On the Quantization of the Monoatomic Ideal Gas

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Introduction

A recent experiment [1] has brought a nearly-ideal gas of Fermi-Dirac particles (^{40}K atoms) to the condition of *quantum degeneracy*, in which the symmetry of the many-particle wavefunction has a dominant effect on the equation of state of the gas.

In the above-mentioned experiment, the gas atoms were confined by a magnetic field, whose effect is expressed by the harmonic potential,

$$V(x,y,z) = \frac{M}{2}\left(w_r^2(x^2+y^2) + w_z^2 z^2\right)$$

where x, y, z are Cartesian particle coordinates, M is the particle mass, $\omega_r = 2\pi\,137$ Hz, and $\omega_z = 2\pi\,19.5$ Hz. This situation is close to that portrayed in the original model used by Fermi to elucidate the effects of quantum degeneracy on the equation of state of an ideal gas, in the paper translated here.[2] Fermi confined the gas with an isotropic harmonic oscillator potential ($\omega_r = \omega_z$). This approach contrasts with that of most modern textbook treatments, which put the particles in a volume of constant potential, subject to either hard-wall or periodic boundary conditions, as are appropriate to the treatment of extended, homogeneous systems, *e.g.* electrons in a metal. The utility of such an approach was recognized by Fermi, but he adopted the harmonic confining potential so as to allow the invocation of the Bohr-Sommerfeld quantization rule in its simplest form.

In passing to the thermodynamic limit, the essential physics of the ideal Fermi- Dirac gas emerges independently of the choice of confining potential. Thus Fermi's treatment can be enjoyed without reference to recent developments. However, since some details of his original derivation have just come to have specific relevance to experiments, it seems appropriate to make them more accessible to an English-speaking audience.

The translation provided here is based on the Italian original,[2] "Sulla quantizzazione del gas perfetto monoatomico," as reprinted in the first volume of Fermi's collected papers.[3] A longer, German-language paper, presenting the argument in greater detail, was subsequently published by Fermi in *Zeitschrift für Physik*.[4] That paper is also reprinted in Ref. ([3]).

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1. According to classical thermodynamics, the specific heat at constant volume of a monoatomic ideal gas (referred to a single molecule) is given by $c = 3k/2$. It is clear however that if we also want to admit the validity of the Nernst principle for an ideal gas, we need to consider the previous expression for c as only an approximation for high temperatures, and in reality c goes to zero for $T = 0$, so that we can extend down to absolute zero the integral that expresses the value of the entropy without leaving the constant undetermined. To realize how this kind of variation in c can take place, it is necessary to admit that also the motions of the ideal gas have to be quantized. It is understandable also that such quantization will affect not only the amount of energy of the gas, but also its equation of state, giving the so-called degeneracy phenomena of the ideal gas for low temperatures.

The purpose of this work is to present a method that makes the quantization of the ideal gas possible, and which is, we believe, as independent as possible from unjustified hypotheses concerning the statistical behavior of the molecules of the gas.

Recently many attempts have been made to establish the equation of state for an ideal gas.[5] The formulae given by the various authors and ours differ from each other and from the classical equation of state, only for very low temperatures and very high densities; unfortunately these are the same conditions for which the differences between the laws of real gases and ideal gases are most important. Since under conveniently attainable experimental conditions, the deviations from the equation of state $pV = kT$ caused by the degeneracy 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, so that up to the present the former have been masked by the latter; it cannot be excluded that, with an improved knowledge of the forces acting between the molecules of a real gas, it might be possible, more or less in the near future, to separate the two deviations, so as to decide experimentally between the different theories of the degeneration of the ideal gas.

2. In order to be able to perform the quantization of the motion of the molecules of an ideal gas it is necessary to put ourselves in a position to apply Sommerfeld's rules to their motion: this can clearly be done in an infinite number of ways which, of course, all give the same result. For example, we can suppose the gas to be enclosed in a parallelepiped receptacle with elastic walls, quantizing the triply periodic motion of the molecule that bounces between the six faces of the receptacle; or, more generally, we can apply to the molecules a suitable system of forces such that their motion becomes periodic and can then be quantized. The hypothesis that the gas is ideal allows us to neglect in all these cases the forces acting between the molecules, so that the mechanical motion of each one of these takes place just as if the others did not exist. It is possible however to realize that the simple quantization, with Sommerfeld's rules, of the motion of the molecules considered as completely independent from each other is not sufficient to get correct results; because, even if in this way the specific heat goes to zero for $T = 0$, we find that its value depends not only on the temperature and density, but also on the total amount of gas, and goes, for every temperature, to the limit $3k/2$ when, while keeping the density constant, the total amount of gas goes to infinity. Thus it seems necessary to admit that we must add some complements to Sommerfeld's rules, in the case of systems, like ours, in which the elements are not distinguishable from each other.[6]

To have a hint of what is the most plausible hypothesis that we can make, it is convenient for us to examine how things work for other systems that, like our ideal gas, have indistinguishable elements; and precisely, we want to examine the behavior of atoms heavier than hydrogen, all containing more than one electron. If we consider the deepest parts of a heavy atom, we find conditions such that the forces that act on the electrons are very small compared with those created by the nucleus. In these circumstances the pure and simple application of Sommerfeld's rules would lead us to predict that, in the normal state of the atom, a considerable number of electrons should be found in an orbit of total quantum 1. In reality we observe that the K ring is already saturated when it contains two electrons, and in the same way the L ring is saturated when it contains 8 electrons, etc. This fact was interpreted by Stoner,[7] and even more precisely by Pauli,[8] in the following way: let us characterize a possible electronic orbit in a complex atom with 4 quantum numbers; n,k,j,m that have respectively the meaning of total quantum, azimuthal quantum, internal quantum and magnetic quantum. Given the inequalities that those four numbers have to satisfy, it is found that for $n = 1$, there exist only two triples of values k, j, m; for $n = 2$, there exist 8 triples of values, etc. To realize this fact, it is sufficient to assume that in the atom there can not be two electrons with the orbits described by the same quantum numbers; in other words it is required to admit that an electronic orbit is already "occupied" when it contains only one electron.

3. We now want to find out if such a hypothesis can give good results also in the problem of the quantization of the ideal gas: we shall thus assume that in our gas there can be at the most one molecule, whose motion is characterized by certain quantum numbers, and we shall show that this hypothesis leads us to a perfectly consistent theory for the quantization of the ideal gas that, in particular, accounts for the expected decrease of the specific heat for low temperatures, and that yields the exact value for the constant of the entropy of the ideal gas.

Reserving publication of the mathematical details of this theory to another occasion, we limit ourselves in this Note to showing the principles of the method and the results.

First of all we have to subject our gas to such conditions that the motion of its molecules can be quantized. As we have seen this can be done in an infinite number of ways; however as the result is independent of the specific way chosen, we shall choose the one that makes the calculations easy; and precisely we shall assume that an attractive force toward a fixed point O acts on our molecules, with strength proportional to the distance r of the molecule from O; so that each molecule will become a single spatial harmonic oscillator, with a frequency that we call ν. The orbit of the molecule will be characterized by its three quantum numbers s_1,s_2,s_3, that are related to its energy through the relation

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

The energy of a molecule can thus take all the multiple integer values of $h\nu$, and the value $sh\nu$ can be taken in $Q_s = \frac{1}{2}(s+1)(s+2)$ modes.

The zero energy can thus be realized only in one way, the energy $h\nu$ only in 3 ways, the energy $2h\nu$ in 6 ways, etc. To realize the consequences of our hypothesis, that given quantum numbers can not correspond to more than one molecule, let us consider the limiting case of having N molecules at the absolute zero. At this temperature the gas has to be in the state of minimum energy. Thus, if there was no restriction on the number of molecules that can have a certain energy, all the molecules would be in the state of zero energy, and all the three quantum numbers of each of them would be zero. Instead, according to our hypothesis, it is not possible to have more than one molecule with all the three quantum numbers equal to zero; so if $N = 1$, the only molecule will occupy the place with zero energy, if instead $N = 4$, one of the molecules will occupy the place with zero energy, and the other three the places with energy $h\nu$; if $N = 10$, one of the molecules will occupy the place of zero energy, three will occupy the three places of energy $h\nu$, and the remaining six the six places of energy $2h\nu$, etc.

Let us suppose now that we have to distribute among our N molecules the total energy $W = Eh\nu$ ($E=$ integer number); and let us label with $N_s \leq Q_s$ the number of molecules of energy $sh\nu$. It is easy to find 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 some constants dependent on W and N. To find the relation between these constants and the temperature, we observe that, because of the effect of the attraction toward O, the density of our gas will be a function of r, that must go to zero for $r = \infty$. So, for $r = \infty$ the degeneracy phenomena must cease, and in particular the distribution of the velocities, easily obtainable from (2), must become Maxwell's law. It is thus found that it has to be that

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

Now we are able to find from (2) the function $n(L)dL$, that represents, for a fixed value of r, the density of molecules with an energy that ranges from L to $L + dL$ (Analogous to Maxwell's law), and from that we can find the mean kinetic energy $\bar{L}$ of the molecules at distance r, that is a function not only of the temperature, but also of the density n. It is found precisely that

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

Here we have indicated by $P(x)$ a function, with a fairly complicated analytic expression, whose evaluation is possible when x is very large or very small using the asymptotic formulae

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

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

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

In the limit of high temperatures, that is for small degeneracy, the equation of state thus takes the following form

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

The pressure is therefore greater than that predicted from the classical equation of state. For an ideal gas of the atomic weight of helium, at a temperature of 5^o absolute, and at a pressure of 10 atmospheres the difference would be of 15%. From (4) and (5) we can also deduce the expression of the specific heat for low temperatures. It is found that

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

In the same way we can find the absolute value of the entropy. Performing the calculation we find, for high temperatures

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

which coincides with the value of the entropy given by Tetrode and by Stern.[9]

References

[1] "Onset of Fermi degeneracy in a trapped atomic gas," B. DeMarco and D. Jin, *Science* **285**, 1703-1706 (1999)

[2] "Sulla quantizzazione del gas perfetto monoatomico," E. Fermi, *Rend. Lincei* **3**, 145-149 (1926), reprinted in Ref. ([3]), pp. 181-185

[3] *Collected Papers (Note e Memorie), Volume I Italy 1921-1938,* E. Fermi (ed. E. Amaldi, H. L. Anderson, E. Persico, F. Rasetti, C. S. Smith, A. Wattenberg, and E. Segré), University of Chicago Press, Chicago, 1962)

[4] "Zur quantelung des idealen einatomigen Gases," E. Fermi, *Z. Physik* **36**, 902-912 (1926), reprinted in Ref. ([3]), pp. 186-195)

[5] See for example 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).

[6] E. Fermi, *N. C.* **I**, 145 (1924)

[7] E. C. Stoner, *Phil. Mag.* **48**, 719 (1924)

[8] W. Pauli, *Zs. f. Phys.* **31**, 765 (1925)

[9] Eq.(9) is reproduced here exactly from ref. 3; it is missing a factor of k on the right hand side.