\lambda = -\frac{E_0}{\theta}$$

That is, the value we find for $\theta \to 0$. If we put this value into the parenthesis on the left side, we obtain the second approximation:

(11.35) $$\lambda = \frac{E_0}{\theta}\frac{1}{\left(1+\frac{\pi^2}{8}\frac{\theta^2}{E_0^2}\right)^{\frac{2}{3}}} \cong \frac{E_0}{\theta}\left(1-\frac{2}{3}\frac{\pi^2}{8}\frac{\theta^2}{E_0^2}\right) \qquad \Rightarrow$$

(11.36) $$\lambda = -\frac{E_0}{\theta}+\frac{\pi^2}{12}\frac{\theta}{E_0}$$

When this is inserted in (11.31) we get in the same approximation:

(11.37) $$E = \frac{3}{5}N_0\theta\left(\frac{E_0}{\theta}-\frac{\pi^2}{12}\frac{\theta}{E_0}\right)\left(1+\frac{\pi^2}{2}\frac{\theta^2}{E_0^2}\right) = \frac{3}{5}N_0\theta\left(\frac{E_0}{\theta}-\frac{5\pi^2}{12}\right)$$

(11.38) $$E = \frac{3}{5}N_0 E_0 + N_0\frac{\pi^2}{4}\frac{\theta^2}{E_0^2} = E_0 + \frac{\pi^2}{4}\frac{k^2 T^2}{E_0}$$

From (11.26) $P_0 = \frac{2}{3}\frac{<H>_0}{V} = \frac{2}{5}n_0 E_0$, we the get:

(11.39) $$P = P_0 + \frac{\pi^2}{6}\frac{k^2 T^2}{E_0}$$

The Fermi function now becomes, with λ given by (11.36)

(11.40) $$F(E,\theta) = \frac{1}{e^{\frac{E-E_0}{\theta}+\frac{\pi^2\theta}{12 E_0}}+1}$$

This function is displayed in the figure above as the second graph.

When $\dfrac{\theta}{E_0}$ is sufficiently small, near the absolute zero, this function can be replaced by

(11.41) $$F(E,\theta) = \frac{1}{e^{\frac{E-E_0}{\theta}}+1}$$

And the two cross hatched areas separated by $E = E_0$. are equal.
In the case $\theta = kT << E_0$, when the gas is in a degenerated staet, the variation of the energy with temperature, as displayed in (11.36) is entirely different from the classical expression (11.25).

Not only has the energy a finite value when T approaches zero, but what is more important the specific heat at constant pressure c_P , which in the classical description is constant, is given by:

(11.42)
$$c_P = \frac{dE}{dT} = \frac{\pi^2}{2} \frac{N_0 k^2}{E_0} T$$

That is the specific heat goes to zero when the temperature does.

Sommerfeld brought forward this issue, to explain why the conducting electrons in a metal apparently contributed less to the specific heat, than what one should expect. The explanation was for electrons that the formula (11.42) already has an influence at normal temperatures.