Einstein's second manuscript on the ideal Bose gas — the paper in which Bose–Einstein condensation was discussed for the first time — again was announced in a session of the Prussian Academy of Sciences, held on 8 January 1925. The work was published in the *Sitzungsberichte* I of 1925, with its abstract included in the session's survey on p. 1:

2. Mr. EINSTEIN handed in a work on the quantum theory of the monoatomic ideal gas (second treatise).

The theory of the degeneracy of gases developed previously by myself is elaborated further. It turns out that for every temperature there exists a saturation density of the ideal gas, such that the molecules in excess of this density do not take part in the thermal agitation. The statistical properties (density-fluctuations) are investigated. The equation of state is discussed, and a convenient approximate formula for it is stated.

The paper then follows on pp. 3–14:

## Quantum theory of the monoatomic ideal gas Second treatise.

BY A. EINSTEIN.

In a treatment which has appeared recently in these proceedings (XXII 1924, p. 261) a theory of the "degeneracy" of ideal gases has been given, applying a method devised by Mr. D. BOSE for the derivation of PLANCK's radiation formula. The interest in this theory stems from the fact that it is based on a far-reaching relationship between radiation and gas. According to this theory, the degenerate gas deviates from the gas of mechanical statistics in a manner analogous to the deviation of the radiation described by PLANCK's law from the radiation described by WIEN's law. If BOSE's derivation of PLANCK's radiation formula is taken seriously, then one will not be allowed to ignore this theory of the ideal gas; since if it is justified to regard the radiation as a quantum gas, then the analogy between the quantum gas

and the molecule gas has to be a complete one. In the following the previous deliberations shall be augmented by some new ones, which in my opinion enhance the interest in this matter. For the sake of convenience I will write the following formally as a continuation of the treatment cited.

#### §6. The saturated ideal gas.

In the theory of the ideal gas it seems to be an unquestionable requirement that volume and temperature of a sample of gas can be prescribed arbitrarily. The theory then determines the energy, or the pressure of the gas. However, studying the equation of state contained in the equations (18), (19), (20), (21) shows that for a given number of molecules n and a given temperature T the volume can not be made arbitrarily small. Namely, equation (18) demands that  $\alpha^s \ge 0$  for all s, which according to (20) means that  $A \ge 0$  has to hold. This means that in the equation (18b), which is relevant in this case,  $\lambda \ (= e^{-A})$  has to lie between 0 and 1. Hence, from (18b) it follows that the number of molecules in such a gas, at given volume V, can not be larger than

$$n = \frac{(2\pi m\kappa T)^{3/2}V}{h^3} \sum_{s}^{\infty} \tau^{-3/2} .$$
 (24)

But what happens now if I let at this temperature the density  $\frac{n}{V}$  of the substance increase (*e.g.*, by isothermal compression) to even higher values?

I claim that in this case a number of molecules which always grows with the total density makes a transition to the 1. quantum state (state without kinetic energy), whereas the remaining molecules distribute themselves according to the parameter value  $\lambda = 1$ . The claim thus asserts that something similar happens as when isothermally compressing a vapour beyond the volume of saturation. A separation occurs; a part "condenses", the rest remains a "saturated ideal gas" ( $A = 0, \lambda = 1$ ).

The fact that both parts indeed form a thermodynamic equilibrium can be grasped by showing that the "condensed" substance and the saturated ideal gas have the same PLANCKian function  $\Phi = S - \frac{\overline{E} + pV}{T}$  per mole. For the "condensed" substance  $\Phi$  vanishes, since  $S, \overline{E}$ , and V vanish individually [1]. For the "saturated gas" one first has from (12) and (13) for A = 0

$$S = -\kappa \sum_{s} \ln\left(1 - e^{-\alpha^{s}}\right) + \frac{E}{T} \,. \tag{25}$$

The sum can be written as an integral and manipulated by integrating by parts. In this way one finds

$$\sum_{s} = -\int_{0}^{\infty} s \cdot \frac{e^{-\frac{cs^{2/3}}{\kappa T}}}{1 - e^{-\frac{cs^{2/3}}{\kappa T}}} \cdot \frac{2}{3} \frac{cs^{-1/3}}{\kappa T} \,\mathrm{d}s \;,$$

or, by virtue of (8) and (11) and (15),

$$\sum_{s} = -\frac{2}{3} \int_{0}^{\infty} n_{s} E^{s} \,\mathrm{d}s = -\frac{2}{3} \frac{\overline{E}}{\kappa T} = -\frac{pV}{\kappa T} \,. \tag{26}$$

Thus, from (25) and (26) it follows for the "saturated ideal gas"

$$S = \frac{\overline{E} + pV}{T}$$

or — as it is required for the coexistence of the saturated ideal gas with the condensed substance —

$$\Phi = 0 . \tag{21}$$

(97)

Therefore, we obtain the following theorem:

According to the developed equation of state of the ideal gas there is for every temperature a maximum density of molecules being in agitation. If this density is exceeded, the excess molecules fall out into an unmoving state (they "condense" without attractive forces). The remarkable point lies in the fact that the "saturated ideal gas" represents both the state of maximum possible density of moving gas molecules and that density at which the gas is in thermodynamic equilibrium with the "condensate". Hence, an analogue of "oversaturated vapour" does not exist for the ideal gas.

### §7. Comparison of the gas theory developed here with the one that follows from the hypothesis of the mutual statistical independence of the gas molecules.

An aspect of BOSE's theory of radiation and of my analogous theory of the ideal gases which has been criticized by Mr. EHRENFEST and other colleagues is that in these theories the quanta or molecules are not treated as mutually statistically independent entities; this matter not being pointed out explicitly in our treatments. This is absolutely correct. If the quanta are treated as mutually statistically independent in their localization, one arrives at WIEN's displacement law; if one treats the gas molecules in an analogous manner, one arrives at the classical equation of state of the ideal gases, even when proceeding in all other respects exactly as BOSE and I have done. I want to iuxtapose both views for gases here, in order to make the difference fairly clear, and in order to be able to compare our results with those provided by the theory of independent molecules in a convenient manner.

According to both theories, the number  $z_{\nu}$  of "cells" belonging to the infinitesimal domain  $\Delta E$  of molecular energy (denoted as "elementary domain" in the following) is given by

$$z_{\nu} = 2\pi \frac{V}{h^3} (2m)^{3/2} E^{1/2} \Delta E .$$
(2a)

Let the state of the gas be (macroscopically) defined by the statement how many molecules  $n_{\nu}$  lie in each such infinitesimal domain. One is asked to calculate the number W of possible realizations (PLANCKian probability) of the state defined in this way,

#### a) following BOSE:

A state of the gas is microscopically defined by specifying how many molecules are sitting in each cell (complexion). The number of complexions for the  $\nu$ -th infinitesimal domain then is

$$\frac{(n_{\nu} + z_{\nu} - 1)!}{n_{\nu}! (z_{\nu} - 1)!} . \tag{28}$$

By forming the product over all infinitesimal domains one obtains the total number of complexions of a state, and from this, according to BOLTZMANN's theorem, the entropy

$$S = \kappa \sum_{\nu} \left\{ (n_{\nu} + z_{\nu}) \ln(n_{\nu} + z_{\nu}) - n_{\nu} \ln n_{\nu} - z_{\nu} \ln z_{\nu} \right\} .$$
(29a)

The fact that this method of calculation does not treat the distribution of the molecules over the cells as statistically independent is easy to see. This is connected with the circumstance that those cases which are denoted as "complexions" here would not be regarded as cases of equal probability if the hypothesis of the independent distribution of the individual molecules over the cells were adopted. Counting the "complexions" equipped with different probabilities then would not yield the correct entropy if the molecules were actually statistically independent. Therefore, the formula indirectly expresses a certain hypothesis concerning a mutual influence of the molecules of a, at present, totally mysterious kind; this influence just effectuates the equal statistical probability of the cases defined here as "complexions".

b) according to the hypothesis of the statistical independence of the molecules:

A state is microscopically defined by specifying for each molecule the cell it is sitting in (complexion). How many complexions belong to a macroscopically defined state? I can distribute  $n_{\nu}$  given molecules in

 $z_{\nu}^{n_{\nu}}$ 

different ways over the  $z_{\nu}$  cells of the  $\nu$ -th elementary domain. If the assignment of the molecules to the elementary domains in a certain way has already been done, then there is a total number of

$$\prod \left( z_{\nu}^{n_{\nu}} \right)$$

different distributions of the molecules over the cells. In order to obtain the number of complexions in the sense defined above, this amount still has to be multiplied by the number

$$\frac{n!}{\prod n_{\nu}!}$$

of possible assignments of all molecules to the elementary domains, when n is given. BOLTZ-MANN's principle then yields for the entropy the expression

$$S = \kappa \left\{ n \ln n + \sum_{\nu} \left( n_{\nu} \ln z_{\nu} - n_{\nu} \ln n_{\nu} \right) \right\} .$$
 (29b)

The first term in this expression does not depend on the choice of the macroscopic distribution, but only on the total number of molecules. When comparing the entropies of different macroscopic states of the same gas, this term plays the role of a meaningless constant which we may omit. We *have to* omit it, if — as is usual in thermodynamics — we want to achieve that, the inner state of the gas being given, the entropy be proportional to the number of molecules. Thus, we have to set

$$S = \kappa \sum_{\nu} n_{\nu} (\ln z_{\nu} - \ln n_{\nu}) .$$
 (29c)

One usually justifies this omission of the factor n! in W for gases by regarding complexions which are generated by a mere interchange of identical molecules not as different, and therefore counts them only *once*.

Now we have to determine for both cases the maximum of S, subject to the constraints

$$\overline{E} = \sum E_{\nu} n_{\nu} = \text{const.}$$
$$n = \sum n_{\nu} = \text{const.}$$

In case a) one obtains

$$n_{\nu} = \frac{z_{\nu}}{e^{\alpha + \beta E} - 1},\tag{30a}$$

which, apart from the notation, agrees with (13). In case b) one obtains

$$n_{\nu} = z_{\nu} e^{-\alpha - \beta E} . \tag{30b}$$

In both cases, one has  $\beta \kappa T = 1$ .

One also sees that in case b) MAXWELL's distribution law results. The quantum structure does not make itself felt here (at least not if the total volume of the gas is infinitely large). It is now easy to see that case b) is irreconcilable with NERNST's theorem. Namely, in order to calculate the value of the entropy at the absolute zero point of temperature for this case, one has to evaluate (29c) for the absolute zero point. At this point, all molecules will occupy the first quantum state. Therefore, we have to set

$$n_{\nu} = 0 \quad \text{for } \nu \neq 1$$
  
 $n_1 = n$   
 $z_1 = 1$ .

(29c) thus yields for T = 0

$$S = -n\ln n . ag{31}$$

Thus, when adopting the method b) there exists a contradiction to the statement made by NERNST's theorem. In contrast, the method a) is in accordance with NERNST's theorem, as can be seen immediately when considering that at the absolute zero point there exists only a single complexion (W = 1) in the sense of the method a). According to the above deliberations, the viewpoint b) leads either to a violation of NERNST's theorem or to a violation of the requirement that the entropy be proportional to the number of molecules when the inner state is given. For these reasons I believe that the method a) (*i.e.*, Bose's statistical ansatz) has to be preferred, even if the preference of this method to others can not be proven a priori. This result, in its turn, provides support for the notion of a deep inner relationship between radiation and gas, insofar as the same statistical viewpoint which leads to PLANCK's formula establishes, when applied to ideal gases, the agreement of the gas theory with NERNST's theorem.

#### §8. The fluctuation properties of the ideal gas.

Let a gas of volume V communicate with a gas of the same kind in an infinitely large volume. Both volumes be separated by a wall penetrable only for molecules in an infinitesimal energy domain  $\Delta E$ , and reflecting molecules with any other kinetic energy. The fiction of such a wall is analogous to the quasi-monochromatically penetrable wall in the area of radiation theory. We ask for the fluctuation  $\Delta_{\nu}$  of the number  $n_{\nu}$  of molecules belonging to the energy domain  $\Delta E$ . It is assumed that there be no exchange of energy among molecules of different energy domains within V, so that there be no fluctuations of numbers of molecules belonging to energies no covered by  $\Delta E$ .

Let now  $n_{\nu}$  be the mean value of the molecules belonging to  $\Delta E$ , and  $n_{\nu} + \Delta_{\nu}$  its instantaneous value. Then (29a) yields the value of the entropy as a function of  $\Delta_{\nu}$ , if one inserts  $n_{\nu} + \Delta n_{\nu}$  instead of  $n_{\nu}$  into this equation. Proceeding up to the quadratic terms, one obtains

$$S = \overline{S} + \frac{\overline{\partial S}}{\partial \Delta_{\nu}} \Delta_{\nu} + \frac{1}{2} \frac{\overline{\partial^2 S}}{\partial \Delta_{\nu}^2} \Delta_{\nu}^2 \,.$$

A similar relation holds for the infinitely large remaining system, namely

$$S^0 = \overline{S^0} - \frac{\overline{\partial S^0}}{\partial \Delta_\nu} \Delta_\nu$$

Here, the quadratic term is relatively infinitely small because of the relatively infinite size of the remaining system. If one denotes the total entropy by  $\sum (=S+S^0)$ , one has  $\frac{\partial \overline{\Sigma}}{\partial \Delta_{\nu}} = 0$ , since on the average there is equilibrium. Thus, adding these equations one obtains for the total entropy the relation

$$\Sigma = \overline{\Sigma} + \frac{1}{2} \frac{\overline{\partial^2 S}}{\partial \Delta_{\nu}^2} \Delta_{\nu}^2 .$$
(32)

According to BOLTZMANN's principle one finds from this for the probability of  $\Delta_{\nu}$  the law

$$\mathrm{d}W = \mathrm{const.} \, e^{S/\kappa} \, \mathrm{d}\Delta_{\nu} = \mathrm{const.} \, e^{\frac{1}{2\kappa} \frac{\overline{\partial^2 S}}{\partial \Delta_{\nu}^2} \Delta_{\nu}^2} \, \mathrm{d}\Delta_{\nu} \, .$$

Hence, it follows for the mean square fluctuation

$$\overline{\Delta_{\nu}^2} = \frac{\kappa}{\left(-\frac{\overline{\partial^2 S}}{\partial \Delta_{\nu}^2}\right)} \,. \tag{33}$$

From this one obtains, taking into account (29a),

$$\overline{\Delta_{\nu}^2} = n_{\nu} + \frac{n_{\nu}^2}{z_{\nu}} \,. \tag{34}$$

This fluctuation law is entirely analogous to the one for the quasi-monochromatic PLANCKian radiation. We write it in the form

$$\overline{\left(\frac{\Delta_{\nu}}{n_{\nu}}\right)^2} = \frac{1}{n_{\nu}} + \frac{1}{z_{\nu}} . \tag{34a}$$

The square of the mean relative fluctuation of the molecules of the considered kind is composed of two parts. The first would appear alone if the molecules were independent from each other. In addition, there is a part of the mean square of fluctuation which is entirely independent of the mean molecule density, determined only by the elementary domain  $\Delta E$ and the volume. It corresponds to the interference fluctuations of the radiation. One can interpret this term also for gases in the corresponding manner, if one assigns to the gas in a suitable way a radiation process and calculates the interference fluctuations of the latter. I will explain this interpretation in more detail, because I believe that this concerns more than a mere analogy.

How a (scalar) wave field can be assigned to a material particle or a system of material particles has been pointed out by Mr. E. DE BROGLIE in a very noteworthy treatment [2]. To a material particle of mass m one first assigns a frequency  $\nu_0$  according to the equation

$$mc^2 = h\nu_0 . aga{35}$$

The particle be now at rest with respect to a galilean system K', in which we have an oscillation with the frequency  $\nu_0$  which is everywhere synchronous. Relative to a system K, with respect to which K' with the mass m moves with velocity v along the (positive) X-axis, there then exists a wavelike process of the kind

$$\sin\left(2\pi\nu_0\frac{t-\frac{v}{c^2}x}{\sqrt{1-\frac{v^2}{c^2}}}\right)$$

Thus, the frequency  $\nu$  and the phase velocity V of this process are given by

$$\nu = \frac{\nu_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$
(36)

$$V = \frac{c^2}{v} \,. \tag{37}$$

v then also is — as has been shown by Mr. DE BROGLIE — the group velocity of this wave. Moreover, it is interesting that by virtue of (35) and (36) the energy  $\frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}}$  of the particle is just equal to  $h\nu$ , in accordance with the basic relation of quantum theory.

One now sees that to such a gas one can assign a scalar wave field, and I have convinced myself by calculation that the mean square fluctuation of this wave field is  $\frac{1}{z_{\nu}}$ , as far as it corresponds to the energy domain  $\Delta E$  studied above.

These deliberations throw light on the paradox which has been pointed out at the end of my first treatment. In order to be able to interfere in a notable manner, two trains of waves have to be nearly identical with respect to V and  $\nu$ . According to (35), (36) and (37), this requires that v and m be almost identical for both gases. Therefore, the wave fields assigned to two gases of notably different molecular masses can not interfere notably. Hence, one can deduce that according to the theory presented here the entropy of a mixture of gases is composed in the same additive manner from that of its constituents as according to the classical theory, at least as long as the molecular masses of the components deviate somewhat from each other.

#### §9. Remark concerning the viscosity of the gases at low temperature.

According to the considerations of the previous paragraph it appears that there is an undulatoric field associated with every process of motion, just as the optical undulatoric field is associated with the motion of light quanta. This undulatoric field — the physical nature of which is still in the dark, has, in principle, to be observable through its corresponding phenomena of motion. Thus, a beam of gas particles traversing a slit should be subject to a diffraction which is analogous to the one of a beam of light. In order to observe such a phenomenon, the wavelength  $\lambda$  has to be about comparable to the dimensions of the slit. From (35), (36), and (37) it follows now that for velocities small compared to c,

$$\lambda = \frac{V}{\nu} = \frac{h}{mv} \,. \tag{38}$$

This  $\lambda$  is always exceedingly small for gas molecules moving with thermal velocities, in most cases even substantially smaller than the molecular diameter  $\sigma$ . Hence, it follows that one can not even think about observing this diffraction with manufacturable slits or screens.

However, it is evident that at low temperatures  $\lambda$  becomes of the order of magnitude of  $\sigma$  for the gases Hydrogen and Helium, and it indeed seems that the coefficient of friction will suffer the influence which we have to excpect according to the theory.

Namely, if a bunch of molecules moving with velocity v hits another molecule, which, for the sake of convenience, we imagine to be at rest, then this is comparable to the case that a train of waves with a certain wavelength  $\lambda$  hits a leaflet with the diameter  $2\sigma$ . Then a diffraction phenomenon (in the sense of FRAUNHOFER) occurs, which equals the one furnished by a slit of the same size. Large angles of diffraction occur if  $\lambda$  is of the order of  $\sigma$  or larger. Therefore, apart from the deflections on impact which occur according to mechanics, there will then also be deflections of the molecules which can not be understood in mechanical terms, occurring with similar frequency as the former ones and diminishing the free path. Therefore, close to that temperature an accelerated decrease of the viscosity with decreasing temperature will set in rather abruptly. An estimate of that temperature on the basis of the relation  $\lambda = \sigma$  yields 56° for H<sub>2</sub>, 40° for He. Needless to say, these are quite rough estimates; they can, however, be replaced by more accurate calculations. This amounts to a new interpretation of the experimental results obtained by P. GÜNTHER with Hydrogen, following a suggestion by NERNST, on the dependence of the coefficient of viscosity on temperature. For explaining these, NERNST has already worked out a quantum theoretical view [3].

# §10. Equation of state of the saturated ideal gas. Remarks on the theory of the equation of state for gases and on the electron theory of metalls.

In § 6 it has been shown that for an ideal gas in equilibrium with "condensed substance" the degeneracy parameter  $\lambda$  equals 1. Concentration, energy, and pressure of the part of the molecules equipped with motion then are determined, according to (18b), (22), and (15), by T alone. Thus, we have the equations

$$\eta = \frac{n}{NV} = \frac{2.615}{Nh^3} (2\pi m\kappa T)^{3/2} = 1.12 \cdot 10^{-15} (MRT)^{3/2}$$
(39)

$$\frac{E}{n} = \frac{1.348}{2.615} \cdot \kappa T \tag{40}$$

$$p = \frac{1.348}{2.615} RT\eta \,. \tag{41}$$

Here,  $\eta$  means the concentration in moles,

N means the number of molecules in moles,

M means the molar mass (molecular weight).

One then finds with the help of (39) that the gases existing in reality do not reach such values of the density which ensure that the corresponding ideal gas would be saturated. However, the critical density of Helium is only about five times smaller than the saturation density  $\eta$  of an ideal gas with the same temperature and molecular weight. For Hydrogen, the corresponding ratio is about 26. Since the real gases thus exist at densities which by order of magnitude come close to the saturation density and since, according to (41), the degeneracy substantially influences the pressure, a non-negligible quantum influence on the equation of state will make itself felt if the present theory is correct; in particular, one will have to investigate whether the deviations from VAN DER VAAL's law of corresponding states can be explained in this manner [4].

By the way, one also will have to expect that the diffraction phenomenon pointed out

in the previous paragraph influencees the equation of state, since at low temperatures it generates an apparent enlargement of the molecular volume.

There is one case in which nature possibly has essentially realized the saturated ideal gas, namely with conduction electrons in the interior of metals. As is well known, the electron theory of metals has explained the relation between electrical and thermal conductivity with remarkable accuracy in a quantitative manner (DRUDE-LORENTZ formula) by assuming that there be free electrons in the interior of metals, which conduct both electricity and heat. In spite of its great success, however, that theory is presently not regarded as correct, partly because it could not account for the fact that the free electrons do not yield a notable contribution to the specific heat of the metal. However, this difficulty vanishes if one starts from the present theory of the gases. Namely, from (39) it follows that the saturation concentration of the (moving) electrons at room temperature is about  $5.5 \cdot 10^{-5}$ , so that only a vanishingly small fraction of the electrons could yield a contribution to the specific heat. The mean thermal energy per electron participating in the thermal motion then is about half as large as according to the classical molecule theory. If there are even only very small forces which bind the non-moving electrons in their rest position, then it also becomes understandable that these do not take part in the electical conduction. Possibly even the disappearance of these weak binding forces at very low temperatures could effectuate superconductivity. The thermo-forces could not be understood at all on the basis of this theory, as long as one treats the electron gas as an ideal gas. Needless to say, such an electron theory of the metals should not be based on the MAXWELLian velocity distribution, but on the one for the saturated ideal gas according to the present theory; from (8), (9), (11) one obtains for this special case

$$\mathrm{d}W = \mathrm{const.} \, \frac{E^{1/2} \,\mathrm{d}E}{e^{\frac{E}{\kappa T}} - 1} \,. \tag{42}$$

When elaborating this theoretical possibility one arrives at the difficulty that in order to explain the measured conductivity of the metals for heat and electricity one has to assume a very large free path (order of magnitude  $10^{-3}$  cm), because of the very low volume density of the electrons which, according to our results, take part in the thermal agitation. Moreover, it does not seem possible to understand the behaviour of the metals with respect to infrared radiation (reflection, emission) on the basis of this theory.

#### §11. Equation of state of the unsaturated gas.

We now want to consider the deviation of the equation of state of the ideal gas from the classical equation of state in the unsaturated regime in more detail. To this end, we take up the equations (15), (18b), and (19b) again.

For abbreviation, we set

$$\sum_{\substack{\tau=1\\\tau=\infty\\\tau=\infty}}^{\tau=\infty} \tau^{-3/2} \lambda^{\tau} = y(\lambda)$$
$$\sum_{\tau=1}^{\tau=\infty} \tau^{-5/2} \lambda^{\tau} = z(\lambda)$$

and pose to ourselves the problem to express z as a function of y ( $z = \Phi(y)$ ). The solution of this problem, which I owe to Mr. J. GROMMER, is based on the following general theorem (LAGRANGE):

Under the condition, satisfied in our case, that y and z vanish for  $\lambda = 0$ , and that yand z are regular functions of  $\lambda$  in a certain interval around zero, there exists for sufficiently small y the TAYLOR-expansion

$$z = \sum_{\nu=1}^{\nu=\infty} \left(\frac{\mathrm{d}^{\nu}z}{\mathrm{d}y^{\nu}}\right)_{\lambda=0} \frac{y^{\nu}}{\nu!},\tag{43}$$

where the coefficients can be obtained from the functions  $y(\lambda)$  and  $z(\lambda)$  by means of the recursion formula

$$\frac{\mathrm{d}^{\nu}(z)}{\mathrm{d}y^{\nu}} = \frac{\frac{\mathrm{d}}{\mathrm{d}\lambda} \left(\frac{\mathrm{d}^{\nu-1}z}{\mathrm{d}y^{\nu-1}}\right)}{\frac{\mathrm{d}y}{\mathrm{d}\lambda}} \,. \tag{44}$$

In this way, one obtains in our case the expansion

$$z = y - 0.1768 y^2 - 0.0034 y^3 - 0.0005 y^4 ,$$

convergent up to  $\lambda = 1$  and convenient for numerical evaluation. We now introduce the notation

$$\frac{z}{y} = F(y)$$

Then the following relations hold for the unsaturated ideal gas, *i.e.*, between y = 0 and y = 2.615:

$$\frac{E}{n} = \frac{3}{2}\kappa T F(y) \tag{19c}$$

$$p = RT\eta F(y) ; \qquad (22c)$$

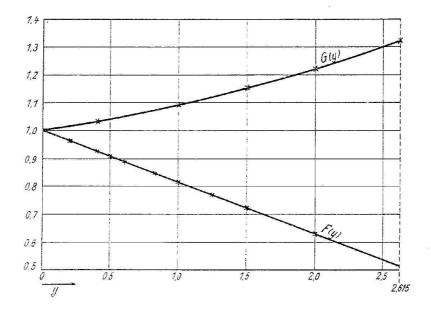
where

$$y = \frac{h^3}{(2\pi m\kappa T)^{3/2}} \frac{n}{V} = \frac{h^3 N\eta}{(2\pi MRT)^{3/2}}$$
(18c)

has been set. From (19b) one gets for the specific heat per mole at constant volume,  $c_V$ :

$$c_V = \frac{3}{2}R\left(F(y) - \frac{3}{2}yF'(y)\right) = \frac{3}{2}RG(y)$$
.

For easy orientation we give a graphical representation of the functions F(y) and G(y):



Taking into account the approximately linear behaviour of F(y), one obtains for p the good approximate equation

$$p = RT\eta \left[ 1 - 0.186 \frac{h^3 N^4 \eta}{(2\pi M RT)^{3/2}} \right] .$$
 (22d)

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- The "condensed" part of the substance claims no particular volume, since it contributes nothing to the pressure.
- [2] LOUIS DE BROGLIE. Thèses. Paris. (Edit. Musson & Co.), 1924. In this dissertation one also finds a very remarkable geometric interpretation of the BOHR-SOMMERFELD quantum rule.

- [3] Cf. W. NERNST, Sitzungsber. 1919. VIII, p. 118. P. GÜNTHER, Sitzungsber. 1920. XXXVI,
   p. 720.
- [4] This is not the case, as I have found out afterwards by comparison with experience. The searched for influence is masked by molecular interactions of other kinds.