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Quantum mechanical disclosure of the classical adiabatic constancy of pV^γ for both an ideal and a photon gas

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In our recent paper (Yarman et al., 2010), we established a connection between the macroscopic adiabatic transformation law ($Pressure \times Volume^{5/3} = Constant$) of an ideal gas and the quantum mechanical description of its molecules. This connection was unique in embodying just the Planck constant and quantum numbers, instead of the classical temperature quantity and Boltzmann constant. It was shown that for an ideal gas enclosed in a macroscopic cubic box of volume V , the constant, arising along with the classical law of adiabatic expansion, comes to be proportional to h^2/m ; here h is the Planck constant and m is the rest mass of the molecule the gas is made of. In this paper, we first check the relationship of concern in general parallelepiped geometry, displaying how the quantum numbers are affected throughout. We then show that our results hold for a photon gas, too, although the related setup is quite different from the previous ideal gas setup. At any rate, for a photon gas we come out with $PV^{4/3} \sim hc = Constant$, where c is the speed of light in vacuum. No matter what, the dimensions of the two constants in question are different from each other; they are still rooted to universal constants, more specifically to h^2 and to hc , respectively, while their ratio, that is, $V^{1/3} \sim h/mc$, interestingly points to the de Broglie relationship's cast.

Key words: Classical thermodynamics, quantum mechanics, ideas gas, photon gas.

INTRODUCTION

It is known that the question of finding a connection between the Boltzmann constant k and the Planck constant h remains unanswered. In a previous work, Yarman et al. (2010) have shown that such an effort is in vain. Instead, we established an organic bridge between the macroscopic classical laws of gases and the quantum mechanical description of molecules of an ideal gas, within the framework of a sole gas relationship involving neither k nor h . Along this line, it would be fair to recall that in particular, de Broglie (1925) already in his doctorate thesis has brilliantly applied his relationship

(associating a wavelength with the momentum of a moving particle) to the statistical equilibrium of gases, but did not advance his idea, to see whether one can, along such a line, obtain anything related to the laws of gases established long ago, in 1650. Modern statistical physics, despite huge efforts to draw a 'parallelism' between the classical law of gases and quantum mechanics, does not yet appear at the level of fully implementing the two disciplines in question, into each other, the way Yarman et al. (2010) did.

In an ideal gas, by definition, one proposes to consider the motion of each molecule independently on all other molecules. Accordingly the macroscopic parameters of the ideal gas, such as pressure P , can be introduced as a result of simple averaging over all individual motions of

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molecules. The aforementioned work (Yarman et al., 2010) thus show that for an ideal gas enclosed in a macroscopic 'cubic' box of volume V , the classical law of adiabatic expansion is:

$$PV^\gamma = \text{Constant}, \quad (1)$$

this law can (had the cube expanded uniformly) be derived based on simple quantum mechanics. A principal advantage of such a quantum mechanical analysis is the explicit determination of the constant of Equation 1, which turned out to be $h^2 n^2 / (4m_0)$ for just one molecule of mass m_0 . Here n is the integer number characterizing the energy level of the molecule in consideration, within the framework of the simplifying 'cubic' container assumption, where all three quantum numbers n_x , n_y and n_z are equal to the given number n , thus equal to each other. The result obtained for just one molecule, can easily be extended, and via averaging, generalized to a given set of molecules of ideal gas.

Subsequently, we first summarize the previous work (Yarman et al., 2010), which constitutes the basis of the present contribution. At this stage, though, we provide the solution of the problem in (just not a cube, but in the general case) a parallelepiped, in this case we find out how the quantum numbers of the molecules of an ideal gas are altered through an adiabatic transformation. Further we undertake the case of a photon gas. We show that the relationship $PV^\gamma = \text{constant}$ holds for a photon gas, too, together with the exponent $\gamma = 4/3$. The constant coming into play, however, is still nailed to the Planck constant h . Finally we draw a conclusion.

THE ADIABATIC TRANSFORMATION LAW, $PV^\gamma = \text{CONSTANT}$ FOR AN IDEAL GAS: QUANTUM MECHANICAL APPROACH

As anticipated previously (Yarman et al., 2010), the relationship (Equation 1) for an adiabatic transformation of ideal gas constitutes an efficient check point of the compatibility of the macroscopic laws of gases and quantum mechanics. Subsequently, for simplicity, we will operate with one mole of gas. We could well operate with just a single molecule, and the respective results would still be the same, since in an ideal gas the molecules are supposed not to interact with each other, and their wave functions are not mixed. Hence, the overall internal energy of the ideal gas can be found as a simple sum of energy eigenvalues tapped for different molecules. One should notice that the average principal quantum number for any given molecule confined in a container of macroscopic size can be very large, near the room temperature, but this does not create any conceptual difficulty. On the contrary, this allows us to neglect the

exchange interaction (thus omitting the spin effects), and to apply classical kinetic theory of gases to characterize the macroscopic parameters of an ideal gas such as the pressure.

Equation 1 involves the usual definition:

$$\gamma = C_P / C_V, \quad (2)$$

where

$$C_V = \frac{3}{2} R, \quad (3)$$

$$C_P = \frac{5}{2} R, \quad (4)$$

C_V being the heat to be delivered to one mole of ideal gas at 'constant volume' to increase the temperature of the gas as much as 1 °K, C_P being the heat to be delivered to one mole of ideal gas at 'constant pressure' to increase its temperature, still as much as 1 °K and R is the gas constant. Equations 3 and 4 are exact, when internal energy levels of molecules are not excited. By definition, such an approximation is fulfilled for an ideal gas. Hence, we have:

$$\gamma = 5/3. \quad (5)$$

Subsequently, we shortly summarize the derivation of the constant in Equation 1 within a quantum mechanical framework, suggested in Yarman et al. (2010) for the case of uniformly expanded (or compressed) cubic container. Further, we explore the general case of parallelepiped geometry of container for a non-uniform transformation of its sizes, where we not only arrive at the specific constant in the *rhs* of Equation 1, but also determine the law of variation of quantum numbers of the molecules of ideal gas under an adiabatic transformation.

Non-relativistic case considered in a cube

Let us consider a non-relativistic particle of rest mass m_0 at a fixed internal energy state, located in a macroscopic 'cube' of side L . The non-relativistic Schrödinger equation written for the 'cubic' container at hand, furnishes the n th energy E_n , that is:

$$E_n = \frac{h^2}{8m_0} \left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2} \right) = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8m_0 L^2} \quad (6)$$

where we denoted $n_x=1,2,3,\dots$, $n_y=1,2,3,\dots$, $n_z=1,2,3,\dots$ the quantum numbers to be associated with the

corresponding wave function dependencies on the respective directions x , y and z . Hereinafter, for brevity, while writing E_n , we introduced the subscript “ n ” to denote the given state characterized by the integer numbers n_x , n_y and n_z , so each “ n ” in fact, represents a set of three integer numbers. For an ideal gas confined in an infinitely high box, the potential energy input to the Schrödinger equation is null everywhere inside the box (It is evidently infinite at the borders). Hence for a non-relativistic particle we have:

$$E_n = \frac{1}{2} m_0 v_n^2, \tag{7}$$

v_n being the velocity of the particle at the n th energy level. At the given energy level, the pressure p_n exerted by just one particle on the walls, after averaging over three dimensions, becomes (Yarman et al., 2010):

$$p_n = \frac{m_0 v_n^2}{3L^3} = \frac{2}{3} \frac{E_n}{L^3}. \tag{8}$$

Now let us calculate the product $p_n V^\gamma$ for the cube at hand, confining the single particle in consideration:

$$p_n V^\gamma = \frac{2}{3} \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8m_0 L^2} \frac{(L^3)^{5/3}}{L^3} = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{12m_0}. \tag{9a}$$

We observe that the *rhs* of Equation 9a indeed turns out to be a constant for the given discrete energy level n (specified by the set of n_x , n_y and n_z) of the particle of mass m_0 . Recall that the total quantized energy E_n in Equation 6 ultimately determines the quantized velocity v_n of Equation 7 along with its three quantized components. When it is a question of many particles instead of just one, we have to consider all particles each lying at different, possible, quantized states. We can anyway visualize the ‘average particle’ at the \bar{n}^{th} level, thus corresponding to the given temperature of the gas¹ at the given state, and suppose that all other particles behave the same. Furthermore, all three components of the average velocity are expected to be the same in equilibrium state. Thus, we can rewrite Equation 9a for the macroscopic pressure $P_{\bar{n}}$ exerted at the given average state \bar{n} by one mole of gas on the walls of the

¹ Note that through a uniform, adiabatic transformation of particles in a box, the “temperature” will evidently get changed, whereas the set of quantum numbers associated with the respective energy levels of the particles in consideration, will remain the same; that is, the quantum numbers coming into play, shall not get altered. Thus we have to precise what we mean here, by “temperature”; thus we mean, the “average energy of the constituents in the box, at the given state, prior to the transformation”.

container:²

$$P_{\bar{n}} V^\gamma = N_A \frac{h^2 \bar{n}^2}{4m_0}, \tag{9b}$$

where N_A is the Avagadro number.

Given that the transformation is adiabatic, the quantum numbers would not change, if the transformation is achieved uniformly in all directions, and this is what, in effect, we meant so far. Thus, equation 9b discloses not only the ‘constancy’ of the quantity $P V^\gamma$, but also the value of the constant delineated by the adiabatic transformation relationship, that is, Equation 1. Note that at the average state \bar{n} (that is, at the given temperature), the mean square speed of the gas molecules is $v_{\bar{n}}^2 = \overline{v_n^2}$; the average energy $E_{\bar{n}} = \overline{E_n}$ is furnished accordingly via the framework of Equation 7.

Under the given circumstances, we conclude that the constancy $P_{\bar{n}} V^\gamma$, drawn by an adiabatic transformation of an ideal gas, is nothing but a macroscopic manifestation of its quantum mechanical behavior.

Yet, one needs to develop further care, if the container was not a cube, and the expansion (or compression) occurs ‘non-uniformly’. This problem is analyzed subsequently.

Ideal gas in a parallelepiped container

Let us thus reconsider a non-relativistic particle of mass m at a fixed internal energy state, though, now located in a macroscopic parallelepiped of sides L_x , L_y and L_z . We will have to rewrite the quantized energy E_n of the particle in the box (Equation 6) for the general case at hand:

$$E_n = \frac{h^2}{8m_0} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right), \tag{10a}$$

where h is the Planck constant and n_x , n_y and n_z are the

²Rigorously speaking, one must write (Yarman et al., 2010)

$$P_{\bar{n}} V^\gamma = \sum_{i=1}^{N_A} \frac{h^2(n_{ix}^2 + n_{iy}^2 + n_{iz}^2)}{12m_0} = N_A \frac{h^2 \bar{n}^2}{4m_0} \text{ along with the}$$

definition $\frac{1}{3N_A} \sum_{i=1}^{N_A} (n_{ix}^2 + n_{iy}^2 + n_{iz}^2) = \bar{n}^2$. Hence it becomes clear

that, if all particles bear the same set of quantum numbers, each with equal quantum numbers along all three directions, that is, $n_x = n_y = n_z = \bar{n}$, then \bar{n} becomes $\bar{n} = \sqrt{\bar{n}^2}$.

quantum numbers to be associated with the corresponding wave function dependencies on the respective directions x , y and z . For brevity, we reintroduce the subscript “ n ” which denotes the specific state characterized by the given set of integer numbers n_x , n_y and n_z .

For non-interacting non-relativistic particles of an ideal gas, the potential energy within the box is null. Thus, here again we have:

$$E_n = m_0 v_n^2 / 2$$

(Equation 7); now v_n has three different components v_x , v_y and v_z .

At the given energy level, the pressure p_n exerted by just one particle on either wall, can be written as:

$$p_n = \frac{m_0 v_n^2}{3 L_x L_y L_z} = \frac{2}{3} \frac{E_n}{L_x L_y L_z} = \frac{2 E_n}{3 V} \tag{10b}$$

For convenience, we recall the classical derivation of Equation 10b. The force f_x exerted by the molecule of mass m_0 and non-relativistic velocity $v_n \{v_x, v_y, v_z\}$ on the wall in the plane yz , is given by Newton’s second law $f_x = -\Delta p_x / \Delta t_x$, where $\Delta p_x = -2m_0 v_x$, is the algebraic increase in the momentum, whilst the molecule bounces back from the wall and $\Delta t_x = 2L_x / v_x$, L_x being the size of the container along the x -direction. Thus, one gets $f_x = m_0 v_x^2 / L_x$, and the pressure exerted by the molecule on the wall of concern is $p = f_x / (L_y L_z) = m_0 v_x^2 / V$. At the equilibrium state, characterized evidently by the same temperature, one can write $v_x^2 = v_y^2 = v_z^2 = v_n^2 / 3$. Hence, we arrive at Equation 10b.

Equations 10a and b, via the gas law $p_n V = kT$, written for just one molecule, k being the Boltzmann constant (so that $R = N_A k$, where N_A is the Avagadro Number), allow us to write:

$$E_n = \frac{h^2}{8m_0} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) = \frac{1}{2} m_0 (v_x^2 + v_y^2 + v_z^2) = \frac{3}{2} kT \tag{10c}$$

At the given stationary state, delineated by the temperature T , one can conjecture that;

$$\frac{h^2 n_x^2}{8m_0 L_x^2} = \frac{1}{2} m_0 v_x^2 = \frac{h^2 n_y^2}{8m_0 L_y^2} = \frac{1}{2} m_0 v_y^2 = \frac{h^2 n_z^2}{8m_0 L_z^2} = \frac{1}{2} m_0 v_z^2, \tag{10d}$$

or, in short

$$\frac{n_x}{L_x} = \frac{n_y}{L_y} = \frac{n_z}{L_z} \tag{10e}$$

This is the ‘equilibrium condition’ for the ‘parallelepiped geometry’.

Combining Equation 10a and 10b, let us calculate (for just one particle, at the quantum level n) the product $p_n V^{5/3}$:

$$p_n V^{5/3} = \frac{2}{3} \frac{8m_0 \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)}{V} V^{5/3} = \frac{h^2}{12m_0} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) (L_x L_y L_z)^{2/3} \tag{10f}$$

The second equality can further be arranged based on Equation 10e:

$$p_n V^{5/3} = \frac{h^2}{4m_0} \left(\frac{n_x^2}{L_x^2} \right) (L_x L_y L_z)^{2/3} \tag{10g}$$

When it is the question of many particles instead of just one (made of one type of gas molecule), normally we would have particles, in general, at different quantized states. This means that here again we deal with some energy distribution of molecules at the given temperature, instead of the fixed eigenvalue given by Equation 10a and derived for a gas consisting in just a single molecule. In order to describe the distribution of energy over the molecules within an elaborated quantum mechanical approach, as we have done previously (Yarman et al., 2010), we have to abandon the strict ideal gas approximation, and to introduce into the Schrödinger equation a potential energy term as a perturbation responsible of the weak interaction of molecules, whose averaged value will somewhat randomly affect all of the molecules of gas at each fixed temperature.

We have to stress that such a distribution of perturbation energy is to be compatible with the Maxwellian distribution of velocities. However, the analysis of this problem falls outside the scope of the present paper.

Thus, for our immediate purpose, it is sufficient to take into consideration an “average molecule” at the given temperature T . We can visualize the average molecule as a single particle, obeying Equation 10a and 10b, thus situated at the n th level and, associate the given temperature with this energy.

For the ideal gas, we can straightforwardly generalize Equation 10f for the macroscopic pressure P_n exerted at the given average state n by ‘one mole’ of gas on the walls of the container:

$$P_n V^{5/3} = \frac{h^2}{12m_0} \sum_{i=1}^{N_A} \left(\frac{n_{xi}^2}{L_x^2} + \frac{n_{yi}^2}{L_y^2} + \frac{n_{zi}^2}{L_z^2} \right) (L_x L_y L_z)^{2/3}; \quad (11)$$

where the quantum numbers n_{ix} , n_{iy} and n_{iz} coming into play are associated with the i th molecule.

The right hand sides of Equation 11 for a cubic container ($L_x=L_y=L_z$) indeed turns out to be constant. However, for a parallelepiped geometry ($L_x \neq L_y \neq L_z$), the constancy of $P_n V^{5/3}$ is not that obvious. More specifically, if one, as a first inclination, assumes that the quantum numbers n_{ix} , n_{iy} , and n_{iz} stay invariant under a given adiabatic transformation of the ideal gas, the *rhs* of Equations 11 then becomes dependent on the size of container, which though in the much hasty way we sketched, appears to contradict the classical result $PV^{5/3} = \text{Constant}$.

Thereby, one can see that in the three-dimensional case, the quantum numbers n_{ix} , n_{iy} and n_{iz} , in general, have to be altered through the adiabatic transformation of an ideal gas. The exception is the case, where the adiabatic transformation is achieved uniformly (that is, $L_x \rightarrow fL_x$, $L_y \rightarrow fL_y$ and $L_z \rightarrow fL_z$; f being the given multiplier), and in such a case the constancy of the *rhs* of Equation 11 for the fixed initial set of quantum numbers n_{ix} , n_{iy} and n_{iz} is clearly seen.

In short, the ‘uniform transformation’ of a three-dimensional box containing an ideal gas actually does not alter the quantum numbers of the molecules of the gas, when a uniform expansion or contraction is carried out adiabatically. From the physical viewpoint this result can be grasped via the observation that the uniform expansion of the container preserves the equilibrium condition (Equation 10e) untouched. In contrast, any non-uniform transformation of the container breaks the original equilibrium (Equation 10e) and leads to a new equilibrium, achieved after multiple collisions of the molecules with the walls of the container (recall, we assumed that in an ideal gas the molecules do not collide with each other). In this case the quantum numbers n_x , n_y and n_z should, in general, be altered (here we omitted the subscript “ i ” for brevity).

In order to determine the law of transformation of quantum numbers, we reconsider the uniform expansion of a parallelepiped container, implemented however via three stages:

1. The expansion in the x -direction only: $L_x, L_y, L_z \rightarrow fL_x, L_y, L_z$ (where $f > 1$ for the expansion process);
2. Further transformation in the y -direction: $fL_x, L_y, L_z \rightarrow fL_x, fL_y, L_z$;
3. Final transformation in the z -direction: $fL_x, fL_y, L_z \rightarrow fL_x, fL_y, fL_z$.

Next we assume that the quantum number n_x at the first stage is modified by ε_{xx} , at the second stage by a

further coefficient ε_{xy} and at the third stage by a final coefficient ε_{xz} , so that at this latter stage we landed at the overall transformation $n_x \rightarrow \varepsilon_{xy} \varepsilon_{xx} \varepsilon_{xz} n_x$. Similar coefficients can be introduced for the quantum numbers n_y and n_z . Thus, at the first stage, we have the transformation $n_y \rightarrow \varepsilon_{yx} n_y$, at the second stage, we have the transformation $\varepsilon_{yx} n_y \rightarrow \varepsilon_{yy} \varepsilon_{yx} n_y$ and at the third stage the transformation $\varepsilon_{yy} \varepsilon_{yx} n_y \rightarrow \varepsilon_{yz} \varepsilon_{yy} \varepsilon_{yx} n_x$.

Now we notice that after the implementation of all these stages, we get the ‘uniform expansion’ of a container, where the quantum numbers n_x , n_y and n_z become equal to their original values. Hence we get the equalities, $\varepsilon_{xx} \varepsilon_{xy} \varepsilon_{xz} = 1$, $\varepsilon_{yx} \varepsilon_{yy} \varepsilon_{yz} = 1$, $\varepsilon_{zx} \varepsilon_{zy} \varepsilon_{zz} = 1$, which, in combination with Equation 10e, yield³:

$$\varepsilon_{ll} = f^{2/3}, \quad \varepsilon_{l \neq m} = f^{-1/3} \quad (l, m = x, y, z). \quad (12)$$

Equation 12 discloses the law of transformation of quantum numbers.

$$n_l(f) \rightarrow \varepsilon_{lm}(f) n_l \quad (13)$$

for the expansion ($f > 1$) or compression ($f < 1$) of a container in the dimension m by f times. In particular, for the adiabatic transformation of the container along the x -axis (L_x, L_y, L_z), we obtain from Equations 11, 12 and 13:

$$P_n V^{5/3} = \frac{h^2}{12m_0} \sum_{i=1}^{N_A} \left(\frac{n_{xi}^2 f^{4/3}}{f^2 L_x^2} + \frac{n_{yi}^2 f^{-2/3}}{L_y^2} + \frac{n_{zi}^2 f^{-2/3}}{L_z^2} \right) f^{2/3} (L_x L_y L_z)^{2/3} = \frac{h^2}{12m_0} \sum_{i=1}^{N_A} \left(\frac{n_{xi}^2}{L_x^2} + \frac{n_{yi}^2}{L_y^2} + \frac{n_{zi}^2}{L_z^2} \right) (L_x L_y L_z)^{2/3}, \quad (14)$$

which, via the comparison with Equation 11, indeed shows the constancy of the product $PV^{5/3}$ in such an adiabatic transformation.

Analogously, one can derive the constancy of $PV^{5/3}$ for the transformation of the size of a container along the y - and z -axes⁴.

Further, we have to interpret the quantum numbers n_{xi} , n_{yi} and n_{zi} , and the sizes L_x , L_y and L_z in the *rhs* of Equation 14, as the ‘initial parameters’ of the ideal gas confined in the container at the given initial temperature T_0 . Any further adiabatic transformation of the ideal gas

³ Here we have to remember that both the initial and the final sets of quantum numbers must be presented by the integers, in order to keep the boundary condition of the vanished wave function on the walls of the container. This means that the coefficients ε_{ij} cannot be presented, in general, by continuous functions. However, the quantum numbers are huge for an ideal gas confined in a macroscopic container near the room temperature and thus, we can easily overlook the mentioned constraint of non-continuity on the coefficients ε_{ij} .

⁴ The general case of a non-uniform transformation of a container in all three dimensions simultaneously can be processed as a succession of corresponding non-uniform transformations in each dimension with application of Equation (13).

keeps the constancy of $PV^{5/3}$, in full agreement with the classical result. Thus, the “Constant” of the adiabatic transformation can be written in the form:

$$Constant = \frac{h^2}{12m_0} \sum_{i=1}^{N_A} \left[\frac{n_{xi}^2(T_0)}{L_x^2(T_0)} + \frac{n_{yi}^2(T_0)}{L_y^2(T_0)} + \frac{n_{zi}^2(T_0)}{L_z^2(T_0)} \right] [V(T_0)]^{2/3}, \quad (15)$$

and any further adiabatic transformation of an ideal gas keeps the constancy of $PV^{5/3}$, in perfect harmony with the classical result.

Equation 15 fulfils our goal with regards to evaluating, in the general case, the constancy of the long lasting adiabatic transformation relationship, $PV^\gamma = Constant$, at the extension of what was done (Yarman et al., 2010). We have indeed come to obtain not only this classical relationship via non-relativistic quantum mechanics, geared to the classical definition of ideal gas, but we also obtained the specific value of the constant (the *rhs* of Equation 15); we further disclosed the pattern through which the quantum numbers of molecules must be modified, as expressed via Equations 12 and 13.

For the special case of a cube, the *rhs* of Equation 15 evidently becomes:

$$Constant_{cubic\ container} = \frac{h^2}{4m_0} \sum_{i=1}^{N_A} n_{ix}(T_0)^2 = N_A \frac{h^2 n(T_0)^2}{4m_0}, \quad (16)$$

where n pertains to the average molecule.

ADIABATIC TRANSFORMATION OF THE PHOTON GAS

The basic finding we proposed to provide here, is whether or not a photon gas would fulfill our disclosure about the adiabatic constancy of the quantity (*Pressure*) \times (*Volume*) $^\gamma$. We will subsequently see that it does. We will accordingly specifically calculate the constant coming into play in the law (*Pressure*) \times (*Volume*) $^\gamma = Constant$.

Thus, to simplify things, without any loss of generality (as we have seen), we consider once again, a cube of side L , containing just a single photon of frequency ν . The total energy E of it, is, as usual:

$$E = h\nu = mc^2 = \mathcal{A}c \quad (17)$$

where \mathcal{A} is the relativistic momentum mc of the photon. Let us first consider the x -component \mathcal{A}_x of it. The force F_x , that the photon exerts on the wall, is given as:

$$F_x = \frac{\Delta \mathcal{A}_x}{\Delta t} = \frac{2\mathcal{A}_x}{2L/c} = \frac{\mathcal{A}_x c}{L}. \quad (18)$$

Thus, the pressure p created by the given photon's hits the sides of the cube perpendicular to the x -direction is given as:

$$p = \frac{F_x}{L^2} = \frac{\mathcal{A}_x c}{L^3} = \frac{E}{V}. \quad (19)$$

As can be shown easily (Equation 10b), the same expression, as expected, is obtained for the pressure, the photon exerts on another side of the cube, along with the changes its related momentum component would experience through a bouncing process from this side. This, at the equilibrium state, in the cube of concern we get as:

$$p = \frac{\mathcal{A}c}{3L^3} = \frac{E}{3V}, \quad (20)$$

or

$$E = 3pV. \quad (21)$$

A photon, on the other hand, has altogether $3 \times 2 = 6$ degrees of freedom, that is, three components of momentum, along with two kinds (right handed or left handed) of circular polarization. Thus, at the given temperature T , one can write similarly to equation 10c:

$$E = 6 \frac{kT}{2} = 3kT. \quad (22)$$

This makes that for the photon, the specific heat c_V at constant volume becomes:

$$c_V = \frac{dE}{dT} = 3k. \quad (23)$$

In order to derive an expression for c_p (the specific heat at constant pressure), we recall the first law of thermodynamics, that is:

$$dE = \delta Q - pdV, \quad (24)$$

which expresses an increase of the total energy as much as dE , if an amount of heat δQ is received from the outside, upon which the constituent delivers to the outside the work pdV . At constant pressure, the first law of thermodynamics, based on equation 21, yields:

$$(\delta Q)_p = dE + pdV = 3pdV + pdV = 4pdV = \frac{4}{3}dE.$$

Hence, via Equation 22,

$$c_p = \left(\frac{\partial Q}{\partial T} \right)_p = \frac{4}{3} \frac{dE}{dT} = 4k, \quad (25)$$

which, via Equation 23, leads to the following equation:

$$\gamma = \frac{c_p}{c_v} = \frac{4}{3}. \quad (26)$$

Let us finally calculate the product pV^γ for the photon at hand, again, taking into account Equations 17 and 21:

$$pV^\gamma = pV^{4/3} = \frac{\Lambda_x c}{V} V^{4/3} = \Lambda_x cL, \quad (27)$$

where v , as conveyed, is the frequency of the photon of concern.

To proceed further, we note that via the de Broglie relationship we have:

$$\Lambda_x = \frac{nh}{2L}. \quad (28)$$

When this is inserted in Equation 27, then we obtain:

$$p_n V^{4/3} = \Lambda_x cL = \frac{nhc}{2L} L = \frac{nhc}{2}. \quad (29)$$

The generalization of Equation 29 for an arbitrary number N of (non-interacting) photons, confined inside a cube, that immediately follows, visualized the ‘average photon’:

$$P_{\bar{n}} V^{4/3} = N \frac{\bar{n}hc}{6}. \quad (30)$$

$P_{\bar{n}}$ stands for the overall pressure, and \bar{n} for the quantum number defined in the same way as that followed earlier, with regards to the ‘average photon’ at the n th energy level inside the three dimensional box.

Thence, we see that the product $P_{\bar{n}} V^\gamma$ is a constant, supposing evidently that N , the number of photons stays the same throughout (that is, there is no absorption of photons by the walls of the box).

Note here again, that the quantum numbers associated with particles are not affected if the adiabatic expansion takes place uniformly.

Conclusions

The fact that $PV^{5/3}$ stays constant through an adiabatic

transformation of an ideal gas derived practically in all books on thermodynamics (Kestin and Dorfman, 1971; Moore and Aberdam, 1955; Souchay, 1964) is based on the long lasting phenomenological description of the gas. However, the specific alphanumeric expressed the constant delineated by $PV^{5/3}$, if any, to our recollection, is something totally missed. As far we could see indeed, no one even seems to have wondered about the possible value of this constant.

In a previous work (Yarman et al., 2010), we had calculated this constant for an ideal gas confined in a *cube*, expanding uniformly, thus succeeding at the same time to establish an organic link between classical thermodynamics and quantum mechanics (Yarman et al., 2010), thus free of the classical quantity of temperature and the Boltzmann constant. The essence of our approach was to express the energy, entered in Equation 8 for the pressure exerted by just ‘one molecule’, through the quantum mechanical energy eigenvalue relationship, expressed by Equation 6. We are fully convinced that this is a warranted procedure, even if the molecule is confined inside a macroscopic recipient.

This way, we could derive the value of the constant delineated by the quantity $PV^{5/3}$ for the given average discrete energy level n related to the particle, no matter what, the number n might be huge for a macroscopic cube. Then the value of this constant is obtained via simple quantum mechanics and an ordinary averaging (Equation 10).

Although our derivation may still look somewhat simple for the case of a gas confined in a cube expanding adiabatically and uniformly; it is not so for a gas confined in a ‘parallelepiped’, expanding still adiabatically, but now ‘non-uniformly’. Thus, herein we were able to generalize our previous plain derivation, providing us with an interesting rule (Equation 13) about how quantum numbers are affected through a non-uniform adiabatic expansion (compression).

In this article, we have further extended our approach to the photon gas. Because, it is a question of a photon, the setup is, as expected, different than the one we have established previously. Nevertheless the result, ‘cast-wise’, is the same. In other words, the quantity pV^γ for a photon is i) a constant, and ii) nothing but $N\bar{n}hc/6$ (Equation 30).

Note that in our approach the classical temperature quantity drops off, together with the Boltzmann constant, suggesting the formulation of a new thermodynamics not embodying these two quantities, which will then be merely based on the Planck constant and quantum numbers, symbolizing the energy of the particle in consideration.

Recall that for an ideal gas, the exponent γ in all expressions of $(Pressure) \times (Volume)^\gamma$ is 5/3. It became 4/3 for the photon gas, though it still indicates the ratio of specific heats at, respectively constant pressure and

constant volume.

No matter what the dimensions of the constants in question are different from each other, it seems of course, striking that they are still rooted to universal constants, more specifically to h^2 and to hc , respectively. Interestingly, their dimensional ratio, that is, $[Volume]^{1/3} = [h]/[mc]$, points to the de Broglie relationship's cast.

We believe that the results presented herein have a general significance and show that the phenomenological laws for the ideal gas and for the photon gas can be interpreted as a macroscopic manifestation of quantum phenomena.

Thence any deviation from $PV^\gamma = Constant$ must mean that one then deals with something else than an ideal gas.

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