

Quantum Theory of a Monoatomic Ideal Gas

A translation of *Quantentheorie des einatomigen idealen Gases* (Einstein, 1924)

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This is a translation of the paper appeared in Sitzungsber. phys.-math. Kl. 1924, Gesamtsitzung vom 10. Juli 1924, p.261-267. It seems this paper has never been translated in English so far. In this paper Einstein develops for the first time the Bose-Einstein statistics, applying the ideas first discussed in a paper by D. Bose and extending them to massive particles (here called atoms or molecules). In 1925 Einstein publishes a second part of this paper (Sitzungsberichte der Preussischen Akademie der Wissenschaften, Berlin, Physikalisch-mathematische Klasse, 1925, p. 3-14; we refer to this as the second paper) in which he investigates, among other, the existence of what is now known as the Bose-Einstein condensates. Except for abstract, footnotes in italic and final acknowledgments, all the text is from the original paper (o.p. in the following). The equation numbering does not conform to the original one.

A quantum theory of ideal gases free from arbitrary Ansätzen does not yet exist today. This gap will be filled in the following on the basis of a new approach proposed by Mr. D. Bose, from which that author has obtained a most remarkable derivation of Planck's radiation formula [1].

The method following Bose can be characterized as follows. The phase space of an elementary object (in this case monoatomic molecules) with respect to a given (three dimensional) volume is divided into "cells" of extension h^3 . Considering many elementary objects, their thermodynamic can be characterized by how the objects are distributed among these cells. The "probability" of a macroscopically defined state (in Planck's sense) is equal to the number of different microscopic states through which the macroscopic state can be thought realized. The entropy of the macroscopic state and thus the statistical and thermodynamic behavior of the system is then determined by Boltzmann's theorem.

I. THE CELLS

The phase-space volume to which a certain range of coordinates x, y, z and corresponding momenta p_x, p_y, p_z of a monoatomic molecule belongs, can be estimated through the integral

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

If V is the volume available to the molecule, then the phase volume of all states whose energy $E = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$ is smaller than a certain value E , is given by

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

The number Δs of the cells belonging to a given elementary range ΔE of energy is as follows

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

No matter how small a $\Delta E/E$ is given, one can always choose V so large that Δs is a very large number.

II. STATE PROBABILITY AND ENTROPY

We define now the macroscopic state of the gases.

Let be present in the volume V a number n [2] of molecules with mass m . A number Δn of these will have energies between E and $E + \Delta E$. These will distribute themselves among the Δs cells. Of these Δs cells, a number

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

and so on. The probability p_r associated to the s -th cell is then clearly function of the cell number s and of the integer r and will be therefore denoted in the following with p_r^s . It is evident that for any s

$$\sum_r p_r^s = 1 \quad (4)$$

For a given p_r^s and a given Δn the number of possible distributions of the Δn molecules over the considered energy range is

$$\frac{\Delta s!}{\prod_{r=0}^{r=\infty} (p_r^s \Delta s)!} \quad (5)$$

which can be replaced by[3]

$$\frac{1}{\prod_r (p_r^s)^{p_r^s \Delta s}} \quad (6)$$

by employing Stirling's formula[4] and Eq. (4), which can also be written as a productory over all values of r and s

$$\frac{1}{\prod_{r,s} (p_r^s)^{p_r^s}} \quad (7)$$

By extending the product to all values of s from 1 to ∞ , the expression (7) represents clearly the total number of complexions[5], i.e. the probability in the Planckian sense of the macroscopic state of a gas defined though the p_r^s . The Boltzmann theorem gives for the entropy S of these states the expression[6]

$$S = -k \log \sum_{r,s} (p_r^s \log p_r^s) \quad (8)$$

III. THERMODYNAMIC EQUILIBRIUM

In thermodynamic equilibrium S is a maximum, for which additional conditions to be satisfied, beside Eq. (4), are that the total number n of atoms and their total energy \bar{E} are fixed. These conditions can be clearly expressed as[7]

$$n = \sum_{r,s} r p_r^s \quad (9)$$

$$\bar{E} = \sum_{r,s} E^s r p_r^s \quad (10)$$

where E^s denotes the energy of a molecule that belongs to the s -th phase-space cell. From Eq. (3) it follows that

$$E^s = c s^{2/3} \quad (11)$$

$$c = (2m)^{-1} h^2 \left(\frac{4}{3} \pi V\right)^{-\frac{2}{3}}$$

Performing the variation [8] with the p_r^s as variables, one finds with an appropriate choice of the constants β^s , A and B [9] that [10]

$$p_r^s = \beta^s e^{-\alpha^s r} \quad (12)$$

$$\alpha^s = A + B s^{\frac{2}{3}} \quad (13)$$

Because of Eq. (4) one has therefore

$$\beta^s = 1 - e^{-\alpha^s} \quad (14)$$

This results in the average number of molecules per cell

$$\sum_r r p_r^s = \beta^s \sum_r r e^{-\alpha^s r} = -\beta^s \frac{d}{d\alpha^s} (\sum_r e^{-\alpha^s r}) = -\beta^s \frac{d}{d\alpha^s} \left(\frac{1}{1 - e^{-\alpha^s}}\right) = \frac{1}{e^{\alpha^s} - 1} \quad (15)$$

The equations (9) and (10) become then

$$n = \sum_s \frac{1}{e^{\alpha_s} - 1} \quad (16)$$

$$\bar{E} = c \sum_s \frac{s^{\frac{2}{3}}}{e^{\alpha_s} - 1} \quad (17)$$

which, together with

$$\alpha^s = A + Bs^{\frac{2}{3}} \quad (18)$$

determine the constants A and B . In this way the distribution law in thermodynamic equilibrium is completely determined.

Inserting the results of this paragraph in Eq. (8) gives the following expression for the equilibrium entropy

$$S = -k \left\{ \sum_s \left[\log(1 - e^{-\alpha^s}) \right] - An - \frac{B}{c} \bar{E} \right\} \quad (19)$$

We should now estimate the temperature of the system. To this scope we employ the definition of entropy in a infinitesimally small isopycnal heating [11] and obtain

$$d\bar{E} = TdS = -kT \left\{ \sum_s \frac{d\alpha^s}{1 - e^{\alpha^s}} - ndA - \frac{\bar{E}}{c} dB - Bd \left(\frac{\bar{E}}{c} \right) \right\} \quad (20)$$

which in consideration of Eqs. (12,9 and 10) gives

$$d\bar{E} = kT B d \left(\frac{\bar{E}}{c} \right) = kT \frac{B}{c} d\bar{E} \quad (21)$$

or

$$\frac{1}{kT} = \frac{B}{c} \quad (22)$$

In this way the temperature is also expressed indirectly through the energy and the other quantities given above. From Eq. (21) and (22) it follows also that the free energy F of the system is given by

$$F = \bar{E} - TS = kT \left\{ \log \sum_s (1 - e^{-\alpha^s}) - An \right\} \quad (23)$$

The pressure p of the gas is given by

$$p = -\frac{\partial F}{\partial V} = -kT \frac{\bar{E}}{c} \frac{\partial B}{\partial V} = -\bar{E} \frac{\partial \log c}{\partial V} = \frac{2}{3} \frac{\bar{E}}{V} \quad (24)$$

This yields the remarkable result that the relation between the kinetic energy and the pressure is the same as in the classical theory, where it is obtained by the virial theorem.

IV. THE CLASSICAL THEORY AS LIMITING CASE

By discarding the unity next to e^{α^s} one recovers the result of the classical theory; in the following it will be shown under which conditions this is legitimate. In view of (15), (12) and (22), the average number n^s of molecules per cell is given by

$$n^s = e^{-\alpha^s} = e^{-A} e^{-\frac{E^s}{kT}} \quad (25)$$

Because of (11) the number of molecules with energy within the small range dE^s is also given by

$$\frac{3}{2} c^{-\frac{3}{2}} e^{-A} e^{-\frac{E}{kT}} E^{\frac{1}{2}} dE \quad (26)$$

in agreement with the classical theory. Eq. (9) gives then, under the same condition of neglecting the unity term,

$$e^A = \pi^{\frac{3}{2}} h^{-3} \frac{V}{n} (2mkT)^{\frac{3}{2}} \quad (27)$$

For hydrogen at atmospheric pressure this quantity is roughly $6 \cdot 10^4$, that is much larger than unity. This shows that the classical theory is a rather good approximation. The error however grows with larger densities and smaller temperatures and for helium at the critical state is quite considerable; in this case however one can not any longer speak of an ideal gas.

We now estimate from (21) the entropy for our limiting case. Replacing $\log(1 - e^{-\alpha^s})$ with $-e^{-\alpha^s}$ and this with $-1/(e^{\alpha^s} - 1)$, one obtains, also in view of (16),

$$S = \nu R \log \left[e^{\frac{5}{2}} \frac{V}{h^3 n} (2\pi mkT)^{\frac{3}{2}} \right] \quad (28)$$

where ν is the number of moles of gas and R is the ideal gas constant. This result for the absolute value of entropy is in agreement with well-known results of quantum statistics.

According to the theory presented here, Nernst theorem[12] is satisfied for ideal gases. In reality, our formulas can not be applied directly to extremely low temperatures, as we have assumed in their derivation that the p_r^s change only relatively infinitely little when s changes by 1. However, one can see immediately that the entropy must vanish at absolute zero. In fact, in that case all the molecules lie in the first cell; for this state there is only a single distribution of molecules according to our counting. From this it immediately follows the correctness of the assertion.

V. THE DEPARTURE OF THE GAS EQUATION FROM THE CLASSICAL THEORY

Our results for as concerns the equation of state are contained into the following equations[13]:

$$n = \sum_s \frac{1}{e^{\alpha^s} - 1} \quad (29)$$

$$\bar{E} = \frac{3}{2} pV = c \sum_s \frac{s^{\frac{2}{3}}}{e^{\alpha^s} - 1} \quad (30)$$

$$\alpha^s = A + \frac{cs^{\frac{2}{3}}}{kT} \quad (31)$$

$$c = \frac{E^s}{s^{\frac{2}{3}}} = \frac{h^2}{2m} \left(\frac{4}{3} \pi V \right)^{-\frac{2}{3}} \quad (32)$$

We wish now to transform and discuss these results. From the argument in Sect. 4 it follows that the quantity e^{-A} , which we will denote with λ [14], is smaller than unity. This is a measure of the “degeneration” of the gas. We can now put Eqs. (29) and (30) in form of a double sum

$$n = \sum_{s,\tau} \lambda^\tau e^{-\frac{cs^{2/3}\tau}{kT}} \quad (33)$$

$$\bar{E} = c \sum_{s,\tau} s^{\frac{2}{3}} \lambda^\tau e^{-\frac{cs^{2/3}\tau}{kT}} \quad (34)$$

where τ is to be summed for all s from 1 to ∞ .

The sum over s can be performed by replacing it with an integration from 0 to ∞ . This is allowed since the exponential function is slowly changing with s [15]. We obtain then

$$n = \frac{3\sqrt{\pi}}{4} \left(\frac{kT}{c} \right)^{\frac{3}{2}} \sum_{\tau} \tau^{-\frac{3}{2}} \lambda^\tau \quad (35)$$

$$\bar{E} = c \frac{9\sqrt{\pi}}{8} \left(\frac{kT}{c} \right)^{\frac{5}{2}} \sum_{\tau} \tau^{-\frac{5}{2}} \lambda^\tau \quad (36)$$

Eq. (35) determines the degeneracy parameter λ as a function of V, T and n , while Eq. (36) gives the energy and therefore also the pressure of the gas. A general discussion of these equations consists in finding the function that expresses the sum in (36) through the sum in (35). One obtains through division

$$\frac{\bar{E}}{n} = \frac{3}{2}kT \frac{\sum_{\tau} \tau^{-\frac{5}{2}} \lambda^{\tau}}{\sum_{\tau} \tau^{-\frac{3}{2}} \lambda^{\tau}} \quad (37)$$

The average energy of the gas molecules for a given temperature (and also the pressure) is then always smaller than the classical value and in fact the factor that expresses this reduction is the smaller the larger the degeneracy parameter λ . In turn this parameter, in view of Eqs (35) and (32), is a function of $(V/n)^{\frac{2}{3}}mT$.

If λ is so small that λ^2 is negligible with respect to unity then one obtains[16]

$$\frac{\bar{E}}{n} = \frac{3}{2}kT \left[1 - 0.0318h^3 \frac{n}{V} (2\pi mkT)^{-\frac{3}{2}} \right] \quad (38)$$

We consider now in which way the Maxwellian distribution is influenced by the quantum effects. Expanding Eq. (15) in powers of λ and taking into account Eq. (31) one obtains

$$n^s = const \times e^{-\frac{E^s}{kT}} (1 + \lambda e^{-\frac{E^s}{kT}} + \dots) \quad (39)$$

The parenthesis expresses the quantum effects on the Maxwellian distribution. One sees that there are more slow molecules with respect to fast ones than would be the case with Maxwell law.

Finally, I would like to draw attention to a paradox whose resolution I have not succeeded to obtain [17]. There is no difficulty to handle by the method given here also the case of the mixture of two different gases. In this case, each type of molecule has its special ‘‘cell’’. This yields the additivity of the entropy of the components of the mixture. Each component behaves, with respect to molecular energy, pressure and statistical distribution, as if it alone were present. A mixture of molecule numbers n_1, n_2 , with molecules of the first and second kind no matter how little different from each other (in particular with respect to the molecular mass m), yields a different pressure and a different state distribution when compared to a single gas of $n_1 + n_2$ molecules at the same temperature having practically the same molecular mass and the same volume. But this seems really impossible.

Acknowledgments

I thank Davide Amendola for help with the German translation. The original paper can be found at <http://nausikaa2.mpiwg-berlin.mpg.de/cgi-bin/toc/toc.x.cgi?dir=PG8B073X>. An English translation of the second paper by Einstein and of Bose’s paper can be found at wavewatching.net/lost-papers/

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- [1] To appear in ‘‘Zeitschr. fuer Physik’’.
 - [2] (in the o.p. the symbols V, n appeared as if multiplied together)
 - [3] (in the o.p. the symbol p_r^s at exponent appeared without subscript and superscript)
 - [4] (i.e. $n! \approx n^n e^{-n}$)
 - [5] (i.e. microstates)
 - [6] (Boltzmann’s constant k was denoted as χ in the o.p.)
 - [7] $n^s = \sum_r r p_r^s$ is the corresponding number of molecules in the s -th cell.
 - [8] (of the entropy)
 - [9] (in the symbols $p_r^s, \alpha^s, \beta^s, E^s$ the symbol s is a superscript index, not an exponent)
 - [10] (The constant A turns out to be related to what in modern notation is called the chemical potential μ , $A = -\mu/kT$)
 - [11] (i.e. a constant density transformation; since the number of particle is here also assumed constant, constant density implies constant volume)
 - [12] (that the entropy vanishes at zero absolute temperature)
 - [13] (in the o.p. the sum index is denoted by σ)
 - [14] (this quantity is often called fugacity in modern literature)
 - [15] (‘‘with σ ’’ in the o.p.)
 - [16] (The numerical factor was corrected to 0.1768 in the second paper by Einstein)
 - [17] (This is sometimes called Gibbs’ paradox; Einstein solves it in the second paper)