THERMODYNAMIC FUNCTIONS FOR TWO DIMENSIONAL QUANTUM STATISTICS*

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In recent years the Fermi-Dirac statistics applied to the case of electron gas has found numerous applications. The case in which the electron gas is restricted to two dimensions is also of interest in certain special cases. In the first part of the present paper the various thermodynamical functions for a ν-dimensional space for a gaseous assembly obeying Fermi-Dirac statistics or Bose-Einstein statistics have been evaluated in the usual familiar way,[1] and the values of these functions for a two dimensional space have been deduced as a special case. An application of the results has been made in a following paper[2] in deducing the magnetic susceptibility of a free electron gas when the electrons are confined to a plane.

1. We first determine the distribution laws for a ν-dimensional space. The wave function for an allowed state of a free particle in a space of 'volume' L^{ν} is

$$\psi = C \sin\frac{l_1 \pi x_1}{L} \sin\frac{l_2 \pi x_2}{L} \dots\dots\dots \sin\frac{l_\nu \pi x_\nu}{L},$$

$$= C \prod_{\alpha=1}^{\alpha=\nu} \sin\frac{l_\alpha \pi x_\alpha}{L}, \qquad \dots \quad (1)$$

where
$$C = \left(\frac{2}{L}\right)^{\frac{\nu}{2}}.$$

The wavelength λ associated with a normal mode of vibration is given by

$$\frac{1}{\lambda} = \frac{l_\alpha}{2L},$$

and, therefore,
$$p^2 = \Sigma \frac{h^2}{\lambda^2} = \frac{h^2}{4L^2} \Sigma\, l_\alpha^2,$$

where p is the momentum.

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Now, taking account of relativistic mechanics,

since $$p=\frac{m\beta c}{\sqrt{1-\beta^2}}, \quad \text{and} \quad \epsilon=mc^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right),$$

we have $$\epsilon_0\Sigma(l_a)^2=\epsilon\left(\frac{\epsilon}{2mc^2}+1\right),$$

where $$\epsilon_0=\frac{h^2}{8mL^2}.$$

The number of states $C_\nu(\epsilon)$ for which the energy is less than ϵ is equal to $2^{-\nu}$ times the volume of a sphere of radius $\{\Sigma(l_a)^2\}^{\frac{1}{2}}$ and is given by

$$C_\nu(\epsilon)=\frac{\pi^{\frac{\nu}{2}}2^{-\nu}}{\Gamma\left(\frac{\nu}{2}+1\right)}\left\{\frac{\epsilon}{\epsilon_0}\left(\frac{\epsilon}{2mc^2}+1\right)\right\}^{\frac{\nu}{2}}. \quad \ldots \quad (2)$$

Therefore $a_\nu(\epsilon)\,d\epsilon$, the number of states of energy lying between ϵ and $\epsilon+d\epsilon$, is given by

$$a_\nu(\epsilon)d\epsilon=gC'_\nu(\epsilon),$$

$$=2g\left(\frac{\pi L^2}{h^2c^2}\right)^{\frac{\nu}{2}}\frac{1}{\Gamma\left(\frac{\nu}{2}\right)}(\epsilon+mc^2)(\epsilon^2+2mc^2\epsilon)^{\frac{\nu}{2}-1}, \quad \ldots \quad (3)$$

g being the weight factor.

In the completely non-relativistic case $\left(\frac{mc^2}{kT}>>1\right)$, this reduces to

$$a_\nu(\epsilon)d\epsilon=\frac{g}{\Gamma\left(\frac{\nu}{2}\right)}\left(\frac{2\pi mL^2}{h^2}\right)^{\frac{\nu}{2}}\epsilon^{\frac{\nu}{2}-1}d\epsilon, \quad \ldots \quad (4)$$

and in the completely relativistic case $\left(\frac{mc^2}{kT}<<1\right)$, we have

$$a_\nu(\epsilon)d\epsilon=\frac{2g}{\Gamma\left(\frac{\nu}{2}\right)}\left(\frac{\pi L^2}{h^2c^2}\right)^{\frac{\nu}{2}}\epsilon^{\nu-1}d\epsilon. \quad \ldots \quad (5)$$

Equations (4) and (5) for the two limiting cases can be written as

$$a_\nu(\epsilon)d\epsilon=D\epsilon^{s-1}d\epsilon, \quad \ldots \quad (6)$$

where, in the non-relativistic case,

$$s=\frac{\nu}{2}, \qquad D=\frac{g}{\Gamma(s)}\left(\frac{2\pi m L^2}{h^2}\right)^s, \qquad \dots \quad (7)$$

and, in the relativistic case,

$$s=\nu, \qquad D=\frac{2g}{\Gamma\left(\frac{s}{2}\right)}\left(\frac{\pi L^2}{h^2 c^2}\right)^{s/2}. \qquad \dots \quad (8)$$

It is to be noted that for the three dimensional case s takes the values $3/2$ and 3 in the non-relativistic and relativistic cases respectively. For the two dimensional case its values are 1 in the non-relativistic case and 2 in the relativistic case.

The distribution function $f(\epsilon)=\dfrac{1}{\frac{1}{A}e^{\epsilon/kT}+\beta}$ is not affected by the number of dimensions. $\beta=+1$ for Fermi-Dirac statistics and $\beta=-1$ for Bose-Einstein statistics. The number of particles, therefore, possessing energy in the range ϵ to $\epsilon+d\epsilon$ is given by

$$N(\epsilon)d\epsilon=\frac{D\epsilon^{s-1}}{\frac{1}{A}e^{\epsilon/kT}+\beta}d\epsilon. \qquad \dots \quad (9)$$

2. We shall first consider the case of non-degeneracy.

In this case $A \ll 1$ and the distribution function is easily expanded as a series.

The total number N of the particles in the assembly is given by

$$N=\int_0^\infty N(\epsilon)d\epsilon=D(kT)^s\int_0^\infty \frac{u^{s-1}}{\frac{e^u}{A}+\beta}du \qquad \dots \quad (10)$$

$$=D(kT)^s A\Gamma(s)\left\{1-\frac{\beta A}{2^s}+\frac{\beta^2 A^2}{3^s}-\dots\right\}. \qquad \dots \quad (11)$$

And, therefore,

$$A_1\equiv\frac{N}{D(kT)^s\Gamma(s)}=\sum\frac{A^n}{n^s}(-\beta)^{n-1}. \qquad \dots \quad (12)$$

The total energy of the assembly E is given by

$$E=\int_0^\infty \epsilon.N(\epsilon)d\epsilon=D(kT)^{s+1}\int_0^\infty\frac{u^s}{\frac{e^u}{A}+\beta}du, \qquad \dots \quad (13)$$

$$=sNkT[1+a\beta A_1-b\beta^2 A_1^2+c\beta^3 A_1^3+\dots], \qquad \dots \quad (14)$$

where $a=\dfrac{1}{2^{s+1}}$, $b=\left(\dfrac{2}{3^{s+1}}-\dfrac{1}{4^s}\right)$, $c=\dfrac{3}{4^{s+1}}+\dfrac{5}{2.8^s}-\dfrac{3}{6^s}$.

From (12) and (14), we easily obtain, noting that $E = spV$, the general formulae for the non-degenerate case

$$\frac{G}{NkT} = \log A = \log A_1 + 2a\beta A_1 - \tfrac{3}{2}b\beta^2 A_1^2 + \tfrac{4}{3}c\beta^3 A_1^3 \ldots \qquad \ldots (15)$$

$$\frac{F}{NkT} = \frac{G - pV}{NkT} = \log A_1 - 1 + a\beta A_1 - \tfrac{1}{2}b\beta^2 A_1^2 + \tfrac{1}{3}c\beta^3 A_1^3 \ldots\ldots\ldots, \qquad \ldots (16)$$

and

$$\frac{S}{Nk} = \frac{E - F}{NkT} = (s+1) - \log A_1 + (s-1)a\beta A_1 - \frac{(2s-1)}{2}b\beta^2 A_1^2$$

$$+ \frac{3s-1}{3}c\beta^3 A_1^3 \ldots\ldots\ldots, \qquad \ldots (17)$$

where G, F and S are respectively the Thermodynamic Potential, Free Energy and Entropy of the assembly.

As a special case we write down the values of the above functions in the non-relativistic two-dimensional case.

We have $s = \frac{\nu}{2} = 1, \qquad D = \frac{g 2\pi m L^2}{h^2},$

and

$$A_1 = \frac{N}{DkT} = \frac{nh^2}{g 2\pi m kT}, \qquad \ldots (18)$$

where n is the surface density. Also $a = \frac{1}{4}$, $b = \frac{-1}{36}$ and $c = 0$.

$$\frac{E}{NkT} = 1 + \beta\frac{A_1}{4} + \frac{1}{36}\beta^2 A_1^2 + \ldots\ldots\ldots, \qquad \ldots (19)$$

$$\frac{G}{NkT} = \log A_1 + \beta\frac{A_1}{2} + \frac{\beta^2 A_1^2}{24} + \ldots\ldots\ldots, \qquad \ldots (20)$$

$$\frac{F}{NkT} = \log A_1 - 1 + \frac{\beta A_1}{4} + \frac{\beta^2 A_1^2}{72} + \ldots\ldots\ldots, \qquad \ldots (21)$$

and

$$\frac{S}{Nk} = 2 - \log A_1 + \frac{\beta^2 A_1^2}{72} + \ldots\ldots\ldots \qquad \ldots (22)$$

We shall now take up the degenerate case.

In degeneracy the Fermi-Dirac and Bose-Einstein cases are considered separately. In Bose-Einstein statistics $A = 1$, $\beta = -1$ and equation (13), therefore, easily gives

$$E = \Gamma(s+1)D(kT)^{s+1}\zeta(s+1), \qquad \ldots (23)$$

$$G = 0, \qquad \ldots (24)$$

$$F = -\frac{E}{S} = -\Gamma(s)D(kT)^{s+1}\zeta(s+1), \qquad \ldots (25)$$

$$S = \frac{s+1}{s} \cdot \frac{E}{T} = (s+1)\Gamma(s)D(kT)^s k\,\zeta(s+1), \qquad \ldots (26)$$

$$C_L = \left(\frac{\partial E}{\partial T}\right)_L = (s+1)\frac{E}{T}, \qquad \ldots (27)$$

where C_L is the specific heat when the size of the space ("volume") occupied by the assembly remained fixed.

In the two-dimensional non-relativistic case these reduce to

$$E = \frac{g 2\pi m L^2}{h^2}(kT)^2\zeta(2), \qquad \ldots (28)$$

$$G = 0, \qquad \ldots (29)$$

$$F = -E, \qquad \ldots (30)$$

$$S = \frac{2E}{T}, \qquad \ldots (31)$$

$$C_\sigma = \frac{2E}{T}, \qquad \ldots (32)$$

where C_σ denotes specific heat at constant area.

The degenerate case of the Fermi-Dirac statistics is characterised by $A >> 1$ and $\beta = +1$. The integrations are carried out by using Sommerfeld's formula according to which, for large A,

$$\int_0^\infty \frac{u^s du}{\frac{e^u}{A}+1} = \frac{u_0^{s+1}}{s+1}\left\{1 + \frac{\pi^2 s(s+1)}{6\,u_0^2} + \frac{7\pi^4(s+1)s(s-1)(s-2)}{360\,u_0^4}\ldots\right\}, \qquad \ldots (33)$$

where $u_0 = \log A$. Equation (10) yields

$$N = D(kT)^s \frac{u_0^s}{s}\left\{1 + \frac{\pi^2(s-1)s}{6\,u_0^2} + \frac{7\pi^4}{360} \cdot \frac{s(s-1)(s-2)(s-3)}{u_0^4}\ldots\right\}. \qquad \ldots (34)$$

And, defining A_1 by relation (12), we have

$u_0 = \log A =$

$$\{\Gamma(s+1)A_1\}^{1/s}\left\{1 - \frac{\pi^2(s-1)}{6\{\Gamma(s+1)A_1\}^{2/s}} - \frac{\pi^4}{720} \cdot \frac{(s-1)(4s^2-30s+54)}{\{\Gamma(s+1)A_1\}^{4/s}}\ldots\right\}\ldots \qquad (35)$$

Similarly, integrating equation (13) for large A, we have

$$E = \frac{s}{s+1}\,NkT\{\Gamma(s+1)A_1\}^{1/s}\left[1 + \frac{\pi^2(s+1)}{6\{\Gamma(s+1)A_1\}^{2/s}} - \ldots\ldots\ldots\right], \qquad \ldots (36)$$

from which we easily obtain

$$\frac{G}{NkT} = \{\Gamma(s+1)A_1\}^{1/s}\left\{1 - \frac{\pi^2}{6}\,\frac{(s-1)}{\{\Gamma(s+1)A_1\}^{2/s}}\ldots\ldots\ldots\right\}, \qquad \ldots (37)$$

$$\frac{F}{NkT}=\frac{s}{s+1}\{\Gamma(s+1)A_1\}^{1/s}\left\{1-\frac{\pi^2}{6}\,\frac{s+1}{\{\Gamma(s+1)A_1\}^{2/s}}\,\cdots\cdots\cdots\right\}, \qquad (38)$$

$$\frac{S}{Nk}=\frac{s}{3}\,\frac{\pi^2}{\{\Gamma(s+1)A_1\}^{1/s}}, \qquad \cdots \quad (39)$$

$$C_L=\frac{s}{3}\,\frac{Nk\pi^2}{\{\Gamma(s+1)A_1\}^{1/s}}. \qquad \cdots \quad (40)$$

In the two dimensional case $s=1$ and the values obtained for the various thermodynamic functions are entered in Table I, where for the sake of comparison results for the three dimensional case are also shown.

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TABLE I

	Two dimensional	Three dimensional
log A	(A_1+1)*	$\left(\frac{3\pi^{\frac{1}{2}}}{4}\right)^{\frac{2}{3}}A_1^{\frac{2}{3}}\left\{1-\frac{\pi^{\frac{4}{3}}\,2^{\frac{2}{3}}}{3^{\frac{7}{3}}\,A_1^{\frac{4}{3}}}\cdots\right\}$
$\frac{E}{NkT}$	$\frac{A_1}{2}\left\{1+\frac{\pi^2}{3A_1^2}\cdots\right\}$	$\frac{3}{5}\left(\frac{3\pi^{\frac{1}{2}}}{4}\right)^{\frac{2}{3}}A_1^{\frac{2}{3}}\left\{1+\frac{5\pi^{\frac{4}{3}}\,2^{\frac{2}{3}}}{3^{\frac{7}{3}}\,A_1^{\frac{4}{3}}}\cdots\right\}$
$\frac{G}{NkT}$	A_1+1	$\left(\frac{3\pi^{\frac{1}{2}}}{4}\right)^{\frac{2}{3}}A_1^{\frac{2}{3}}\left\{1-\frac{\pi^{\frac{4}{3}}\,2^{\frac{2}{3}}}{3^{\frac{7}{3}}\,A_1^{\frac{4}{3}}}\cdots\right\}$
$\frac{F}{NkT}$	$\frac{A_1}{2}\left\{1-\frac{\pi_2}{3A_1^2}\cdots\right\}$	$\frac{3}{5}\left(\frac{3\pi^{\frac{1}{2}}}{4}\right)^{\frac{2}{3}}A_1^{\frac{2}{3}}\left\{1-\frac{5\pi^{\frac{4}{3}}\,2^{\frac{2}{3}}}{3^{\frac{7}{3}}\,A_1^{\frac{4}{3}}}\cdots\right\}$
$\frac{S}{Nk}$	$\frac{1}{3}\,\frac{\pi^2}{A_1}=\frac{C_\sigma}{Nk}$	$\frac{\pi^2 mkT}{h^2}\left(\frac{4\pi g}{3n}\right)^{\frac{2}{3}}=\frac{C_v}{Nk}$

* In the case of two dimensions the equation can be integrated exactly and log A comes out equal to A_1+1. It may be noted that the series in Sommerfeld's integration formula for the degenerate case are correct to an order of $1/A$.

REFERENCES

[1] Fowler & Guggenheim. "Statistical Thermodynamics," p. 239.
[2] "Magnetic Susceptibility of two dimensional electron gas."