

On Quantizing an Ideal Monatomic Gas

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In classical thermodynamics the molecular heat (an constant volume) is

$$c = (3/2)k. \tag{1}$$

If, however, we are to apply Nernst's heat theorem to a gas we must consider (1) merely as an approximation for high temperatures since c must vanish in the limit as $T = 0$. We are therefore forced to assume that the motion of a molecule in an ideal gas is quantized; this quantization manifests itself for low temperatures by certain degeneracy phenomena so that the specific heat and the equation of state depart from their classical counterparts.

The aim of the present paper is to present a method of quantization of an ideal gas which, according to our opinion, is as independent of arbitrary assumptions about the statistical of the gas molecules as is possible.

In recent times, numerous attempts have been made to determine the equation of state of a perfect gas. The equations of state of the various authors and ours differ from each other and from the classical equation of state

$$PV = NkT$$

by the terms, which become appreciable only at very low temperatures and high pressures; unfortunately, real gases depart most strongly from ideal gases under these conditions so that the significant degeneracy phenomena have not been observable up until now. In any case, it may well be that a deeper knowledge of the equation of state may enable us to separate the degeneracy from the remaining deviations from the equation $PV = NkT$ so that it may be possible to decide experimentally which of the degeneracy theories is correct.

To apply the quantum rules to the motions of the molecules, we can proceed in various ways; the result, however, is always the same. For example, we may picture the molecules as being enclosed in a parallelepiped container with elastically reflecting walls; then the motion of the molecules flying back and forth between the walls is conditionally periodic and can therefore be quantized; more generally, we may picture the molecules as moving in an external force field, such that their motion is conditionally periodic; the assumption that the gas is ideal permits us to neglect the interactions of the molecules, so that their mechanical motions occur only under the influence of the external field. It is clear, however, that the quantization of the molecular motion made under the assumption of the complete independence of the molecules from one another is not sufficient to account for the expected degeneracy. We can see this best in the example of molecules in a container if we note that as linear dimensions of the container increase, the energy levels of the quantum states of each molecule become denser and denser, so that for vessels of macroscopic dimensions all influences of the discontinuity of the energy values practically disappear. This influence, moreover, depends on the volume of the container, even if the number of molecules in it are so chosen that the density remains constant.

By analyzing this state of affairs quantitatively, we can convince ourselves that we only then obtain a degeneracy of the expected magnitude when we choose the vessel so small that it contains, on the average, just one molecule.

We therefore surmise that the quantization of ideal gases requires an addition to the Sommerfeld quantum condition.

Now recently Pauli, following upon an investigation by E.C. Stoner, proposed the rule that if an electron inside an atom has quantum numbers (including the magnetic quantum number) with definite values, then no other electron can exist in the atom in an orbit which is characterized by the same quantum numbers. In other words, a quantum state (in an external magnetic field) is already completely filled by a single electron.

Since this Pauli rule has proved extremely fruitful in the interpretation of spectroscopic phenomena, we want to see whether it may not also be useful in the problem of the quantization of ideal gases.

We shall show that this is, indeed, the case, and that the application of Pauli's rule allows us to present a completely consistent theory of the degeneracy of an ideal gas.

We therefore assume in the following that, at most, one molecule with given quantum numbers can exist in our gas: as quantum numbers we must take into account not only those that determine the internal motions of the molecule but also the numbers that determine its translational motion.

We must first place our molecules in a suitable external force field so that their motion is conditionally periodic. This can be done in an infinitude of ways; since, however, the result does not depend on the choice of the force field, we shall impose on the molecules a central elastic force directed toward a fixed point O (the coordinate origin) so that each molecule becomes a harmonic oscillator. This central force will keep our gas mass in the neighborhood of O ; the gas density will decrease with increasing distance from O and vanish at infinity. If

ν is proper frequency of the oscillators, then the force exerted on the molecules is

$$4\pi^2\nu^2mr$$

where m is the mass of the molecule and r its distance from O . The potential energy of the attractive force is then

$$u = 2\pi^2\nu^2mr^2$$

Let s_1, s_2, s_3 be the quantum numbers of a molecule oscillator. These quantum numbers are essentially not sufficient to characterize the molecule, for we must add to these the quantum numbers of the internal motions. We limit ourselves, however, to monatomic molecules and assume, in addition, that all the molecules in our gas are in the ground state and that this state is single (does not split in a magnetic field). We need not worry about the internal motion then, and we may then consider our molecules simply as mass points. The Pauli rule, therefore, states in our case that in the entire mass of gas at most only one molecule can have the given quantum numbers s_1, s_2, s_3 .

The total energy of this molecule is given by

$$w = h\nu (s_1 + s_2 + s_3) = h\nu s. \quad (2)$$

The total energy can thus be an arbitrary integral multiple of $h\nu$; the value $sh\nu$, however, can be realized in many ways. Each realization implies a solution of the equation

$$s = s_1 + s_2 + s_3 \quad (3)$$

where s_1, s_2, s_3 can assume the values 1,2,3 . . . We know that (3) has

$$Q_s = \frac{(s+1)(s+2)}{2} \quad (4)$$

solutions. The energy 0 can thus be realized in one way, the energy $h\nu$ in three ways, the energy $2h\nu$ in six ways, and so on. We shall simply call a molecule with energy $sh\nu$ an $((s))$ - molecule.

According to our assumption, there can be in our entire gas mass only $Q_s((s))$ - molecules; thus, at most, one molecule with energy zero, at most, three with energy $h\nu$ at most, six with energy $2h\nu$, and so on.

To see early the results of this state of affairs, we consider the extreme case in which the absolute temperature of our gas is zero. Let N be the number of molecules. At absolute zero our gas must be in its lowest energy state. If there were no restrictions on the number of molecules of a given energy, then every molecule would be in a state of zero energy ($s_1 = s_2 = s_3 = 0$). According to the foregoing, however, at most, only one molecule can have zero energy; hence, if N were 1, then this single molecule would have energy zero; if N were 4, one molecule would have energy zero and the three other would occupy the three available places with energy $h\nu$; if N were 10 one molecule would be in the zero energy position, three others in the three places with energy $h\nu$, and the six remaining ones in the six places with energy $2h\nu$ and so on.

At the absolute zero point, our gas molecules arrange themselves in a kind of shell-like structure which has a certain analogy to the shell-like arrangement of electrons in an atom with many electrons.

We now want to investigate how a certain amount of energy

$$W = E h \nu \quad (5)$$

($E = \text{integer}$) is distributed among our molecules.

Let N_s be the number of molecules in a state with energy $s h \nu$. According to our assumption

$$N_s \leq Q_s \quad (6)$$

We have, further, the equations

$$\sum N_s = N \quad (7)$$

$$\sum s N_s = E \quad (8)$$

which state that the total number and total energy of the molecules are N and $E h \nu$, respectively.

We now want to calculate the number P of arrangements of our N molecules for which N_0 are at places with energy 0, N_1 at places with energy $h \nu$, N_2 at places with energy $2 h \nu$, etc. Two such arrangements are to be considered identical if the places occupied by the molecules are the same; thus two arrangements which differ only in a permutation among the molecules in their places are to be considered as one. If we considered two such arrangements as different, we would have to multiply P by the constant $N !$; we can easily see, however, that this can have no influence on what follows. In the above-defined sense, the number of arrangements of N_s molecules among the Q_s places of energy, $s h \nu$ is given by

$$\binom{Q_s}{N_s}.$$

We therefore find for P the expression

$$P = \binom{Q_0}{N_0} \binom{Q_1}{N_1} \binom{Q_2}{N_2} \dots = \prod \binom{Q_s}{N_s}. \quad (9)$$

We obtain the most probable values of the N_s by seeking the maximum of P under the constraints (7) and (8). By applying Stirling's theorem we may write sufficient approximation for our case

$$\log P = \sum \log \binom{Q_s}{N_s} = - \sum \left(N_s \log \frac{N_s}{Q_s - N_s} + Q_s \log \frac{Q_s - N_s}{Q_s} \right) \quad (10)$$

We thus seek the values of N_s that satisfy (7) and (8) and for which $\log P$ becomes a maximum. We find

$$\alpha e^{-\beta s} = \frac{N_s}{Q_s - N_s}$$

where α and β are constants. This equation gives us

$$N_s = Q_s \cdot \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}} \quad (11)$$

The values of α and β can be found from equation (7) and (8) or, conversely, we may consider α and β as given; then (7) and (8) determine the total number and total energy of our configuration. We find, namely,

$$N = \sum_0^{\infty} Q_s \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}} \quad (12)$$

$$\frac{W}{h\nu} = E = \sum_0^{\infty} s \cdot Q_s \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}}$$

The absolute temperature T of the gas is a function of N and E or also of α and β . This function can be determined by two methods, which, however, lead to the same result. We could, for example, according to the Boltzmann entropy principle set

$$S = k \log P$$

and then calculate the temperature from the formula

$$T = \frac{dW}{dS}$$

This method, however, has the disadvantage common to all methods based on the Boltzmann principle, that for its application we must make a more or less arbitrary assumption about the probability of a state. Therefore, we proceed as follows: we note that the density of our gas is a function of the distance which vanishes for infinite distances. For infinitely large r , therefore, the degeneracy phenomena also vanish and the statistics of our gas go over to classical statistics. In particular, for $r = \infty$ the mean kinetic energy of a molecule must become $(2/3)kT$ and the velocity distribution must go over to the Maxwellian. We can thus obtain the temperature from the distribution of velocities in the region of infinitesimal densities; and since the entire gas is at the same constant temperature, we then at the same time obtain the temperature of the high density region also. For this determination we use, so to speak, a gas thermometer with an infinitely attenuated ideal gas.

To begin with, we calculate the density of molecules with kinetic energy between L and $L + dL$ at the distance r . The total energy of these molecules lies, according to (1), between

$$L + 2\pi^2\nu^2mr^2 \quad \text{and} \quad L + 2\pi^2\nu^2mr^2 + dL.$$

Now the total energy of a molecule is $sh\nu$. For our molecules s must therefore lie between s and $s + ds$, where

$$s = \frac{L}{h\nu} + \frac{2\pi^2\nu mr^2}{h} \quad ds = \frac{dL}{h\nu} \quad (13)$$

We now consider a molecule whose motion is characteristic by the quantum numbers s_1, s_2, s_3 . Its coordinates x, y, z are given by

$$\begin{aligned} x &= \sqrt{Hs_1} \cos(2\pi\nu t - \alpha_1), & y &= \sqrt{Hs_2} \cos(2\pi\nu t - \alpha_2) \\ z &= \sqrt{Hs_3} \cos(2\pi\nu t - \alpha_3) \end{aligned} \quad (14)$$

as functions of the time. Here

$$H = \frac{h}{2\pi^2\nu m}; \quad (15)$$

$\alpha_1, \alpha_2, \alpha_3$ are phase constants which may take on all sets of values with equal probability. From this and from equation (14) it follows that

$$|x| \leq \sqrt{Hs_1}, \quad |y| \leq \sqrt{Hs_2}, \quad |z| \leq \sqrt{Hs_3},$$

and that the probability that x, y, z lie between the limits x and $x + dx, y$ and $y + dy, z$ and $z + dz$, has the value

$$\frac{dx dy dz}{\pi^3 \sqrt{(Hs_1 - x^2)(Hs_2 - y^2)(Hs_3 - z^2)}}$$

If we do not know the individual values of s_1, s_2, s_3 but only their sum, then our probability is given by

$$\frac{1}{Q_s} \cdot \frac{dx dy dz}{\pi^3} \cdot \sum \frac{1}{\sqrt{(Hs_1 - x^2)(Hs_2 - y^2)(Hs_3 - z^2)}} \quad (16)$$

The sum is to be extended over all integer solutions of equation (3) which satisfy the inequalities

$$Hs_1 \geq x^2, \quad Hs_2 \geq y^2, \quad Hs_3 \geq z^2$$

If we multiply the probability (16) with the number N_s of $((s))$ - molecules, we obtain the number of $((s))$ - molecules in the volume element $dx dy dz$. Taking account of (11) we thus find that the density of $((s))$ - molecules at the position x, y, z is given by

$$N_s = \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}} \cdot \frac{1}{\pi^3} \cdot \sum \frac{1}{\sqrt{(Hs_1 - x^2)(Hs_2 - y^2)(Hs_3 - z^2)}}$$

For sufficiently large s we can replace the sum by a double integral; after carrying out the integration we find

$$N_s = \frac{2}{\pi^2 H^2} \cdot \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}} \cdot \sqrt{Hs - r^2}.$$

Using (13) and (15) we now find that the density of molecules with kinetic energy between L and $L + dL$ at the position x, y, z is given by the following expression

$$N(L)dL = N_s ds = \frac{2\pi(2m)^{3/2}}{h^3} \cdot \sqrt{L} dL \cdot \frac{\alpha e^{-\frac{2\pi^2\nu m\beta r^2}{h}} e^{-\frac{\beta L}{h\nu}}}{1 + \alpha e^{-\frac{2\pi^2\nu m\beta r^2}{h}} e^{-\frac{\beta L}{h\nu}}} \quad (17)$$

This formula must be compared with the classical expression for the Maxwellian distribution:

$$N^*(L)dL = K\sqrt{L} dLe^{-L/kt} \quad (17')$$

We see then that in the limit for $\nu = \infty$ (17) goes over into (17') if we just set

$$\beta = \frac{h\nu}{kT} \quad (18)$$

Now (17) can be written as follows:

$$N(L)dL = \frac{(2\pi)(2m)^{3/2}}{h^3} \cdot \sqrt{L} dL \cdot \frac{Ae^{-L/kT}}{1 + Ae^{-L/kT}} \quad (19)$$

where

$$A = \alpha e^{-\frac{2\pi^2\nu^2mr^2}{kT}} \quad (20)$$

The total density of molecules at the distance r now becomes

$$N = \int_0^{\infty} N(L) dL = \frac{(2\pi mkT)^{3/2}}{h^3} F(A), \quad (21)$$

where we have placed

$$F(A) = \frac{2}{\sqrt{\pi}} \cdot \int_0^{\infty} \frac{A\sqrt{x}e^{-x}dx}{1 + Ae^{-x}} \quad (22)$$

The mean kinetic energy of the molecules at the distance r is

$$\bar{L} = \frac{1}{N} \int_0^{\infty} LN(L)dL = (3/2) \cdot kT \cdot \frac{G(A)}{F(A)} \quad (23)$$

where

$$G(A) = \frac{4}{3\sqrt{\pi}} \int_0^{\infty} \frac{Ax^{3/2}e^{-x}dx}{1 + Ae^{-x}}. \quad (24)$$

Through (21) we can determine A as a function of density and temperature; when we put this into (19) and (20) we obtain the velocity distribution and the mean kinetic energy as a function of density and temperature.

To obtain the equation of state we use the virial theorem. According to this pressure is given by

$$p = \frac{2}{3} \cdot N\bar{L} = NkT \cdot \frac{G(A)}{F(A)}; \quad (25)$$

again A is to be found from (12) as a function of density and temperature.

Before we go further we give some of the mathematical properties of $F(A)$ and $G(A)$.

For $A \leq 1$ we can express both functions by convergent series

$$\begin{cases} F(A) = A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} - \dots \\ G(A) = A - \frac{A^2}{2^{3/2}} + \frac{A^3}{3^{3/2}} - \dots \end{cases} \quad (26)$$

For large A we have the asymptotic expressions

$$\begin{cases} F(A) = \frac{4}{3\sqrt{\pi}} (\log A)^{3/2} \left[1 + \frac{\pi^2}{8(\log A)^2} + \dots \right], \\ G(A) = \frac{8}{15\sqrt{\pi}} (\log A)^{5/2} \left[1 + \frac{5\pi^2}{8(\log A)^2} + \dots \right]. \end{cases} \quad (27)$$

Further, the relationship

$$\frac{dG(A)}{F(A)} = d \log A \quad (28)$$

holds.

We must still introduce another function $P(\Theta)$ defined by

$$P(\Theta) = \Theta \cdot \frac{G(A)}{F(A)}, \quad F(A) = \frac{1}{\Theta^{3/2}} \quad (29)$$

For very large and very small θ respectively, $P(\theta)$ can be calculated from the approximations

$$\begin{cases} P(\Theta) = \Theta \left\{ 1 + \frac{1}{2^{5/2} \Theta^{3/2}} + \dots \right\} \\ P(\Theta) = \frac{3^{3/2} \pi^{1/3}}{5 \cdot 2^{1/3}} \frac{3^{2/3} \pi^{1/3}}{5 \cdot 2^{1/3}} \left\{ 1 + \frac{5 \cdot 2^{2/3} \pi^{4/3}}{3^{7/3}} \Theta^2 + \dots \right\} \end{cases} \quad (30)$$

Using (29), (28), (27), we see further that

$$\int_0^\Theta \frac{dP(\Theta)}{\Theta} = {}^5/3 \cdot \frac{G(A)}{F(A)} - {}^2/3 \log A. \quad (31)$$

We can now eliminate A from the equation of state (25) and (23) and we obtain the pressure and the mean kinetic energy as explicit functions of density and temperature:

$$p = \frac{h^2 N^{5/3}}{2\pi m} \cdot P \cdot \left(\frac{2\pi m k T}{h^2 N^{2/3}} \right) \quad (32)$$

$$\bar{L} = {}^3/2 \cdot \frac{h^2 N^{2/3}}{2\pi m} \cdot P \cdot \left(\frac{2\pi m k T}{h^2 N^{2/3}} \right) \quad (33)$$

In the limit of weak degeneracy (T large and N small) the equation of state has the following form:

$$p = N k T \left\{ 1 + ({}^1/16) \cdot \frac{h^3 N}{(\pi m k T)^{3/2}} + \dots \right\}. \quad (34)$$

The pressure is thus large than the classical pressure $P = (NkT)$. For an ideal gas with the atomic weight of helium at $T = 5^\circ$ and a pressure of 10 atm, the difference is about 15%.

In the limit of large degeneracy, (32) and (33) become

$$\begin{aligned} p &= (1/20) \cdot \left(\frac{6}{\pi}\right)^{2/3} \cdot \frac{h^2 N^{5/3}}{m} + \frac{2^{4/3}}{3^{5/2}} \pi^{8/3} \cdot \frac{m N^{1/3} k^2 T^2}{h^2} + \dots \\ \bar{L} &= (3/40) \cdot \left(\frac{6}{\pi}\right)^{2/3} \cdot \frac{h^2 N^{2/3}}{m} + \frac{2^{1/3} \pi^{8/3}}{3^{2/3}} \cdot \frac{mk^2 T^3}{h^2 N^{2/3}} + \dots \end{aligned} \quad (35)$$

From this we see that the degeneracy leads to a zero point pressure and a zero point energy.

From (35) we can also obtain the specific heat at low temperatures.

We find

$$C_v = \frac{d\bar{L}}{dT} = \frac{2^{4/3} \pi^{8/3}}{3^{2/3}} \frac{mk^2 T}{h^2 N^{2/3}} + \dots \quad (36)$$

The specific heat vanishes at absolute zero and is proportional to the absolute temperature at low temperatures . . .