Full Length Research Paper

The classical adiabatic constancy of PV$^\gamma$ for an ideal gas as a quantum mechanical occurrence

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In this paper we find a connection between the long lasting macroscopic classical laws of gases and the quantum mechanical description of non-interacting particles confined in a box, thus constituting an ideal gas. In such a gas, the motion of each individual molecule can be considered to be independent of all other molecules, and the macroscopic parameters of an ideal gas, mainly, pressure *P* and temperature *T*, can be defined as simple average quantities based on individual motions of all molecules in consideration. It is shown that for an ideal gas enclosed in a macroscopic box of volume *V*, the constant γ appearing in the classical law of adiabatic expansion law, that is, $PV^\gamma = cons\tan t$, can be derived based on quantum mechanics. Physical implications of the result we disclose are discussed.

Key words: Adiabatic transformation, quantum mechanics, kinetic theory of gases.

INTRODUCTION

From time to time, most of us, no doubt, just like many scientists of the 20th century, were puzzled with the question of finding a link between the Boltzmann Constant *k* and the Planck Constant *h*. In particular, one can refer to the de Broglie doctorate thesis, where he brilliantly has applied his relationship (associating a wave length with the momentum of a moving particle) to the statistical equilibrium of gases (de Broglie, 1925), but did not advance his idea, to see whether one can along such a line, obtain anything related to the law of gases, established long ago, in 1650. At the second half of the past century a possible relationship between *k*, *h* as well as the light velocity in vacuum *c* has been explored in details by Dannenhower (Dannenhower, 1977). However, he concluded that the existence of a solution is not evident; thus according to him the issue remains unresolved. We will see below that this is actually a vain effort.

Let us assume that the gas is made of just one kind of molecule. The Boyle-Mariotte law of ideal gas is given as usual by

$$PV = n_m RT = kNT \qquad (1)$$

where *P* is the pressure of the gas, *V* the volume of the gas, *T* the temperature of the gas, n_m the number of *moles* the gas is made of, *N* the number of molecules making the gas, *R*= 8.31 J/K is the gas constant,

$$k = R / N_A \qquad (2)$$

is the Boltzmann constant, and N_A the Avagadro number.

The kinetic theory of gases allows us to derive the same casing as that of Equation (1) via considering the momentum change of each molecule separately, when bouncing back from a wall of the given container (Halliday et al., 1997). Assuming for simplicity a cubic geometry, one obtains through simple averaging:

$$PV = \frac{N}{3} m \overline{v^2} = \frac{2}{3} N \overline{E} \ , \qquad (3)$$

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where $\overline{E} = m\overline{v^2}/2$ being the average translational energy of molecules of mass m.

For the sake of completeness, let us recall the classical derivation of Equation (3). The force f_x exerted by the molecule of mass m and velocity $\mathbf{v}\{v_x, v_y, v_z\}$ on the wall in the plane yz, is given by Newton's second law $f_x = -\Delta p_x/\Delta t$, where $\Delta p_x = -2mv_x$ is the algebraic increase in the momentum, whilst the molecule bounces back from the wall, and $\Delta t = 2L/v_x$, L being the size of the container along the x-direction. Thus one has $f_x = mv_x^2/L$. We can suppose that we deal with an average molecule, and all molecules behave as this average molecule in the ideal gas. Hence, summing over N molecules the gas is made of, we get the total force

$F_x = N\dfrac{m\overline{v_x^2}}{L} = \dfrac{N}{3}\dfrac{m\overline{v^2}}{L}$, where the mean square velocity can be assumed to have the same value for each molecule at the equilibrium. The pressure P exerted by N molecules on the wall of concern, is thence

$$P = \frac{N}{3}\frac{m\overline{v^2}}{L^3} ,$$

which is Equation (3), along with $V=L^3$.

Now comparing Equations (3) and (1), one as usual derives

$$\overline{E} = \frac{3}{2}kT . \tag{4}$$

Furthermore, Equation (3) can naturally be written for the pressure p that would be built in a volume V, containing just one molecule of translational energy E :

$$pV = kT = \frac{2}{3}E , \tag{5}$$

given that we have started our derivation, based on just one molecule, before we achieved a subsequent averaging.

Now, exploring a possible relationship between the laws of ideal gases and quantum mechanics and supposing the discrete energy levels for each individual molecule (no matter how large the principal quantum number n in the classical limit), one may ask the following questions:

i) Could Equation (3) be the basis for building a bridge between thermodynamics, mainly characterized by the Boltzmann constant, and quantum mechanics, basically the energy quantity $\overline{E}$ averaged over the discrete energy states of all molecules?

ii) More specifically can Equation (3) be the basis for building a bridge between k and the Planck constant h?

Here though, while the equality $pV = kT$ points to the law of gases, the next equality $kT = (2/3)\overline{E}$ of Equation (5), is no more than a definition of temperature in terms of the average translational energy $\overline{E}$ of the molecules, once k is defined via Equation (2). So $kT = (2/3)\overline{E}$ does not in fact provide us with any relationship between k and h.

In other terms, $\overline{E}$ is to be expected to involve the Planck constant, yet this, does not allow us to coin a relationship between h and k, based on Equation (5), and hence with this equation we are bound to fail to establish a relationship between macroscopic properties of an ideal gas and the quantum mechanical description of its molecules.

Thereby we find out that, when we propose to draw a bridge between the phenomenological laws of gases and quantum mechanics, we should not really look for a relationship between h and k. Any such effort will be dissolved through a plain definition of the temperature, in terms of the average translational energy of the molecules, and nothing beyond. However, we can still go ahead to check whether the phenomenological laws of gases could be matched with quantum mechanics, if we could explore those laws of gases, which do not involve the constants R or k. That is the key point of our approach.

CONSTANCY OF PV$^\gamma$ FOR AN ADIABATIC TRANSFORMATION: QUANTUM APPROACH IN SEMICLASSICAL LIMIT

There is, in effect, a relationship satisfying the criteria we have just set; this is the one describing an adiabatic transformation of gases in a wide temperature range, that is,

$$PV^\gamma = constant , \tag{6}$$

obtained in the familiar way based on the laws of gases, considered together with the first law of thermodynamics (Sommerfeld, 1964), along with the usual definition

$$\gamma = C_P/C_V . \tag{7}$$

Here C_V is the heat to be delivered to one mole of an ideal gas at constant volume to increase its temperature

as much as 1K, and C_P is the heat to be delivered to one mole of an ideal gas at constant pressure to increase its temperature till as much as 1K.

For an ideal gas, the internal energy levels of molecules are not excited by definition. In such a case (Van Wylen and Sonntag, 1985) we have

$$C_V = 3R/2,\qquad(8)$$

$$C_P = 5R/2,\qquad(9)$$

and the constant γ in Equation (7) turns to be equal to

$$\gamma = 5/3.\qquad(10)$$

Hence Equation (6) acquires the form

$$PV^{5/3} = constant.\qquad(11)$$

Any reader in the field knows that the derivation of this latter relationship is presented in any related text book.

Haar and Wergeland (1960) suggested a different derivation of Equation (11) based on the fact that the single-particle energy E of a mono-atomic, non-relativistic, diluted gas is proportional to $V^{2/3}$, that is,

$$E \sim V^{-2/3}.\qquad(12)$$

To show this, they write the energy of a single particle in the ith atom as $\varepsilon_i = V^{-2/3} \cdot f_i$, where f_i is some function of quantum numbers and particle mass for the ith particle. Involving the adiabatic theorem of quantum mechanics (which implies the constancy of f_i under slow variation of the volume), they straightforwardly arrive at Equation (12)

Furthermore Haar and Wergeland noticed that the internal energy of one mole of gas can be written in the form

$$\overline{E} = N_A E.\qquad(13)$$

Combining Equations (12) and (13), one obtains:

$$\overline{E}V^{2/3} = constant.\qquad(14)$$

One can additionally write, as usual (cf. Equation (1)),

$$PV = RT,\qquad(15)$$

and via Equation (4), we further derive

$$\overline{E} = \frac{3}{2}PV.\qquad(16)$$

If we now multiply the two sides of this latter equation by $V^{2/3}$, and use the constancy delineated by Equation (14), we arrive at

$$PV^{5/3} = constant,\qquad(17)$$

which is Equation (6), written for the ideal gas.

One should mention that the derivation of Equation (6) proposed in Sommerfeld (1964) is of a general character, and, in particular, does not assume a classical limit. However, neither Equation (6) usually provided by text books, nor Equation (17) obtained by Haar and Wergeland, did tell us, what the "adiabatic constant" on the *rhs* of these equations, specifically is. Moreover, at the moment nobody seems to have even asked what could be the particular alphanumeric expression of this constant, if any.

Our goal thus becomes to derive specifically an expression for this "adiabatic constant", which is worth stressing - still remains classically unknown, by means of a quantum mechanical description of the ideal gas, being applied to the semi-classical limit. This implies that a principal quantum number for any given molecule can be very large, but it does not create any conceptual difficulties. At the same time, it is important that in this limit we can use the standard classical phenomenological laws for the ideal gas without any limitations.

In our further approach, as emphasized, it is essential that the ideal gas is made of non-interacting molecules, each behaving as a simple quantum mechanical particle locked up (potential energy – wise) in an infinitely high box. The wave functions of such non-interacting molecules are not mixed, and thus the internal energy of the ideal gas can be found as a simple sum of eigenvalues of energy for each molecule. Besides, along with the kinetic theory of gases to be valid in the classical limit, we well assume that the Boyle Mariotte law (1) holds for even one molecule. That is, if R is replaced by the Boltzmann constant k, in these equations, then one lands at $c_v = (3/2)k$, $c_p = (5/2)k$, defined for just one molecule. This means we can confidently use the ratio C_p/C_v or the same, the ratio c_p/c_v in the quantum world. It means, in particular, that the expression (10) is well applicable to the one molecule, that is, to a particle in a box.

Let us thus consider a particle of mass m at a fixed internal energy state located in a macroscopic cube of side L. Herein we will consider the non-relativistic case. Our approach however can be extended to the relativistic case with no difficulty. The non-relativistic Schrödinger equation furnishes the energy E_n of the particle in the box at a given energy level, that is,

$$E_n = \frac{h^2}{8m}\left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}\right) = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2},\qquad(18)$$

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

For an ideal gas, the "potential energy" within the box is null. Thus we have

$$E_n = mv_n^2/2, \tag{19}$$

with v_n being the velocity of the particle at the nth energy level.

At the given energy level, the pressure p_n exerted by just one particle on either wall, becomes (cf. Equations (3) and (5))

$$p_n = \frac{mv_n^2}{3L^3} = \frac{2}{3}\frac{E_n}{L^3}. \tag{20}$$

Now let us calculate (for just one particle) the product $p_n V^{5/3}$:

$$p_n V^{5/3} = \frac{2}{3}\frac{\frac{h^2\left(n_x{}^2 + n_y{}^2 + n_z{}^2\right)}{8mL^2}}{L^3}\left(L^3\right)^{5/3} = \frac{h^2\left(n_x{}^2 + n_y{}^2 + n_z{}^2\right)}{12m}. \tag{21}$$

Hence this quantity indeed turns out to be a constant for a given particle of mass m at the given energy level, characterized by the principal quantum numbers n_x, n_y and n_z.

Recall that the total energy E_n of Equation (18) ultimately determines the quantized velocity v_n of Equation (19).

When it is a question of many particles instead of just one, normally we would have particles, in general, at different quantized states. This means that we deal with some energy distribution of molecules at the given temperature, instead of the fixed eigenvalue, Equation (18) derived for a gas consisting of a single molecule.

In order to describe the distribution of energy over the molecules within an elaborated quantum mechanical approach, we have to abandon the strict ideal gas approximation, and add to the Schrödinger equation coming into play, a potential energy term responsible of the weak interaction of molecules, which will randomly affect all of the molecules of gas at each fixed temperature. We have to recall 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. For our immediate purpose, it is sufficient to take into consideration an "average

molecule" at the given temperature T. We can, as conveyed, well visualize the average molecule as a single particle, obeying Equation (21), thus situated at the nth level, and of course associate the given temperature with this energy, along with Equation (4).

Not to complicate things, let us get focused on the average particle, and simply suppose that all others behave the same. Furthermore, all three components of the average velocity at equilibrium are expected to be the same. Thus we can rewrite Equation (21) for the macroscopic pressure P_n exerted at the given average state n by one mole of gas on the walls of the container:

$$P_n V^\gamma = N_A \frac{h^2 n^2}{4m}. \tag{22}$$

Rigorously speaking, one must write

$$P_n V^\gamma = \sum_{i=1}^{N_A} \frac{h^2\left(n_{ix}{}^2 + n_{iy}{}^2 + n_{iz}{}^2\right)}{12m} = N_A \frac{h^2 \overline{n^2}}{4m}, \tag{23}$$

along with the definition

$$\frac{1}{3N_A}\sum_{i=1}^{N_A}\left(n_{ix}{}^2 + n_{iy}{}^2 + n_{iz}{}^2\right) = \overline{n^2}. \tag{24}$$

Thus it becomes clear that, if all particles bared the same set of quantum numbers, each with equal quantum numbers along all three directions, that is, $n_x = n_y = n_z = n$,

then $n = \sqrt{\overline{n^2}}$

Equation (22) does disclose the constant involved by Equation (6). Note that at the average state n (that is, at the given temperature), the mean square speed of the gas molecules is v_n^2. The average energy is furnished accordingly, via the framework of Equation (19). Let us calculate what would n be for 1 mole of H_2, delineating the pressure of 10^5 Pascal (1 atmosphere), in a volume of 1 m^3. From Equation (22) we obtain:

$$n \cong \sqrt{\frac{10^5 \times 4 \times 2 \times 1839 \times 0.9 \cdot 10^{-30}}{6.023 \times 10^{23} \times 6.62^2 \times 10^{-68}}} \approx 7 \times 10^{10}. \tag{25}$$

Thus our result indicates that the behavior of an ideal gas is nothing, but a macroscopic manifestation of quantum mechanics. In particular, the constancy of PV^γ happens to be rooted to quantum mechanics, and seems to be

deep. It is such that the quantity "mass $\times$ PV^{γ}" turns out to be a Lorentz scalar.

Therefore, we expect this scalar to be somehow nailed to a Lorentz invariant universal constant; this constant, more specifically, turns out to be the square of the Planck constant. Accordingly, for a given mass m, the quantity PV^{γ} relates to h^2/m; this is what we have revealed in this paper. Henceforth:

The constancy of PV^{γ} appears to be an extension of quantum mechanics to macroscopic scales, but even more essentially it delineates how the internal dynamics displayed by a gas consisting of quantum mechanical particles made of a given mass is organized in conjunction with the size of the container, the dynamics in question takes place in, and this universally, at all scales (Yarman, 2004a, b). Here we will not go in any further details of this fundamental problem.

We should like to note that Equation (6) is not a relativistic equation anyway. That is, if ever the constituents of the gas move at speeds, which cannot be neglected as compared to the speed of light, then it is not anyway a valid relationship, and it should be replaced, as insinuated by Equations (21) and (22), by

$$\left(\gamma m c^2\right)PV^{\gamma} = constant,\qquad(26)$$

where γ is the Lorentz factor, and γm the relativistic mass of the average particle.

Note further that the above relationship well holds for a photon gas, and we spare the discussion of these interesting points for a future work.

CONCLUSION

In this article we aimed to bridge classical thermodynamics and quantum mechanics. Though we have determined that toward that aim, it is in vain to look for a relationship between Boltzmann constant k and Planck constant h. Indeed, a relationship involving both k and h, such as Equation (5), is nothing more than a definition of say, the temperature, in terms of the translational energy of the particle in hand (see the discussion we provided below Equation (5)). Thus we have chosen on purpose the relationship $PV^{5/3} = constant$ to work with, because it constitutes distinctively a closed form of basic gas relationships, which does not involve the Boltzmann constant.

To avoid possible confusions, let us stress that, our goal was not of course, to show that $PV^{5/3}$ remains constant through an adiabatic transformation; this is evidently a classical relationship. Our goal was to calculate this particular constant, which remained obscure up till now. In the present contribution we have solved this

problem based on quantum mechanics, applied in the semi-classical limit, thus establishing a new link between classical thermodynamics and quantum mechanics in the description of an ideal gas.

The particular value of the constancy of PV^{γ} (Equation (22)) is something totally missed over almost a century in the literature. The whole thing, in fact, is rooted to an intuition, the first author had developed elsewhere (Yarman, 2004a, b, 2009). In other terms, the constancy of PV^{γ} (and, likewise, the frame drawn by the law of gases) seems to be deep, in relation to the fact that the quantity "mass $\times$ PV^{γ}" turns out to be a Lorentz scalar, which must further be in natural harmony with quantum mechanics. Such a universal property, may well allow us to state that the quantity "mass $\times$ P $\times$ (Appropriate volume)$^{\gamma}$", in general, is nailed to the square of the Planck constant; under any circumstances, the volume in question, is being eventually made of the mean free path of a constituent of the gas at hand.

It is also important that Equation (22), being obtained in the semi-classical limit, is in practice well applicable to any ordinary rarefied room-temperature gas, where this equation may well be tested experimentally.

Concurrently we should point out that Equation (22), in general, cannot be applied to low-temperature gases, when their quantum properties become dominant. In such a case the law of adiabatic transformation of such a quantum gas should better be handled via the relationship (cf. Landau and Lifshits, 1981)

$$p = -\frac{\partial H}{\partial q}\frac{1}{S},\qquad(27)$$

where H is the Hamiltonian of quantum particle confined in a container, q stands for the spatial coordinate (x, y or z), and S is the area of the wall of container orthogonal to the coordinate q. Note yet that for the case we handled, the energy of any particle (not interacting with another one, whatsoever), is constant throughout. And the peculiarity drawn by Equation (27) becomes needless.

In addition, one should distinguish between Fermi-gas and Bose-gas, a problem, which can however be overlooked for the case of a semi-classical ideal gas, we have undertaken herein. We only notice that taking into account the exchanged energy through interactions (which we did not have to deal with, herein) requires re-defining the notion of ideal gas, in a quantum mechanical perspective. The analysis of these problems, from the stand point we painted over here, is postponed for a future work.

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