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# The Equation of State of a Non-ideal Einstein-Bose or Fermi-Dirac Gas

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With regard to the question if from isotherm measurements one can obtain an experimental test for the existence of Bose statistics in real gases, as is required by theory, we prove the following general theorem. The "Zustandsumme" of a non-ideal Bose or Fermi gas is given by the classical integral provided one replaces the Boltzmann $\exp(-\phi_{ij}/kT)$ factor by:

$$e^{-\phi_{ij}/kT}(1 \pm \exp\,[-4\pi^2 mkTr_{ij}^2/h^2] \qquad (1)$$

for each pair of molecules $(ij)$. For the second virial coefficient $B$, this has, i.e., in a Bose gas, as a consequence that:

$$B = B_{\text{non-ideal class}} + B_{\text{ideal Bose}} + B' \qquad (2)$$

where:

$$B' = 2\pi N \int_0^\infty drr^2(1 - e^{-\phi(r)/kT}) \exp\,[-4\pi^2 mkTr^2/h^2]. \qquad (3)$$

Only at very low temperatures do the last two terms in (2) become appreciable. They are then of the same order of magnitude, but have opposite signs. Due to this fact, due to the lack of precise knowledge of the molecular forces, and due to the absence of accurate measurements of $B$ at very low temperatures, one can as yet not decide from isotherm measurements alone whether or not real gases obey the Bose statistics.

## I. INTRODUCTION

### 1.

AS IS well known, it has been proved from the fact that electrons and protons obey the Fermi-Dirac (F.D.) statistics, that a gas consisting of particles of even charge obeys the Einstein-Bose (E.B.) statistics.[1] A neutral gas, for example helium, is a special case of this. The question therefore becomes very important, if one could for example verify this theoretical prediction from equation of state measurements, in particular from the experimentally determined values of the second virial coefficient $B$.

The theoretical expression $B_{\text{cl}}$, for a *non-ideal* gas, obeying *Boltzmann* statistics is, as is well known:[2]

$$B_{\text{cl}} = 2\pi N \int_0^\infty drr^2(1 - e^{-\phi(r)/kT}) \qquad (1)$$

$N$ is the number of molecules per mol. It is here assumed that the intermolecular forces are radial and have the potential $\phi(r)$.

The expression $B_{E.B.}$ or $B_{F.D.}$ for an *ideal* gas obeying Einstein-Bose or Fermi-Dirac statistics, is:

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[1] E. Wigner, Sitzungsber. der Ungarischen Acad. 1928, p. 1; P. Ehrenfest and J. R. Oppenheimer, Phys. Rev. **37**, 333 (1931).

[2] See e.g., R. H. Fowler, Statistical Mechanics, Ch. VIII.

$$\left.\begin{matrix} B_{E.B.} \\ B_{F.D.} \end{matrix}\right\} = \mp \frac{1}{2^4}\left(\frac{h^2}{\pi mkT}\right)^{3/2} N \tag{2}$$

In the recent work on the quantum theory of the equation of state of real gases (London, Slater, Kirkwood, Keyes, Margenau) one has made only use of (1), introducing for $\phi(r)$ the theoretical expression obtained from a generalized Heitler-London calculation.[3] The reason that (2) was neglected is, that only at very low temperatures (say below 20°) it becomes appreciable, and *because it was always assumed that the B for a non-ideal Bose gas was the sum of* (1) *and* (2).

We wish to show in this paper that this additivity is not strictly true, but that in addition there occurs a term due to the interaction between the *Boseness* and the non-ideality of the gas. We get for a non-ideal Bose gas:

$$B = B_{\mathrm{cl}} + B_{E.B.} + B'_{E.B.} \tag{3}$$

where:

$$B'_{E.B.} = 2\pi N \int_0^\infty dr r^2 (1 - e^{-\phi(r)/kT}) \exp\left[-4\pi^2 mkTr^2/h^2\right] \tag{4}$$

**2.** The proof of (3) and (4) rests upon a kind of generalization of the exp $(-V/kT)$ theorem of Boltzmann for an E.B. or F.D. gas. Recently Slater[4] has pointed out the analogue of this fundamental theorem in the quantum theory. He remarked that quantum mechanically, due to the orthogonality and normalization of the wave functions $\psi_n$ belonging to the energy values $E_n$, the *Zustandssumme* $S_Q$ may be written:

$$S_Q = \sum_n G_n e^{-E_n/kT} = \int \cdots \int dx_1 \cdots dx_N \sum_n e^{-E_n/kT} \psi_n^2. \tag{5}$$

In *Boltzmann-statistics* for a given $E_n$ *all* the $G_n$ linearly independent wave functions $\psi_n$ belonging to it, are allowed, and must therefore occur in the sum,[5] so that the $G_n$ does not explicitly appear any more. In *Bose statistics* the $G_n = 1$, because only those $E_n$ are allowed, to which belong the symmetric wave functions, and only these have therefore to occur in the sum. Similarly in the *F.D. statistics* we have the $E_n$ to which the antisymmetric functions belong. Hereafter we will distinguish between these three cases by writing $S_{QB}$, $S_{QE.B.}$, $S_{QF.D.}$.

Slater compares (5) now with the classical "Zustandsintegral" after integration over the momenta:

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[3] F. London, Zeits. f. Physik **63,** 245 (1930); Zeits. f. phys. Chem. B. **11,** 222 (1930). J. C. Slater, Phys. Rev. **32,** 349 (1928); J. C. Slater and J. G. Kirkwood, Phys. Rev. **37,** 682 (1931). H. Margenau, Phys. Rev. **36,** 1782 (1930); **37,** 1014, 1425 (1931); **38,** 747, 1785 (1931); Proc. Nat. Acad. **18,** 56, 230 (1932). J. G. Kirkwood and F. G. Keyes, Phys. Rev. **37,** 832; **38,** 576 (1931). J. G. Kirkwood, Phys. Zeits. **33,** 39 (1932). One has made small corrections in (1), though, to allow for the existence of discrete states (formation of polarization molecules).

[4] J. C. Slater, Phys. Rev. **38,** 237 (1931).

[5] Comp. P. Ehrenfest and G. E. Uhlenbeck, Zeits. f. Physik **41,** 24 (1927).

$$S_{\text{cl}} = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \int \cdots \int e^{-V/kT} dx_1 \cdots dz_N \tag{6}$$

where $V(x_1 \cdot \cdot \cdot z_N)$ is the total potential energy due to the intramolecular forces and eventually also due to external forces.

One might expect from the correspondence principle that for sufficient high temperatures where the influence of the discreteness of the translational energy levels can be neglected with respect to the influence of the intermolecular forces (which is already the case, excluding the electron gas, say for $T > 1°$ absolute)[6]

$$\sum_n {}_{B.} e^{-E_n/kT} \psi_n^2 \xrightarrow[(T>1°)]{} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} e^{-V/kT}. \tag{7}$$

Slater makes this also plausible from the meaning of $\psi_n^2$ as a probability density. In Chapter III we will give an analytical proof. This gives the justification even in the quantum theory for the use of (6) in the case of a Boltzmann gas.

For the case of a E.B. or F.D. gas we will prove a theorem analogous to (7):

$$\left.\begin{array}{l} \sum_n {}_{E.B.} e^{-E_n/kT} \psi_n^2 \\ \sum_n {}_{F.D.} e^{-E_n/kT} \psi_n^2 \end{array}\right\} \xrightarrow[(T>1°)]{} \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} e^{-V/kT} \times \prod_{ij} (1 \pm \exp\left[-4\pi^2 mkTr_{ij}^2/h^2\right] \tag{8}$$

where the product has to be taken over all pairs of molecules, and $r_{ij}$ is the distance between the $(ij)$ pair. This again holds as indicated for temperatures so high that the influence of the discreteness of the translational energy levels is negligible, but not yet so high that the deviations due to the E.B. or F.D. statistics from the classical gas laws can be neglected. These are given by (8) in *first* approximation; in addition therefore the volume must not be too small. One sees from (8) that there is an apparent attractive force in the E.B. gas between each pair of molecules with the potential:

$$\phi' = - kT \log \left\{1 + e^{-4\pi^2 mkT/h^2 r^2}\right\} \tag{9}$$

Of course for temperatures so high that the deviations due to E.B. or F.D· statistics can be neglected compared to the non-ideality of the gas ($T$, say for He, $>20°$ absolute) (8) goes over into (7).

**3.** Because the total potential energy $V$ (in absence of external fields) can be written in the form:

$$V = \sum_{ij} \phi(r_{ij})$$

(8) can by using (9) be put in the form,

$$\sum{}_{E.B.} = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \prod_{ij} e^{-(\phi_{ij}+(\phi_{ij}')/kT}. \tag{8a}$$

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[6] We will distinguish the integrands of $S_{QB}$, $S_{QE \cdot B}$ by subscripts $B$, $E.B.$ etc. and sometimes write for the sums simply $\Sigma_B$, $\Sigma_{E \cdot B}$. etc.

Exactly as (7) is carried through by way of (6) to give (1), so (8a) is carried through and will give again (1) when we replace there $\phi$ by $\phi+\phi'$. Introducing then the value of $\phi'$ we immediately obtain (3) and (4).

To obtain an idea of the contribution of $B_{E.B.}'$ to the second virial coefficient, we have made in the case of helium a graphical integration, introducing for $\phi(r)$ the theoretical expression used by Kirkwood and Keyes, and the slightly different one proposed by Margenau, as well as the half empirical one calculated by Lennard-Jones.[7] We got:

a. $T = 20° : B_{E.B.} = -0{\cdot}8 \quad B'_{E.B.} \cong +1{\cdot}2$

b. $T = 5° : B_{E.B.} = -6{\cdot}4 \quad B'_{E.B.} \cong +5.4.$

We see therefore that $B_{E.B.}$ and $B_{E.B.}'$ are of opposite sign and of the same order of magnitude at these low temperatures. At higher temperatures of course both go to zero rapidly. It is clear therefore that because of this fact, it will be still more difficult to decide from the experimentally determined $B$ values at low temperatures, between the classical and the E.B. statistics. In fact, with the uncertainties still existing at present, both in the theory of the intermolecular potential $\phi(r)$ and in the experimental material, in spite of the rather great accuracy and extent of the latter,[8] it seems to us rather hopeless to try to make this distinction with this method.

Quite analogous results are obtained for the F.D. statistics, the signs being merely reversed,

$$B_{F.D.} = -B_{E.B} \qquad B'_{F.D.} = -B'_{E.B}.$$

so that also the existence of the F.D. statistics may not be ruled out.

## II. A New Treatment of the Ideal Gas

**4.** In order to prove (7) and (8), it will be convenient to show it first in the case of the ideal gas, because as we will see in Chapter III, the proof for the general case can be made to rest upon the evaluation of the sum for the ideal gas. Consider first as the simplest case two atoms in a one-dimensional box of length $L$.

*a*. With Boltzmann statistics we have to take *all* linearly independent wave functions belonging to each energy value, and we get therefore for the sum:

$$\begin{aligned}\textstyle\sum_B &= \frac{4}{L^2}\sum_{n_1\geqq n_2}\sum e^{-\alpha\pi^2/L^2(n_1^2+n_2^2)}\left(\tfrac{1}{2}\right)^{\delta_{n_1n_2}}\left\{\sin^2\frac{n_1\pi x_1}{L}\sin^2\frac{n_2\pi x_2}{L}\right.\\ &\qquad\left.+\sin^2\frac{n_1\pi x_2}{L}\sin^2\frac{n_2\pi x_1}{L}\right\}\\ &= \frac{4}{L^2}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}e^{-\alpha\pi^2/L^2(n_1^2+n_2^2)}\sin^2\frac{n_1\pi x_1}{L}\sin^2\frac{n_2\pi x_2}{L}\end{aligned} \tag{10}$$

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[7] Comp. R. H. Fowler, Statistical Mechanics, Ch. X.

[8] Comp. G. P. Nijhoff, Dissertation Leiden, 1928.

$$= \left[\frac{2}{L} \sum_{n_1} e^{-\alpha\pi^2/L^2 n_1^2} \sin^2 \frac{n_1\pi x_1}{L}\right] \cdot \left[\frac{2}{L} \sum_{n_2} e^{-\alpha\pi^2/L^2 n_2^2} \sin^2 \frac{n_2\pi x_2}{L}\right]$$

where:

$$\alpha = h^2/8\pi^2 mkT$$

In the neighborhood of zero values of $x_1$ and $x_2$ we may replace the sums by integrals and obtain:

$$\sum\nolimits_B \cong \frac{2\pi mkT}{h^2}(1 - e^{-x_1^2/\alpha})(1 - e^{-x_2^2/\alpha}). \tag{11}$$

From the symmetry of the problem it is clear that for $x_1$ and $x_2$ in the neighborhood of $L$ we have an analogous expression replacing $x_1$ and $x_2$ in (11) by $L-x_1$ and $L-x_2$. We see therefore that $\Sigma_B$ is zero at the boundary of the square *OABC* and rises rapidly from all sides to the value $2\pi mkT/h^2$. In the center the wave functions in (10) will average out, because of their different phases. Replacing them by the average value 1/4 and the rest of the sum by the integral, (10) again becomes $2\pi mkT/h^2$, so that $\Sigma_B$ remains constant throughout in accordance with (7). As we will see in §5, the exponentials in (11) account for the correction due to the discreteness of the energy levels.

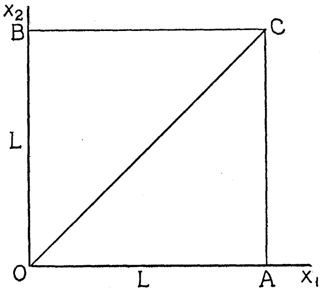

Fig. 1.

*b*. With E.B. or F.D. statistics we get:

$$\left.\begin{matrix}\sum_{E.B.}\\ \sum_{F.D.}\end{matrix}\right\} = \frac{2}{L^2} \sum_{n_1 \geqq n_2}\sum e^{-\alpha\pi^2/L^2(n_1^2+n_2^2)}\left(\tfrac{1}{2}\right)^{\delta_{n_1 n_2}} \left\{\sin\frac{n_1\pi x_1}{L}\sin\frac{n_2\pi x_2}{L} \pm \sin\frac{n_1\pi x_2}{L}\sin\frac{n_2\pi x_1}{L}\right\}^2. \tag{12}$$

We see that *OC* is for each term of the sum a symmetry line; in the F.D. case it is a zero line, in the E.B. case a maximum line. This will therefore also be the case for the total sum. We get working the bracket out and going over from the double sum to products of single sums as in *a*:

$$\left.\begin{matrix}\sum_{E.B.}\\ \sum_{F.D.}\end{matrix}\right\} = \tfrac{1}{2}\sum\nolimits_B \pm \frac{1}{2L^2}\left[\sum_{n=0}^{\infty} e^{-\alpha\pi^2/L^2 n^2}\left\{\cos\frac{n\pi}{L}(x_1 - x_2) - \cos\frac{n\pi}{L}(x_1 + x_2)\right\}\right]^2. \tag{13}$$

All the terms in the first sum of the bracket are in phase along the line $x_1 = x_2$, whereas the second sum has a value only in the corners $O$ and $C$; in the rest of the square the second cos averages out to zero. Therefore we can neglect the second sum with respect to the first sum. Neglecting also the exponentials in $\Sigma_B$ (this can really only be justified for $N$ particles, see §5) and replacing the sum by an integral, we get:

$$\left.\begin{array}{l}\sum_{E.B.}\\ \sum_{F.D.}\end{array}\right\} = \frac{1}{2}\cdot\frac{2\pi mkT}{h^2}\left\{1 \pm e^{-\frac{1}{2\alpha}(x_1 - x_2)^2}\right\}. \tag{14}$$

This is in accordance with (8). We have therefore practically everywhere half the classical value; only along $OC$ it rises in the E.B. statistics sharply to the classical value, and in the F.D. statistics it decreases equally sharp to zero.

## 5.

Going over now to $N$ particles in a one-dimensional box of length $L$, we have:

*a.* for Boltzmann statistics:

$$\sum_B \cong \left(\frac{2\pi mkT}{h^2}\right)^{N/2} \prod_{i=1}^{N}(1 - e^{-x_i^2/\alpha}). \tag{15}$$

This is clearly (11) extended to $N$ particles. From this follows the free energy $\psi$, according to:

$$e^{-\psi/kT} = \int_0^L \cdots \int dx_1 \cdots dx_N \sum_B. \tag{16}$$

Of course one must remember that (15) holds only for every $x_i$ between 0 and $\frac{1}{2}L$, and that for the other half we have an analogous expression replacing $x_i$ by $L - x_i$. Because of this symmetry we can write Eq. (16):

$$e^{-\psi/kT} = \left(\frac{2\pi mkT}{h^2}\right)^{N/2}\cdot 2^N \int_0^{L/2} \cdots \int dx_1 \cdots dx_N \prod_i (1 - e^{-x_i^2/\alpha}).$$

Of all the terms in the product we need only those which after integration give terms proportional to $L^N$ and $L^{N-1}$; because we are only interested in the second virial coefficient. We then obtain:

$$e^{-\psi/kT} = \left(\frac{2\pi mkT}{h^2}\right)^{N/2} V^N\left[1 - \frac{N}{V}\left(\frac{h^2}{8\pi mkT}\right)^{1/2}\right] \tag{17}$$

writing $V$ for $L$ now. This gives for the pressure:

$$p = -\frac{\partial\psi}{\partial V} = \frac{NkT}{V}\left[1 + \frac{1}{V}\cdot\frac{1}{2^{3/2}}\left(\frac{h^2}{\pi mkT}\right)^{1/2}\right]. \tag{18}$$

This agrees with the result obtained by the direct calculation of the Zustandssumme.[9] The second term gives the correction due to the discreteness of the

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[9] For a gas of $N$ particles in a $n$-dimensional vessel this gives:

$$p = \frac{NkT}{V}\left[1 + \frac{1}{2^{3/2}}\,\frac{1}{V^{1/n}}\cdot\left(\frac{h^2}{\pi mkT}\right)^{1/2}\right]$$

energy levels. This correction is *independent of* $N$, in contrast to the correction due to the E.B. or F.D. statistics which are *proportional to* $N$. For this reason the above correction is completely negligible. *Because it arises from the exponentials in* (15) *we will from now on neglect these.*

*b*. For E.B. or F.D. statistics we get for the sum:

$$\left.\begin{matrix}\sum_{E.B.}\\ \sum_{F.D.}\end{matrix}\right\} = \frac{2^N}{L^N}\frac{1}{N!}\sum_{n_1\geqq n_2\geqq\cdots n_N}\sum\cdots\sum e^{-\alpha\pi^2/L^2(n_1{}^2+\cdots n_N{}^2)}g_{n_1\cdots n_N}$$

$$\left[\sum_{P\ (-1)^P}^{+1}\sin\frac{n_1\pi x_1}{L}\cdots\sin\frac{n_N\pi x_N}{L}\right]^2 \tag{19}$$

where the sum goes over all permutations of the $x_i$ keeping the quantum numbers fixed. The factor $g_{n_1\ldots n_N}$ is one, when all the $n_i$ are different; is $\frac{1}{2!}$ when two are the same and the other different; $\frac{1}{3!}$ when three are the same, etc. When we work the square out we get first of all the square terms, which are just the Boltzmann terms evaluated in *a*. From the rest of the terms we must select only those which after integration over $x_i$ will give terms proportional to $L^{N-1}$. One can easily convince oneself that these terms are of the type:

$$\sin\frac{n_1\pi x_i}{L}\sin\frac{n_1\pi x_j}{L}\sin\frac{n_2\pi x_i}{L}\sin\frac{n_2\pi x_j}{L}\cdot\left\{\begin{matrix}\sin^2\frac{n_3\pi x_1}{L}\sin^2\frac{n_4\pi x_2}{L}\cdots\\ \sin^2\frac{n_3\pi x_2}{L}\sin^2\frac{n_4\pi x_1}{L}\cdots\\ \cdots\cdots\cdots\cdots\end{matrix}\right. \tag{20}$$

As in §4 we write for the first four sin:

$$\tfrac{1}{4}\left[\cos\frac{n_1\pi}{L}(x_i-x_j)-\cos\frac{n_1\pi}{L}(x_i+x_j)\right]\times$$

$$\left[\cos\frac{n_2\pi}{L}(x_i-x_j)-\cos\frac{n_2\pi}{L}(x_i+x_j)\right].$$

For the same reason as in §4 we may neglect again the cos of the sum $x_i+x_j$. Going over from the multiple sum to products of single sums, and replacing the sums by integrals, we get:

$$\left.\begin{matrix}\sum_{E.B.}\\ \sum_{F.D.}\end{matrix}\right\} \cong \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{N/2}\left[1\pm\frac{1}{L^2}\cdot\frac{h^2}{2\pi mkT}\times\right.$$

$$\left.\sum_{ij}\left\{\cdot\int_0^\infty e^{-\alpha\pi^2/L^2n^2}\cos\frac{n\pi}{L}(x_i-x_j)dn\right\}^2\right]$$

$$\cong\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{N/2}\left[1\pm\sum_{ij}e^{-(x_i-x_j)^2/2\alpha}\right] \tag{21}$$

$$\cong\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{N/2}\prod_{ij}\left\{1\pm e^{-(x_i-x_j)^2/2\alpha}\right\}.$$

The sum and product are to be taken over all pairs. The last two lines differ only in terms which after integration over $x_i$ give terms proportional to powers of $L$ lower than $N-1$, and therefore they have been neglected. Formula (21) agrees with (8), when we put there $V=0$.

To check (21) further we may calculate the free energy. One obtains:

$$\begin{aligned} e^{-\psi/kT} &= \int_0^L \cdots \int dx_1 \cdots dx_N \left\{ \begin{array}{l} \sum_{E.B.} \\ \sum_{F.D.} \end{array} \right. \\ &= \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{N/2} V^N \left[1 \pm \frac{1}{V}\,\frac{N(N-1)}{2}\left(\frac{h^2}{4\pi mkT}\right)^{1/2}\right] \end{aligned}$$

where again we write $V$ for $L$. Neglecting the 1 with respect to $N$, we get for the pressure:

$$p = -\frac{\partial\psi}{\partial V} = \frac{NkT}{V}\left[1 \mp \frac{N}{V}\cdot\frac{1}{2^2}\left(\frac{h^2}{\pi mkT}\right)^{1/2}\right] \tag{22}$$

which agrees with well known results.[10] Comparing (15) and (21), and their consequences (18) and (22) resp. one sees that the reason why the E.B. or F.D. correction has the factor $N$, in contrast to the discreteness correction, is simply that the number of pairs, which one can form with $N$ objects ($x_i$), is $\frac{1}{2}N(N-1)$.

These considerations can immediately be extended to a gas in a three-dimensional rectangular vessel. One obtains then instead of (21):

$$\left.\begin{array}{l} \sum_{E.B.} \\ \sum_{F.D.} \end{array}\right\} = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \prod_{ij}(1 \pm e^{-(1/2\alpha)\{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2\}} \tag{21a}$$

so that one sees that the apparent potential due to the Bose-ness is radial (see Eq. (9)).

## III. The Non-Ideal E.B. or F.D. Gas

### §6.

The wave equation for the whole gas we write as:

$$(H - E)\psi = 0$$

where:

$$\left.\begin{aligned} H &= \sum_i \frac{1}{2m}(p_{xi}^2 + p_{yi}^2 + p_{zi}^2) + V(x_1 \cdots z_n) \\ V &= \sum_{ij}\phi_{ij} + \sum_i \pi_i \end{aligned}\right\} \tag{23}$$

where $\phi_{ij}$ is the interaction potential between the particles and $\pi_i$ an eventual external potential. We shall abbreviate always all the coordinates by $q$ and all the quantum numbers by $n$. We wish to show in this paragraph that:

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[10] For an E.B. or F.D. gas in an $n$-dimensional vessel one finds according to the usual method:

$$p = \frac{NkT}{V}\left[1 \mp \frac{1}{2^{n+1}}\left(\frac{h^2}{\pi mkT}\right)^{n/2}\frac{N}{V}\right].$$

$$\sum_n e^{-E_n/kT}\psi_n{}^2 = \sum_n \phi_n e^{-H/kT}\phi_n. \tag{24}$$

In the right-hand side $H$ is to be considered as an operator working on $\phi_n$, which are the normalized eigenfunctions for the *ideal* gas.[11] Formula (24) is true *regardless of the statistics*, that is to say, it holds equally well when we take on both sides only the symmetric wave functions (E.B. statistics), or only the antisymmetric wave functions (F.D. statistics), or all the wave functions (Boltzmann statistics).

For the proof one remarks first that for any function (power series) $f(x)$, we have:

$$f(E_n)\psi_n = f(H)\psi_n$$

in which $H$ again is the operator, in particular:

$$e^{-E_n/kT}\psi_n = e^{-H/kT}\psi_n. \tag{25}$$

We develop now $\psi_n$ according to the normalized eigenfunctions of the ideal gas. In the case of a cubicle vessel this is simply a development in a multiple Fourier-series

$$\psi_n(q) = \sum_m c_{nm}\phi_m(q) \tag{26}$$

where one must then remember that $\phi_m(q)$ is an abbreviation for:[12]

$$\phi_{m_1\cdots m_{3N}}(x_1\cdots z_N) = \left(\frac{2}{L}\right)^{3N/2}\sin\frac{m_1\pi x_1}{L}\sin\frac{m_2\pi y_1}{L}\cdots\sin\frac{m_{3N}\pi z_N}{L}\cdot$$

Substituting (25) and (26) in the left-hand side of (24) we get:

$$\sum_n \psi_n e^{-E_n/kT}\psi_n = \sum_n\sum_i\sum_j c_{ni}c_{nj}\phi_i e^{-H/kT}\phi_j = \sum_i \phi_i e^{-H/kT}\phi_i$$

since: $\Sigma_n c_{ni}c_{nj} = \delta_{ij}$.

§7.

Introducing for simplification:

$$V' = 8\pi^2 mV/h^2 \quad E' = 8\pi^2 mE/h^2$$

the wave equation becomes:

$$d^2\psi/dq^2 + (E' - V')\psi = 0$$

and for the sum, using (24) we get:

$$\sum_n e^{-E_n/kT}\psi_n{}^2 = \sum_n e^{-\alpha E'_n}\psi_n{}^2 = \sum_n \phi_n e^{\alpha(d^2/dq - V')}\phi_n$$

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[11] Comp. F. Bloch, Zeits. f. Physik **74**, 295 (1932). We came to this result independently and because our point of view is somewhat different, we thought it not superfluous to repeat the proof.

[12] This is in the case of the Boltzmann statistics. For the E.B. or F.D. statistics one takes the symmetric or antisymmetric combinations, and because these form with respect to symmetric resp. antisymmetric functions a *complete* orthogonal set, the argument remains the same.

where $\alpha$ has again the meaning $h^2/8\pi^2 mkT$ and where $q$ abbreviates again the $3N$ coordinates of the gas.

We will prove now that *when $\alpha$ is very small,* we have *in first approximation:*

$$\sum_n \phi_n e^{\alpha(d^2/\alpha q^2 - V')}\phi_n \cong e^{-\alpha V'} \sum_n e^{-\alpha\epsilon_n'}\phi_n{}^2 \tag{27}$$

where $h^2\epsilon_n'/8\pi^2 m$ are the energy values of the ideal gas. In particular for a cubicle vessel

$$\epsilon_n' = \pi^2(n_1{}^2 + n_2{}^2 + \cdots n_{3N}{}^2)/L^2.$$

In this way the evaluation of the sum for the *non-ideal* gas reduces to that for the *ideal* gas. Using then the results of Chapter II, we will then have proved our main theorems (7) and (8).

Formula (27) is not obvious, because $d^2/dq^2$ and $V'$ are not commutable, so that in general:

$$e^{\alpha(d^2/dq^2 - V')} = e^{\alpha(-V' + d^2/dq^2)} \mp e^{-\alpha V} \cdot e^{\alpha d^2/dq^2}$$
$$\mp e^{\alpha d^2/dq^2} \cdot e^{-\alpha V'}.$$

To prove (27), write:

$$F = e^{\alpha(d^2/dq^2 - V')}\phi_n$$

then $F$ will fulfill the differential equation:[13]

$$\partial F/\partial\alpha = (\partial^2/\partial q^2) - V')F$$

which we rewrite:

$$\partial F/\partial\alpha + (\epsilon_n' + V')F = (\partial^2/\partial q^2 + \epsilon_n')F \tag{28}$$

For $\alpha = 0$, $F = \phi_n$ and the right member is zero. In *first* approximation therefore:

$$F = \phi_n e^{-\alpha(\epsilon_n' + V')} \tag{29}$$

which gives (27). In Note I we will prove that in higher approximations:

$$\sum_n \phi_n e^{\alpha(d^2/dq^2 - V')}\phi_n = e^{-\alpha V'} \sum_n e^{-\alpha\epsilon_n'}\phi_n{}^2 \cdot [1 + \alpha f_1(q) + \alpha^2 f_2(q) + \cdots ] \tag{30}$$

which justifies more strictly that (27) is true for small $\alpha$; $f_1(q)$, $f_2(q)$ are certain functions of the coordinates, which contain $V$ and its derivatives.

As a special example, which is of interest because the summations can be carried out exactly, we will consider in Note II the case of the harmonic oscillator.

*Note I.*

To find the next approximation we substitute (29) in the right-hand side of (28). Considered as a differential equation for $F$ as a function of $\alpha$, we can immediately integrate. Making use of the Schrödinger equation:

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[13] Comp. F. Bloch, reference 11.

$$(d^2/dq^2 + \epsilon_n')\phi_n = 0$$

we obtain:

$$F = \left[\phi_n - \frac{\alpha^3}{2}\left\{\phi_n\frac{d^2V'}{dq^2} + 2\frac{d\phi_n}{dq}\cdot\frac{dV'}{dq}\right\} + \frac{\alpha^3}{3}\phi_n\left(\frac{dV'}{dq}\right)^2\right]e^{-\alpha(\epsilon_n' \ V')} \tag{31}$$

Substituting in the left-hand side of (27) and calling the sum for the ideal gas:

$$S = \sum_n e^{-\alpha\epsilon_n}\phi_n^2$$

we get:

$$\sum_n \phi_n e^{\alpha(d^2/dq^2-V\ )}\phi_n \cong e^{-\alpha V'}\left\{S - \frac{\alpha^2}{2}\left(\frac{d^2V'}{dq^2}S + \frac{dV'}{dq}\cdot\frac{dS}{dq}\right) + \frac{\alpha^3}{3}\left(\frac{dV'}{dq}\right)^2\cdot S\right\}$$

Substituting the value of $S$ from (15) and (21), only the third term of the right-hand member will give a term proportional to $\alpha$. Neglecting the terms which give $\alpha^2$ and $\alpha^3$, we obtain:

*a*. for Boltzmann statistics:

$$\sum\nolimits_{\mathrm{B}} = \left(\frac{1}{4\pi\alpha}\right)^{3N/2} e^{-\alpha V'}\prod_i(1 - e^{-x_i^2/\alpha})\cdot\left[1 - \alpha\sum_i \frac{\partial V}{\partial x_i}\frac{x_i e^{-x_i^2/\alpha}}{1 - e^{-x_i^2/\alpha}} + \cdots\right] \tag{32}$$

*b*. for E.B. or F.D. statistics:

$$\left.\begin{matrix}\sum_{\mathrm{E.B}}\\ \sum_{\mathrm{F.D}}\end{matrix}\right\} = \frac{1}{N'}\left(\frac{1}{4\pi\alpha}\right)^{3N/2} e^{-\alpha V'}\prod_{ij}(1 \pm e^{-(x_i-x_j^2/2\alpha)})$$

$$\cdot\left[1 \pm \frac{\alpha}{4}\sum_{ij}\frac{(x_i-x_j)e^{(-1/2\alpha)(x_i x_j)^2}}{1 \pm e^{-(x_i-x_j)^2/2\alpha}}\left(\frac{\partial V'}{\partial x_i} - \frac{\partial V'}{\partial x_j}\right) + \cdots\right]. \tag{33}$$

We must remark, that the terms proportional to $\alpha$ in (32) and (33) contribute to the second virial coefficient, but as one easily verifies they will give corrections to (3) which are proportional to $\alpha^3$ (for a gas in a three dimensional vessel), whereas (2) is only proportional to $\alpha^{3/2}$.

Further one must remark that the second term in the bracket of (32) and (33) are *not* the $f_1(g)$ of (30), for if one proceeds to the next approximation, one gets another term proportional to $\alpha$, which contains $\partial^2 V'/\partial x_i^2$. One can convince oneself though that in the second virial coefficient these terms give corrections proportional to powers of $\alpha$ higher than $\alpha^3$.

One can approach the proof of (27) from a somewhat more general standpoint. When $f$ and $g$ are any two non-commutable quantities, one can show that for small values of $\alpha$:[14]

$$e^{\alpha(f+g)} = \{1 + (\alpha^2/2)(gf - fg) + \cdots\}e^{\alpha f}\cdot e^{\alpha g}$$

When we identify now $g$ with $d^2/dg^2$ and $f$ with $V'$, and let $\exp[\alpha(f+g)]$ work on $\phi_n$ one obtains again (31).[15]

*Note II.*

For the harmonic oscillator it is possible to carry out the sums exactly. Introducing the abbreviations:

$$y = 2\pi x(m\nu/h)^{1/2} \qquad \theta = h\nu/kT$$

we can write:

$$(2\pi mkT)^{-1/2}\sum_n e^{-E_n/kT}\psi_n^2 = (2\theta)^{1/2}e^{-\theta/2-y^2}\sum_n e^{-n\theta}\frac{H_n^2(y)}{2^n\cdot n!} \tag{34}$$

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[14] Comp. J. E. Campbell, Theory of continuous Groups, pp. 54–57, for analogous questions.

[15] One uses here the special case $n=2$ of a general formula for

$$f\frac{d^n}{dg^n} - \frac{d^n}{dg^n}\cdot f.$$

derived by Hylleras (Zeits. f. Physik **74,** 216 (1932)).

where $\nu$ is the frequency and $H_n$ the $n^{th}$ Hermite polynomial. Introducing Weber's function $D_n(y)$:[16]

$$H_n(2^{-1/2}y) = 2^{n/2}e^{y^2/4}D_n(y)$$

the right-hand side becomes:

$$(2\theta)^{1/2}e^{-\theta/2}\sum_n e^{-n\theta}D_n{}^2(2^{1/2}y)/n!.$$

We distinguish again *two* cases;

*a*. Boltzmann statistics. We have to sum over *all* values of $n$. From the general result:[17]

$$\sum_n \frac{D_n(\xi)D_n(\eta)}{n'}e^{-nx} = (1-e^{-2x})^{-1/2}e^{(\xi^2+\eta^2))/4}\exp\left\{-\frac{\xi^2+\eta^2-2\xi\eta e^{-x}}{2(1-e^{-2x})}\right\} \tag{35}$$

putting $x=\theta$; $\xi=\eta=2^{1/2}y$, we obtain:

$$(2\pi mkT)^{-1/2}\sum_n e^{-E_n/kT}\psi_n{}^2 = \left(\frac{2\theta}{1-e^{-2\theta}}\right)^{1/2}\exp\left(-\frac{\theta}{2}-y^2\operatorname{tgh}\frac{\theta}{2}\right). \tag{36}$$

One sees that for $\theta$ very small the right-hand side goes over into:

$$e^{-\theta y^2/2} = e^{-2\pi^2 m\nu^2x^2/kT} = e^{-V/kT}.$$

*b*. E.B. or F.D. statistics. We must suppose then that we have to do with two particles attracting each other with a force proportional to the distance between them, moving in a one-dimensional vessel. If $x$ stands for the distance between the particles, in E.B. statistics we must take only the eigenfunctions *even* in $x$, and in F.D. statistics we must take the *odd* ones. Separating into center of gravity and relative motion coordinates,[18] we have then to consider for the relative motion simply the sum (34) where in E.B. statistics we have to sum over all even values of $n$, and in F.D. statistics over the odd values[19] and where one must remember to replace $m$ by $\frac{1}{2}m$. Using now the general result;[20]

$$\left.\begin{matrix}\sum\limits_{n\text{even}}\\ \sum\limits_{n\text{odd}}\end{matrix}\right\}\frac{D_n(\xi)D_n(\eta)}{n'}e^{-nx} = (1-e^{-2x})^{-1/2}\exp\left(-\frac{\xi^2+\eta^2}{4}\operatorname{cotgh}x\right)\begin{matrix}\cosh\\ \sinh\end{matrix}\left\{\frac{\xi\eta e^{-x}}{1-e^{-2x}}\right\}. \tag{37}$$

From this follows then immediately:

$$\left.\begin{matrix}(\pi mkT)^{-1/2}\sum\text{E.B.}\\ (\pi mkT)^{-1/2}\sum\text{F.D.}\end{matrix}\right\} = \tfrac{1}{2}\left(\frac{2\theta}{1-e^{-2\theta}}\right)^{1/2}\exp\left(-\frac{\theta}{2}-y^2\operatorname{tgh}\frac{\theta}{2}\right)\cdot\left\{1\pm\exp\left(-\frac{2y^2}{\sinh\theta}\right)\right\} \tag{38}$$

For small $\theta$ the right-hand side goes over into:

$$\tfrac{1}{2}e^{-\pi^2 m\nu^2x^2/kT}(1\pm e^{-4\pi^2 mkTx^2/h^2})$$

in accordance with (8).

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[16] Whittaker-Watson, Modern Analysis, p. 347.

[17] See G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930). F. Bloch reference 11 also gives the result, using a transformation function of Kennard (Zeits. f. Physik **44**, 326, 1927.)

[18] Strictly this is only possible for an infinite vessel. Because we are not interested here in the discreteness effect of the total translational motion, this is quite allowed.

[19] The center of gravity motion will simply give an extra factor $(4\pi mkT/h^2)^{1/2}$.

[20] The proof is quite analogous as given for (35) by G. E. Uhlenbeck and L. S. Ornstein, reference 17.