

1.  
**ON THE QUANTIZATION  
OF AN IDEAL MONATOMIC GAS**

“Sulla quantizzazione  
del gas perfetto monoatomico,”  
*Rend. Lincei* **3**, 145–149 (1926).

§ 1. In classical thermodynamics one takes the specific heat of an ideal monatomic gas at constant volume (referring to a single molecule) to be  $c = 3/2 k$ . However, it is clear that even for an ideal gas, if one wants to admit the validity of the Nerst principle, one must consider the above expression for  $c$  to be only an approximation valid at high temperatures and that actually  $c$  tends to zero for  $T = 0$ , so that the integral expressing the value of entropy can be extended all the way to absolute zero without the indeterminacy of the constant. And to realize how such a variation of  $c$  can occur, it is necessary to admit that the motion of an ideal gas must be quantized as well. Then one understands how such a quantization, besides its effect on the energy content of the gas, will influence the equation of state as well, thus giving rise to the so called phenomena of degeneration of the ideal gas at low temperatures.

The purpose of this work is the exposition of a method for carrying out the quantization of an ideal gas which, in our opinion, is as much as possible independent of unjustified hypotheses on the statistical behaviour of the molecules of the gas.

Recently numerous attempts have been made to arrive at establishing an equation of state for the ideal gas.<sup>1</sup> The formulas given by various authors differ from ours and from the classical equation of state only for very low temperatures and very high densities; unfortunately these are the same circumstances in which the deviations of the laws of real gases from those of ideal gases are more important; and since, under conditions one can easily carry out experimentally, the deviations from the equation of state  $pV = kT$  due to the degeneration of the gas, even if not negligible, are always considerably smaller than those due to the fact that the gas is real and not ideal, the former have so far been hidden by the latter. This does not exclude the possibility that, in the more or less near future, and with a more profound knowledge of the forces which act among the molecules of a real gas,

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<sup>1</sup>See for instance A. Einstein, “Sitzber. d. Pr. Akad. d. Wiss.,” 22, 261 (1924); 23, 3, 18 (1925); M. Planck, “Sitzber. d. Pr. Akad. d. Wiss.,” 23, 49 (1925).

one can separate the two deviations from each other, thus arriving at being able to choose experimentally among the various theories of the degeneration of ideal gases.

§ 2. To be able to carry out the quantization of the motion of the molecules of an ideal gas one must be in such a condition as to be able to apply Sommerfield's rules to their movement; and this can be done in an infinite number of ways all of which, in any case, lead to the same result. One can, for instance, assume the gas to be contained in a parallelepiped vessel with elastic walls, quantizing the three-fold periodic motion of the molecule bouncing off the six walls; or more generally, one can subject the molecules to a system of forces such that their motion becomes periodic and then can be quantized. The hypothesis that the gas is ideal allows us in all these cases to neglect the forces acting among the molecules, so that the mechanical motion of each of them happens as if the other ones did not exist. Nevertheless one can recognize that the mere quantization of the motion of the molecules following Sommerfield's rules, considering them to be mutually independent, is not sufficient to obtain correct results; since, even if in this case the specific heat tends to zero for  $T = 0$ , yet its value, besides on the temperature and density, depends on the total quantity of gas as well, and tends, at any temperature, to the limit  $3/2 k$  when, even if the density remains constant, the quantity of gas tends to infinity. Then it appears necessary to admit that some complement to Sommerfield's rules is needed when calculating systems which, like ours, contain elements indistinguishable from each other.<sup>2</sup>

To have an hint on how to formulate the most plausible hypothesis, it is worth considering how things go in other systems which, like our ideal gas, contain indistinguishable elements; and precisely we want to examine the behaviour of the atoms heavier than hydrogen which all contain more than one electron. If we consider the deep parts of a heavy atom, we are in such conditions that the forces acting among the electrons are very small in comparison with the ones exerted by the nucleus. In these circumstances the mere application of Sommerfield's rules would lead us to expect that, in the normal state of the atom, a considerable number of electrons should lie in an orbit of total quantum number 1. As a matter of fact, instead one sees that the  $K$  ring is already saturated when it contains two electrons, and likewise the  $L$  ring becomes saturated when it contains 8 electrons, etc. This fact has been interpreted by Stoner,<sup>3</sup> and in an even still more precise way by Pauli,<sup>4</sup> as follows: let us characterize an electronic orbit possible in a complex atom by means of 4 quantum numbers;  $n, k, j, m$ , which have respectively the meanings of total quantum, azimuthal quantum, internal quantum and magnetic quantum. Given the inequalities which these 4 numbers must satisfy, one finds that for  $n = 1$ , only two sets of values exist for  $k, j, m$ : for  $n = 2$ , there exist 8, etc. To realize the

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<sup>2</sup>E. Fermi, "N. C.," 1, 145 (1924).

<sup>3</sup>E. C. Stoner, "Phil. Mag.," 48, 719 (1924).

<sup>4</sup>W. Pauli, "Zs. f. Phys.," 31, 765 (1925).

fact previously noted, it is therefore sufficient to admit that in the atom two electrons whose orbits are characterized by the same quantum numbers cannot exist; in other words one must admit that an electronic orbit is already “occupied” when it contains only one electron.

§ 3. We now intend to investigate if such a hypothesis can give good results in the problem of the quantization of an ideal gas as well: therefore we shall assume that in our gas there can be at most one molecule whose motion is characterized by certain quantum numbers, and we shall show that this hypothesis leads to a perfectly consequent theory of the quantization of the ideal gas, and in particular it gives reasons for the expected decrease of the specific heat at low temperatures, and leads to the exact value for the constant of entropy of the ideal gas.

Putting off the publication of the mathematical details of the present theory to another occasion, in this Note we limit ourselves to present the principles of the method we have followed and the results obtained.

First of all we must put our gas in such a condition that the motion of its molecules is quantizable. As we have seen, this can be done in an infinity of ways; but, since the result is independent of the particular way one adopts, we shall choose the most convenient one for the calculation; and precisely we shall assume that our molecules are attracted by a fixed point  $O$ , with a force proportional to the distance  $r$  of the molecule from  $O$ ; so that each molecule will be a spatial harmonic oscillator whose frequency we indicate by  $\nu$ . The orbit of the molecule will be characterized by three quantum numbers,  $s_1, s_2, s_3$ , which are linked to its energy through the relation

$$w = h\nu(s_1 + s_2 + s_3) = h\nu s. \quad (1)$$

Then the energy of a molecule can take all values which are integer multiples of  $h\nu$ , and the value  $sh\nu$  can be assumed in  $Q = \frac{1}{2}(s+1)(s+2)$  ways.

Therefore zero energy can be realized in only one way, the energy  $h\nu$  in 3 ways, the energy  $2h\nu$  in 6 ways, etc. To realize the influence of our hypothesis, i.e., that to given quantum numbers can correspond only one molecule, let us consider the extreme case of  $N$  molecules at absolute zero. At this temperature the gas must lie in the state of minimum energy. If we had no limitation on the number of molecules which can have a certain energy, all the molecules would lie in the state of zero energy, and all three quantum numbers of each of them would be zero. On the contrary, according to our hypothesis, the existence of more than one molecule with all three quantum numbers equal to zero is forbidden; therefore if  $N = 1$ , only one molecule will occupy the place of zero energy; if instead  $N = 4$ , one of the molecules will occupy the place of zero energy, and the other three the place of energy  $h\nu$ ; if  $N = 10$ , one of the molecules will occupy the place of zero energy, three of them the places of energy  $h\nu$ , and the remaining six the six places of energy  $2h\nu$ , etc.

Now let us suppose we have to distribute the total energy  $W = E h\nu$  ( $E =$  whole number) among our molecules; and designate by  $N_s \leq Q_s$  the numbers of molecules

of energy  $s h\nu$ . We find easily that the most probable values of  $N_s$  are

$$N_s = \frac{\alpha Q_s}{e^{\beta s} + \alpha}, \quad (2)$$

where  $\alpha$  and  $\beta$  are constants depending on  $W$  and  $N$ . To find the relation between these constants and the temperature, we observe that, as a consequence of the attraction toward  $O$ , the density of our gas will be a function of  $r$ , which must tend to zero for  $r = \infty$ . Accordingly, for  $r = \infty$  the phenomena of degeneration must cease, and in particular the distribution of velocities, easily deducible from (2), must change into Maxwell's law. Thus one finds that one must have

$$\beta = \frac{h\nu}{kT}. \quad (3)$$

Now we are able to deduce from (2) the function  $n(L) dL$ , which represents, for a given value of  $r$ , the density of the molecules of energy between  $L$  and  $L + dL$  (analogous to Maxwell's law), and from this we can deduce the mean kinetic energy  $\bar{L}$  of the molecules at distance  $r$ , which is a function, besides of the temperature, of the density  $n$  as well. One finds precisely

$$\bar{L} = \frac{3h^2 n^{2/3}}{4\pi m} P \left( \frac{2\pi m k T}{h^2 n^{2/3}} \right). \quad (4)$$

In (4) we have indicated by  $P(x)$  a function, with a bit complicated analytic definition, which for values of  $x$  either very large or very small respectively, can be calculated through the asymptotic formulas

$$\begin{aligned} P(x) &= x \left( 1 + \frac{1}{2^{5/2} x^{3/2}} + \dots \right); \\ P(x) &= \frac{1}{5} \left( \frac{9\pi}{2} \right)^{1/3} \left[ 1 + \frac{5}{9} \left( \frac{4\pi^4}{3} \right)^{1/3} x^2 + \dots \right]. \end{aligned} \quad (5)$$

To deduce from (4) the equation of state, we apply the virial relation. We then find that the pressure is given by

$$p = \frac{2}{3} n \bar{L} = \frac{h^2 n^{5/3}}{2\pi m} P \left( \frac{2\pi m k T}{h^2 n^{2/3}} \right). \quad (6)$$

At the limit of high temperatures, that is for small degeneration, the equation of state then takes the form

$$p = nkT \left[ 1 + \frac{1}{16} \frac{h^3 n}{(\pi m k T)^{3/2}} + \dots \right]. \quad (7)$$

The pressure therefore turns out to be higher than the one coming from the classical equation of state. For an ideal gas having the atomic weight of helium, at the absolute temperature of  $5^\circ$  and at a pressure of 10 atmospheres, the difference would be about 15%.

From (4) and (5) one can also deduce the expression for the specific heat at low temperatures. One finds

$$c_v = \left(\frac{16\pi^8}{9}\right)^{1/3} \frac{mk^2}{h^2 n^{2/3}} T + \dots \quad (8)$$

Likewise we can find the absolute value of the entropy. Carrying out the calculations, one finds at high temperatures

$$S = n \int_0^T \frac{1}{T} d\bar{L} = n \left[ \frac{5}{2} \log T - \log p + \log \frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3} \right], \quad (9)$$

which coincides with the value of the entropy given by Tetrode and Stern.