30) 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 (referring to a single molecule) as specific heat at constant volume of an ideal monatomic gas $c = 3/2k$. However, it is clear that if one wants to admit the validity of the Nerst principle also in the case of an ideal gas, one must think that the above expression of c is only an approximation valid at high temperatures and that in reality c tends to zero for $T = 0$, so that one can extend up to absolute zero the integral expressing the value of entropy without the indeterminacy of the constant. And for realizing how such a variation of c can occur, it is necessary to admit that the motions of an ideal gas must be quantized as well. Then one realizes that such a quantization, besides 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 behavior of the molecules of the gas.[*]

Recently various attempts have been made for arriving to establish an equation of state for the ideal gas.

The formulae given by the 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 the real gases from the ones of ideal gases are more important; and since, on 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 been so far hidden by the latter. This does not exclude the possibility that, in a more or less near future, and with a more profound knowledge of the forces which act among the molecules of a real gas, one can pull the two deviations apart, thus arriving to choose experimentally among the different theories of the degeneration of the ideal gases.

§ 2. – For being able to carry out the quantization of the motions of the molecules of an ideal gas one must be in such a condition to be able to apply Sommerfield's rules to their motion; and this can be made in an infinite number of ways all of which, besides, lead to the same result. One can, for instance, suppose the gas 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

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[*]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).

molecules to a system of forces such as their motion becomes periodic and then can be quantized. The hypothesis that the gas is ideal allow 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 should not exist. Nevertheless one can recognize that the mere quantization, following Sommerfield's rules, of the motion of the molecules, considered mutually independent, is not sufficient for obtaining correct outcomes; since, even if in this case the specific heat tends to zero for $T = 0$, yet his value , besides on temperature and density, comes to depend on the total quantity of gas as well, and tends, at any temperature, to the limit $3/2k$ when, even if the density remains constant, the quantity of gas tends to infinite. Then it appears necessary to admit that some complement to Sommerfield's rules is needed, when calculating systems which, as ours, contain elements indistinguishable between them.[†]

To have an hint on how to formulate the most plausible hypothesis, it is worth to consider how things go in other systems which, as 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 an 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 the Sommerfield's rules would lead 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 ring K is already saturated when contains two electrons, and likewise the ring becomes saturated when contains 8 electrons, etc. This fact has been interpreted by Stoner,[‡] and in an even still more precise way by Pauli,[§] 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 to which these 4 numbers must satisfy, one finds that, for $n = 1$, only two triplets of values exist of k, j, m: for $n = 2$, there are 8, etc. To realize the above fact, therefore it is 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 contains only one electron.

§ 3. – We now intend to investigate if such hypothesis can give good outcomes in the problem of the quantization of the ideal gas as well: therefore we shall admit that in our gas almost a molecule whose motion is characterized by certain quantum numbers can exist, and we shall show that this hypothesis leads to a perfectly consequent theory of the quantization of the ideal gas, and in particular

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[†]E. Fermi, *N. Cimento* **1**, 145 (1924).
[‡]E. C. Stoner, *Phil. Mag.* **48**, 719 (1924).
[§]W. Pauli, *Zs. f. Phys.* **31**, 765 (1925).

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 a next occasion, in this Note we limit ourselves to expose 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 results to be quantizable. As we have seen, this can be made in an infinity of ways; but, since the result is independent of the particular way one adopts, we shall choose the most convenient for the calculation; and precisely we shall admit 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 call ν. 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

$$w = h\nu(s_1 + s_2 + s_3) = sh\nu \ . \tag{1}$$

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

Therefore the 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 to the absolute zero. At this temperature the gas must lie in the state of minimum energy. If we had no limitation to the number of molecules which can have a certain energy, all the molecules would lie in the state of zero energy, and all the three quantum numbers of each of them would be zero. On the contrary, as provided by our hypothesis, the existence of more than one molecule with all the three quantum numbers equal to zero is forbidden; therefore if $N = 1$, the 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 to have to distribute the total energy $W = Eh\nu$ (E = integer) among our molecules; and call $N_s \leq Q_s$ the numbers of molecules of energy $sh\nu$. We find easily that the most probable values of N_s are

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

where α and β 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 $r = 8$. Accordingly, for $r = 8$ the phenomena of degeneration must cease, and in particular the distribution of velocities, easily deducible from (2), must change into Maxwell law. Thus one finds that it must be

$$\beta = \frac{h\nu}{kT} \ . \tag{3}$$

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 the Maxwell 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

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

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

$$P(x) = x\left(1 + \frac{1}{2^{5/2}x^{3/2}} + \dots\right) \ ;$$

$$P(x) = \frac{1}{5}\left(\frac{9\pi}{2}\right)^{1/3}\left[1 + \frac{5}{9}\left(\frac{4\pi^4}{3}\right)^{1/3} x^2 + \dots\right] \ . \tag{5}$$

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

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

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

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

Then the pressure results higher than the one coming from the classical equation of state. For an ideal gas having the atomic weight of the helium, at the temperature of absolute $5°$ and at pressure of 10 atmospheres, the difference would be of 15%. From (4) and (5) one can also deduce the expression of the specific heat for low temperatures. One finds

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

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

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

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