

History is full of anecdotes. Einstein published his papers on the quantum theory of the ideal (Bose) gas in the *Sitzungsberichte der Preussischen Akademie der Wissenschaften*, which, translated literally, means “Reports of the Sessions of the Prussian Academy of Sciences”. When these Proceedings were referenced, they usually were abbreviated as *Sitzungsber. Preuss. Akad. Wiss.*, later shortened to *S. B. preuss. Akad. Wiss.* (as, for instance, in a paper by de Groot, Hooyman and ten Seldam, Proc. Roy. Soc. London A **203**, pp. 266–286 (1950)). But that sequence of symbols posed a tremendous problem to non-German-speaking physicists: How should they possibly have known what “S. B.” meant? — It must have appeared to be a pair of initials, and thus, over the years, Einstein got a collaborator: His work was then attributed to “A. Einstein and S. B. Preus”. The mysterious Mr. Preus has survived up to the present day. He still claims his share of fame, for instance, in ref. [2] of a paper by Kirsten and Toms published in Phys. Rev. E **59**, pp. 158–167 (1999)!

The following is a translation of the first of Einstein’s papers on the ideal Bose gas. It was read in a session of the Prussian Academy held on 10 July 1924 — only eight days after the official date of receipt of Bose’s paper! —, and later was printed in the *Sitzungsberichte* XXII of 1924. The paper’s abstract is found in a survey of the session on p. 241, stating:

4. Mr. EINSTEIN handed in a paper: “Quantum theory of the monoatomic ideal gas.”

The method on which Mr. BOSE based his derivation of PLANCK’s radiation formula can also be applied to ideal gases. In this way, one finds a deviation from the classical equation of state of ideal gases at low temperatures (degeneracy). Finally, a paradox is stated which sheds doubt on the validity of the laws found here.

The paper itself appeared on pp. 261–267:

## Quantum theory of the monoatomic ideal gas

BY A. EINSTEIN.

A quantum theory of the monoatomic ideal gas which is free of uncontrolled assumptions does not exist so far. In the following, this gap shall be closed on the basis of a new point of view introduced by Mr. D. BOSE, which enabled this author to establish a most remarkable derivation of PLANCK's radiation formula [1].

The route which, in accordance with BOSE, has to be taken in the sequel can be characterized as follows: The phase space of an elementary entity (here: a monoatomic molecule) with respect to a given (three-dimensional) volume is divided into "cells" of magnitude  $h^3$ . If there are many elementary entities, then their (microscopic) distribution, which governs the thermodynamics, is characterized by the manner in which the entities are distributed over these cells. The "probability" of a macroscopically defined state (in the sense of PLANCK) is equal to the number of the different microscopic states through which the macroscopic state can be thought to be realized. The entropy, and thus the statistical and thermodynamical behaviour of the system, is then determined by BOLTZMANN's theorem.

### §1. The cells.

The phase space volume belonging to a certain domain of coordinates  $x, y, z$  and conjugate momenta  $p_x, p_y, p_z$  of a monoatomic molecule is expressed by the integral

$$\Phi = \int dx dy dz dp_x dp_y dp_z . \quad (1)$$

If  $V$  is the volume that can be occupied by the molecule, then the phase space volume of all states with an energy  $E = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$  less than a definite value  $E$  is given by

$$\Phi = V \cdot \frac{4}{3} \pi (2mE)^{3/2} . \quad (1a)$$

Therefore, the number  $\Delta s$  of cells belonging to a certain elementary domain  $\Delta E$  of energy is

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

If an arbitrary small  $\frac{\Delta E}{E}$  is given, one can always choose  $V$  so large that  $\Delta s$  becomes a very large number.

### §2. State-probability and entropy.

We now define the macroscopic state of the gas.

Let there now be  $n$  molecules with mass  $m$  in the volume  $V$ . Of these, let  $\Delta n$  possess energy values between  $E$  and  $E + \Delta E$ . These distribute themselves over the  $\Delta s$  cells. Out of these  $\Delta s$  cells,

$$\begin{aligned} p_0 \Delta s & \text{ may contain no molecule,} \\ p_1 \Delta s & \text{ may contain 1 molecule,} \\ p_2 \Delta s & \text{ may contain 2 molecules} \\ & \text{and so on.} \end{aligned}$$

The probabilities  $p_r$  belonging to the  $s$ -th cell then obviously are functions of the cell number  $s$  and of the integer index  $r$ , and shall thus henceforth be denoted more explicitly as  $p_r^s$ . Obviously, for all  $s$  one has

$$\sum_r p_r^s = 1. \quad (3)$$

With  $p_r^s$  and  $\Delta n$  given, the number of possible distributions of the  $\Delta n$  molecules over the considered energy interval equals

$$\frac{\Delta s!}{\prod_{r=0}^{r=\infty} (p_r^s \Delta s)!},$$

which, according to Stirling's formula and equation (3), can be replaced by

$$\frac{1}{\prod_r p_r^{s \Delta s p_r^s}},$$

for which one may also write

$$\frac{1}{\prod_{r,s} p_r^{s p_r^s}}, \quad (4)$$

the product running over all  $r$  and  $s$ . If one extends the formation of the product over all values of  $s$  from 1 to  $\infty$ , then (4) obviously represents the total number of complexions, or the probability, in the sense of PLANCK, of a (macroscopic) state of the gas defined by the  $p_r^s$ . For the entropy  $S$  of this state, BOLTZMANN's theorem provides the expression

$$S = -\kappa \ln \sum_{s,r} (p_r^s \ln p_r^s). \quad (5)$$

### §3. Thermodynamic equilibrium.

In thermodynamic equilibrium  $S$  is a maximum, where, apart from (3), the constraints that the total number  $n$  of atoms and their total energy  $\bar{E}$  be constant have to be satisfied. These constraints obviously express themselves in the two equations [2]

$$n = \sum_{s,r} r p_r^s. \quad (6)$$

$$\bar{E} = \sum_{sr} E^s r p_r^s, \quad (7)$$

where  $E^s$  indicates the energy of a molecule belonging to the  $s$ -th phase cell. From (1a) one easily deduces that

$$\left. \begin{aligned} E^s &= c s^{2/3} \\ c &= (2m)^{-1} h^2 \left( \frac{4}{3} \pi V \right)^{-2/3} \end{aligned} \right\}. \quad (8)$$

By performing the variation with respect to the variables  $p_r^s$  one finds that, with suitable choice of the constants  $\beta^s$ ,  $A$ , and  $B$ ,

$$\left. \begin{aligned} p_r^s &= \beta^s e^{-\alpha^s r} \\ \alpha^s &= A + B s^{2/3} \end{aligned} \right\} \quad (9)$$

has to hold. According to (3),

$$\beta^s = 1 - e^{-\alpha^s} \quad (10)$$

is required. From this, one immediately obtains for the mean number of molecules per cell

$$= \sum_r r p_r^s = \beta^s \sum_r r e^{-\alpha^s r} = -\beta^s \frac{d}{d\alpha^s} \left( \sum_r e^{-\alpha^s r} \right) = -\beta^s \frac{d}{d\alpha^s} \left( \frac{1}{1 - e^{-\alpha^s}} \right) = \frac{1}{e^{\alpha^s} - 1}. \quad (11)$$

The equations (6) and (7) therefore adopt the form

$$n = \sum_s \frac{1}{e^{\alpha^s} - 1} \quad (6a)$$

$$\bar{E} = c \sum_s \frac{s^{2/3}}{e^{\alpha^s} - 1}, \quad (7a)$$

which equations, together with

$$\alpha^s = A + B s^{2/3},$$

determine the constants  $A$  and  $B$ . Thus, the law of the macroscopic distribution of states for the thermodynamic equilibrium is fully determined.

Inserting the results of this paragraph into (5), one obtains for the equilibrium entropy the expression

$$S = -\kappa \left\{ \sum_s [\ln(1 - e^{-\alpha^s})] - An - \frac{B}{c} \bar{E} \right\}. \quad (12)$$

We now have to calculate the temperature of the system. To this end, we apply the defining equation of the entropy to an infinitesimally small, isopycnic heating and get

$$d\bar{E} = T dS = -\kappa T \left\{ \sum_s \frac{d\alpha^s}{1 - e^{\alpha^s}} - n dA - \frac{\bar{E}}{c} dB - B d\left(\frac{\bar{E}}{c}\right) \right\},$$

which, on taking recourse to (9), (6), and (7), yields

$$d\bar{E} = \kappa T B d\left(\frac{\bar{E}}{c}\right) = \kappa T \frac{B}{c} d\bar{E}$$

or

$$\frac{1}{\kappa T} = \frac{B}{c}. \quad (13)$$

Thus, also the temperature has been expressed indirectly in terms of the energy and the other given quantities. From (12) and (13) it also follows that the free energy  $F$  of the system is given by

$$F = \bar{E} - TS = \kappa T \left\{ \ln \sum_s (1 - e^{-\alpha^s}) - An \right\}. \quad (14)$$

This yields for the pressure  $p$  of the gas

$$p = -\frac{\partial F}{\partial V} = -\kappa T \frac{\bar{E}}{c} \frac{\partial B}{\partial V} = -\bar{E} \frac{\partial \ln c}{\partial V} = \frac{2}{3} \frac{\bar{E}}{V}. \quad (15)$$

Thus, one obtains the remarkable result that the relation between the kinetic energy and the pressure turns out to be precisely the same as in the classical theory, where it is derived from the virial theorem.

#### §4. The classical theory as a limiting case.

If one neglects unity in comparison with  $e^{\alpha^s}$  one obtains the results of the classical theory; from the following it will soon become clear under which conditions this neglect is justified. According to (11), (9), (13), the mean number  $n^s$  of molecules per cell is then given by

$$n^s = e^{-\alpha^s} = e^{-A} \cdot e^{-\frac{E^s}{\kappa T}}. \quad (11a)$$

The number of molecules whose energy lies within the elementary interval  $dE^s$  is therefore, by virtue of (8), given by

$$\frac{3}{2} c^{-3/2} e^{-A} e^{-\frac{E}{\kappa T}} E^{1/2} dE, \quad (11b)$$

in accordance with the classical theory. Hence, when applying the same approximation, equation (6) furnishes

$$e^A = \pi^{3/2} h^{-3} \frac{V}{n} (2m\kappa T)^{3/2}. \quad (16)$$

For hydrogen gas under atmospheric pressure this quantity roughly equals  $6 \cdot 10^4$ , and thus is large compared to 1. Therefore, here the classical theory still yields a fairly good approximation. However, the error increases substantially with increasing density and decreasing temperature, and is quite sizeable for Helium in the vicinity of the critical state; on the other hand, one can then no longer consider the gas as ideal.

We now calculate the entropy for our limiting case from (12). By replacing  $\ln(1 - e^{-\alpha^s})$  in (12) by  $-e^{-\alpha^s}$ , and this by  $-\frac{1}{e^{\alpha^s}-1}$  while respecting (6a), one obtains

$$S = \nu R \ln \left[ e^{5/2} \frac{V}{h^3 n} (2\pi m \kappa T)^{3/2} \right], \quad (17)$$

where  $\nu$  means the number of moles, and  $R$  the constant in the equation of state of the ideal gases. The result for the absolute value of the entropy is in agreement with well known results from quantum statistics.

According to the theory developed here, NERNST's theorem is satisfied for ideal gases. It has to be kept in mind that our formulae cannot be applied to extremely low temperatures, because in their derivation we have assumed that the  $p_r^s$  vary only by a relatively infinitesimally small amount when  $s$  varies by 1. On the other hand one recognizes immediately that the entropy has to vanish at the absolute zero point of temperature. Namely, then all molecules are assembled in the first cell; for this state there is only a single distribution of the molecules when adopting our way of counting. From this follows immediately the correctness of our assertion.

### §5. The deviation from the gas equation of the classical theory.

Our results concerning the equation of state are contained in the following equations:

$$n = \sum_s \frac{1}{e^{\alpha^s} - 1} \quad (18) \quad (\text{cf. (16a)})$$

$$\bar{E} = \frac{3}{2} pV = c \sum_s \frac{s^{2/3}}{e^{\alpha^s} - 1} \quad (19) \quad (\text{cf. (7a) and (15)})$$

$$\alpha^s = A + \frac{cs^{2/3}}{\kappa T} \quad (20) \quad (\text{cf. (9) and (13)})$$

$$c = \frac{E^s}{s^{2/3}} = \frac{h^2}{2m} \left( \frac{4}{3} \pi V \right)^{-2/3}. \quad (21) \quad (\text{cf. (8)})$$

We now want to reformulate and discuss these results. From the deliberations in § 4 it follows that the quantity  $e^{-A}$ , which we shall denote as  $\lambda$ , is smaller than 1. It is a measure for the “degeneracy” of the gas. We now can write (18) and (19) in the form of double sums as follows:

$$n = \sum_{s\tau} \lambda^\tau e^{-\frac{cs^{2/3}\tau}{\kappa T}} \quad (18a)$$

$$\bar{E} = c \sum_{s\tau} s^{2/3} \lambda^\tau e^{-\frac{cs^{2/3}\tau}{\kappa T}}, \quad (19a)$$

where  $\tau$  has to be summed for all  $\sigma$  from 1 to  $\infty$ .

We now can perform the summation over  $s$  by replacing it by an integration from 0 to  $\infty$ . This is allowed because the exponential function varies slowly with  $\sigma$ . We thus obtain:

$$n = \frac{3\sqrt{\pi}}{4} \left( \frac{\kappa T}{c} \right)^{3/2} \sum_{\tau} \tau^{-3/2} \lambda^{\tau} \quad (18b)$$

$$\bar{E} = c \frac{9\sqrt{\pi}}{8} \left( \frac{\kappa T}{c} \right)^{5/2} \sum_{\tau} \tau^{-5/2} \lambda^{\tau} . \quad (19b)$$

(18b) determines the degeneracy parameter  $\lambda$  as function of  $V$ ,  $T$ , and  $n$ ; from this, (19b) determines the energy and thus also the pressure of the gas.

The general discussion of these equations can proceed by considering the function which expresses the sum in (19b) in terms of the sum in (18b). In general, one obtains by division

$$\frac{\bar{E}}{n} = \frac{3}{2} \kappa T \frac{\sum_{\tau} \tau^{-5/2} \lambda^{\tau}}{\sum_{\tau} \tau^{-3/2} \lambda^{\tau}} . \quad (22)$$

The mean energy of a molecule of the gas at the temperature (and also the pressure) is therefore always lower than the classical value; more precisely, the factor expressing the reduction is the smaller, the larger the degeneracy parameter  $\lambda$ . According to (18b) and (21), this factor is a certain function of  $\left(\frac{V}{n}\right)^{2/3} mT$ .

If  $\lambda$  is so small that  $\lambda^2$  can be neglected in comparison with 1, one obtains

$$\frac{\bar{E}}{n} = \frac{3}{2} \kappa T \left[ 1 - 0.0318 h^3 \frac{n}{V} (2\pi m \kappa T)^{-3/2} \right] . \quad (22a)$$

We now investigate how MAXWELL's distribution of states is affected by the quanta. Expanding (11) in powers of  $\lambda$ , while respecting (20), one obtains

$$n^s = \text{const.} e^{-\frac{E^s}{\kappa T}} \left( 1 + \lambda e^{-\frac{E^s}{\kappa T}} + \dots \right) . \quad (23)$$

The bracket expresses the influence of the quanta on MAXWELL's distribution law. One sees that the slower molecules occur more frequently, as compared to the fast ones, than they would by virtue of MAXWELL's law.

Finally I would like to draw attention to a paradox which I have been unable to resolve. It is not difficult to treat also the mixing of two different gases by the method explained here. In this case, each molecule species has its own "cells". From this follows the additivity of the entropies of the mixture's components. Therefore, with respect to molecular energy, pressure, and statistical distribution each component behaves as if it were the only one present. A mixture with molecule numbers  $n_1$ ,  $n_2$ , with the molecules of the first kind being distinguishable (in particular with respect to the molecule masses  $m_1$ ,  $m_2$ ) only by an arbitrarily small amount from that of the second, therefore yields, at a given temperature, a pressure and a distribution of states which differs from that of a uniform gas with molecule

number  $n_1 + n_2$  with practically the same molecular mass, occupying the same volume. However, this appears to be as good as impossible.

---

Distributed September 20.

---

---

[1] To appear soon in “Zeitschr. für Physik”.

[2] Namely,  $\sum_r r p_r^s$  is the mean number of molecules falling into the  $s$ -th cell.