



Second law of thermodynamics is ingrained within quantum mechanics

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ARTICLE INFO

Keywords:

Entropy

Classical thermodynamics

Quantum mechanics

ABSTRACT

We show that the second law of thermodynamics is rooted in quantum mechanics, inasmuch as allowing the substitution of the Boltzmann constant k and temperature with respectively the Planck constant and quantum numbers. In particular, we will see that the entropy S becomes proportional to the natural logarithm of the average of the squared quantum numbers $\overline{n^2}$, where each quantum number is associated with a quantum state of the constituents of the thermodynamical system under consideration. It is important to stress that the present approach furnishes the corrected Boltzmann entropy expression. Thus, instead of $S = k \ln \Omega$, with Ω in the former signifying the number of Boltzmann microstates, we land at $S = k \ln \overline{n^2}$. The results obtained are discussed.

Introduction

In the present paper, we will show that the second law of thermodynamics can be understood in terms of a quantum mechanical description of the behavior of the ideal gas on the basis of an approach we introduced previously [1–4].

As is known, both the first and the second laws of thermodynamics plays a principal role in our understanding of the behavior of thermodynamical systems [5–7]. The first law of thermodynamics, briefly speaking, is the “law of energy conservation”. This law states that, should a very small amount of heat δQ delivered to a given system – such as an “ideal gas imprisoned in a cylinder” – and the system subsequently effectuates a very small amount of work δW to the outside (say, via outwardly pushing a piston situated at the upper base of the cylinder filled by the gas), then the internal energy U of the system will be increased on the whole as much dU ; i.e.,

$$dU = \delta Q - \delta W. \quad (1)$$

We remind that δQ and δW are not, in general, total differential quantities (meaning, they are path-dependent, i.e. they are reliant on the manner followed to achieve the given processes), while dU represents a total differential, i.e., it is path-independent.

Let us add that the internal energy U of the ideal gas consisting of N_A molecules can be presented as the product of an average kinetic energy \overline{K} of the given molecules and the number of these molecules; i.e.,

$$U = N_A \overline{K}. \quad (2)$$

It is common practice to take N_A as the Avogadro’s number, so that we deal with one mole of molecules.

One more way to express the internal energy U is based on the notion of temperature T , and the link between U and T is established via the Boyle and Mariotte law [7]; i.e.,

$$PV = nRT, \quad (3)$$

where R is the gas constant, and n is the number of moles the gas at hand embodies.

Based on the kinetic theory of gases [8], we can now bridge U and T by first writing for one mole of gas

$$PV = (2/3)U, \quad (4)$$

and then by considering the equivalent expression

$$RT = (2/3)U. \quad (5)$$

The number 2 in the numerator of the fraction 2/3 right above comes from the expression of the non-relativistic kinetic energy K written for one molecule bearing the mass m and the velocity v , by virtue of the classical mechanics formula $K = (1/2)mv^2$; whereas, the number 3 in the denominator of the fraction points to the three spatial components of the velocity vector, which are expected to be equal to each other for the average velocity the molecules delineate.

Further, we take into account that the internal energy U depends on

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just one parameter – i.e., the temperature T [9]. Accordingly, dU of Eq. (1) can be expressed for one mole of gas as

$$dU = C_v dT, \tag{6}$$

where the quantity C_v is the energy to be furnished to one mole of gas occupying a constant volume in order to increase its temperature by 1°K. As a first undertaking, we assume C_v to be a constant (even though, in the derivation we will offer below, we do not really have to make such an assumption, given that we will operate with just U instead of T).

Next, we retrieve δQ from Eq. (1):

$$\delta Q = dU + \delta W. \tag{7}$$

The work δW , on the other hand, is as usual

$$\delta W = PdV. \tag{8}$$

Therefore, we can rewrite Eq. (7) as

$$\delta Q = C_v dT + PdV. \tag{9}$$

We next divide it by T :

$$\delta Q/T = C_v dT/T + PdV/T, \tag{10}$$

and use Eq. (3) to rephrase it as

$$\delta Q/T = C_v dT/T + RdV/V. \tag{11}$$

Since the rhs of the above equation constitutes a total differential, so too must the lhs $\delta Q/T$; which we shall now call dS . It can be integrated from an initial state (i) up to a final state (f):

$$\int_i^f dS = S_f - S_i = \int_i^f \frac{\delta Q}{T} = \int_i^f C_v \frac{dT}{T} + \int_i^f R \frac{dV}{V}, \tag{12}$$

which leads to

$$\Delta S = \int_i^f \frac{\delta Q}{T} = C_v \ln\left(\frac{T_f}{T_i}\right) + R \ln\left(\frac{V_f}{V_i}\right); \tag{13}$$

where we demarcate

$$\Delta S = S_f - S_i. \tag{14}$$

The function S is the *classic entropy*; and the latter two equations express its variation between the final state f and the initial state i of concern. Henceforth T_f , V_f and T_i , V_i stand for temperatures and volumes at respectively the final and the initial states.

In light of the total differential characteristic, we can straightforwardly write for a fully reversible closed cycle

$$\oint \frac{\delta Q}{T} = 0. \tag{15}$$

This is basically the classic second law of thermodynamics for reversible processes; and we recall that one could arrive at it via merely the law of ideal gases upon embarking from the first law of thermodynamics.

The first law of thermodynamics – i.e., Eq. (1) – can similarly be written thus for a closed cycle as

$$\oint dU = 0. \tag{16}$$

Nothing new is advanced up to this point; we had reminded the foregoing information for the sake of completeness and convenience for the reader with regards to the upcoming presentation.

In Section “*Second law of thermodynamics and the quantum mechanical description of gases*” we introduce a quantum mechanical framework for the second law of thermodynamics based, particularly, on the quantum mechanical expression of the classical *adiabatic constancy* of *Pressure* \times *Volume*^{5/3} obtained from the laws of gas and the first law of thermodynamics, where the *constant* coming into play can be evaluated via non-relativistic or relativistic quantum mechanics (QM) [1–4]. Finally, in Section “*Discussion*”, we discuss the results obtained.

Second law of thermodynamics and the quantum mechanical description of gases

At this stage, we introduce our novel approach. Thus, via referring to the first law of thermodynamics (9), we combine it with Eq. (7) and divide both sides of the outcome by U (thus replacing the temperature T with the internal energy U as the important step in the realization of our approach):

$$\delta Q/U = dU/U + PdV/U. \tag{17}$$

We may further use Eq. (3) along with Eq. (5) to arrive at:

$$\delta Q/U = dU/U + (2/3)dV/V. \tag{18}$$

Here again, as long as the rhs constitutes a total differential, so must the lhs $\delta Q/U$ (i.e., “the infinitesimal heat input over the total internal kinetic energy of one mole of gas”), which we designate below as dS .

Eq. (18) can be integrated from an initial state (i) up to a final state (f):

$$\int_i^f dS = S_f - S_i = \int_i^f \frac{\delta Q}{U} = \int_i^f \frac{dU}{U} + \int_i^f \frac{2}{3} \frac{dV}{V}, \tag{19}$$

which leads to

$$\Delta S = \int_i^f \frac{\delta Q}{U} = \ln\left(\frac{U_f}{U_i}\right) + \ln\left(\frac{V_f}{V_i}\right)^{2/3}, \tag{20}$$

where we designated

$$\Delta S = S_f - S_i. \tag{21}$$

Here, U_f and U_i stand for the internal energies of one mole of gas under consideration at the given final and initial states respectively. Similarly, V_f and V_i are respectively the volumes of the gas at the given final and initial states.

It is clear that S corresponds to the classic entropy S divided by the Boltzmann constant k ; and just for the purpose of distinction, we will denominate it as “*sentropy*”. In such a way, “*sentropy*” is still a measure of “*disorder*” like classic entropy is.

Based on the sentropy function S , and for a closed and entirely reversible cycle, we can write:

$$\oint \frac{\delta Q}{U} = \oint dS = 0, \tag{22}$$

which can be considered as an expression for the second law of thermodynamics that incorporates the sentropy function.

Further, we can explicitly write the function S as referred to a “reference quantity” S_{Ref} :

$$S - S_{Ref} = \int_i^f \frac{\delta Q}{U} = \ln\left(\frac{U}{U_{Ref}}\right) + \ln\left(\frac{V}{V_{Ref}}\right)^{2/3} = \ln\left(\frac{UV^{2/3}}{U_{Ref}V_{Ref}^{2/3}}\right), \tag{23}$$

where the subscript “_{Ref}” signifies the “given state of reference”, while the quantities U and V refer to the actual state the system assumes.

Let us further use Eq. (4) to present Eq. (23) in the equivalent form

$$S - S_{Ref} = \ln\left[\frac{\left(\frac{3}{2}PV\right)V^{2/3}}{\left(\frac{3}{2}P_{Ref}V_{Ref}\right)V_{Ref}^{2/3}}\right] = \ln\left(\frac{PV^{5/3}}{P_{Ref}V_{Ref}^{5/3}}\right). \tag{24}$$

We would like to recall that the combination $PV^{5/3}$ is classically coined as a *constant quantity* under an *adiabatic transformation*, though its particular value (C) had remained undetermined since a long time in the classical approach. So it was evermore considered as an *adiabatic-transformation-invariant* rather than bearing anything special.

Whereas, we have recently shown that the given constant can well be evaluated within the framework of QM [1–4]. Accordingly, as a first approximation, we consider the molecules of gas as non-relativistic non-interacting particles confined in a box of a macroscopic size (e.g., that of a gas container), and solve the corresponding Schrödinger

equation. In particular, for N molecules enclosed in a cube (for simplicity's sake, but without any loss of generality), the constant of concern had been revealed to be [1–4]:

$$C = \frac{h^2}{12m} \sum_{i=1}^N (n_{xi}^2 + n_{yi}^2 + n_{zi}^2). \tag{25a}$$

Here h is the Planck constant, and m the mass of the molecule of the gas. We have to stress the fact that, even in a cubic geometry, each state is normally characterized by the three quantum numbers n_x , n_y and n_z . We anticipate that each molecule would occupy a given set of the three quantum numbers n_x , n_y , and n_z , and normally we would have N such sets.

In order to simplify the notation, we call n_i^2 the summation of the squared quantum numbers in question:

$$n_i^2 = n_{xi}^2 + n_{yi}^2 + n_{zi}^2, \tag{25b}$$

no matter whether or not n_i^2 may be an integer square. Note that n_i^2 is proportional to the total quantum mechanical energy of the molecule situated at the given state [1–4]. Note further that we do not necessarily have to have $n_{xi} = n_{yi} = n_{zi} = 1$ for $i = 1$; on the contrary, the quantum numbers for the lowest and highest energy states are determined by temperature; i.e. the average of n_i^2 .

We now rewrite Eq. (25a):

$$C = \frac{h^2}{12m} \sum_{i=1}^N n_i^2. \tag{25c}$$

In any case, the rhs of Eq. (25a) for an adiabatic transformation indeed stays as a constant, given that the quantum numbers of concern will not get changed throughout such a transformation. In other words, the temperature of the gas under those circumstances will increase (for an adiabatic compression), or decrease (for an adiabatic expansion) with respect to a change of volume, whereas its molecules will remain at their original quantum levels [3].

Note that our approach is not restricted to a cube at all, and can well be generalized to a rectangular parallelepiped [3], and therefore to any other geometry, too.

Eq. (25a) directly establishes the bridge between QM and thermodynamics. While it is true that $PV^{5/3} = \text{Constant}$ is classically derived with respect to an adiabatic transformation, it is at the same time true that the relationship

$$PV^{5/3} = \frac{h^2}{12m} \sum_{i=1}^N n_i^2 \tag{25d}$$

can evidently be considered to hold for any gas at rest, as a whole, and be characterized as a new “system equation”.

While the rhs of the above equation remains constant throughout an adiabatic transformation as mentioned, this is not generally the case, and is in effect shaped by the internal properties of the system at hand.

Henceforth Eq. (25d) becomes the quantum mechanical root of the second law as framed by Eq. (24).

One could wonder how the temperature of the gas, at rest as a whole, can now be determined. The temperature is linked to the average energy of molecules via the Boltzmann constant, while the average energy of molecules is given by the average of n_i^2 . That being the case, the higher the temperature, the greater the quantum numbers appearing in Eq. (25b) for a given volume. In contrast, as mentioned, they stay the same throughout for an adiabatic transformation regardless of the fact that the volume the gas occupies varies together with its pressure (thereby fulfilling the relationship $PV^{5/3} = C$). In short, this latter relationship, where C is coined by Eq. (25c), furnishes a general description of the given gas at rest as a whole, and constitutes a complete quantum mechanical scaffold at any “given particular status” the system should assume.

Under the given circumstances, the sentropy quantity \mathbf{S} , as referred

to the reference sentropy \mathbf{S}_{Ref} , along with the self-explanatory additional notations, becomes

$$\mathbf{S} - \mathbf{S}_{Ref} = \ln \left(\frac{\frac{h^2}{12m} \sum_{i=1}^N n_i^2}{\frac{h^2}{12m} \sum_{i=1}^N n_{iRef}^2} \right) = \ln \left(\frac{\sum_{i=1}^N n_i^2}{\sum_{i=1}^N n_{iRef}^2} \right). \tag{26}$$

Let us call $\overline{n_{Ref}^2}$ the average of the squared quantum numbers at the reference state. This is directly linked to the average energy of the molecules at this state.

At the same time, let us call $\overline{n^2}$ the average of the squared quantum numbers pertaining to the “overall status” the system of concern assumes, which is directly linked to the average energy of the molecules at the given status. We can, accordingly, simplify Eq. (26) as

$$\mathbf{S} - \mathbf{S}_{Ref} = \ln \left(\frac{N_A \overline{n^2}}{N_A \overline{n_{Ref}^2}} \right) = \ln \left(\frac{\overline{n^2}}{\overline{n_{Ref}^2}} \right). \tag{27}$$

Further, we can choose the reference state practically with $T = 0$, and simultaneously infer in tandem that this reference state is characterized with the lowest average quantum number – i.e., *unity* (e.g., molecules of Helium-4 at a very low temperature and very low pressure confined in a macroscopic container). Therefore,

$$\mathbf{S} - \mathbf{S}_{Ref} = \ln(\overline{n^2}) - \ln(\overline{n_{Ref}^2}) = \ln(\overline{n^2}) - \ln(1) \tag{28}$$

Via correlating \mathbf{S}_{Ref} with $\ln(1) = 0$, we can finally write

$$\mathbf{S} = \ln(\overline{n^2}) \tag{29}$$

with regards to the “overall status” of the system we are dealing with.

Remarkably, the sentropy \mathbf{S} we introduced exactly corresponds to the natural logarithm of the “average of squared quantum numbers”; where each integer quantum number is associated with a constituent of the thermodynamical system under consideration. On top of this, one does not even have to bother with what kind of energy distribution governs the system under scrutiny to write the above equation, nor does one need to take into account which quantum numbers the constituents of the system exhibit. When everything is taken into consideration, it may just as well be a question of a classical Boltzmann distribution, or a Maxwellian distribution [10], etc., and this really does not matter for the present derivation. In any case, the determination of energy distribution within the framework of the present approach is a very interesting problem, and we propose to deal with it elsewhere.

Whatever the case may be, the relationship (29) holds valid. We could furthermore discern that \mathbf{S} is independent of the number of molecules the system is composed of. In other words, what counts as important is just the average of the squared quantum numbers coming into play, no matter how many of these there may be.

Nevertheless, one still has to be able to show that Eq. (29) is somehow related to the classical Boltzmann relationship, i.e.,

$$\mathbf{S} = \ln(\overline{n^2}) = S/\mathcal{K} = \ln(\Omega), \tag{30}$$

where Ω is, as known classically, the “number of microstates” the system delineates.

Recall that the Boltzmann entropy expression $S = k \ln(\Omega)$ is based on the Boltzmann distribution, which yet is only an approximate distribution; whereas, Eq. (29) has a more general character and does not depend on the choice of any concrete distribution.

Anyway, the average $\overline{n^2}$ is the straight average of the summation of squared N quantum numbers, so that

$$\overline{n^2} = \frac{1}{N} \sum_{i=1}^N n_i^2, \tag{31}$$

where N is the number of constituents making up the system.

Resuming from where we last left, Eq. (31) necessitates that

$$\overline{n^2} = \frac{1}{N} \sum_{i=1}^N n_i^2 = \Omega. \tag{32}$$

This means the average of the squared quantum numbers (each associated with a constituent making the system at hand) – i.e., consequentially the average energy of the constituents of the system – would be proportional to the number of Boltzmann microstates.

It is, most likely, not exact, and the reason is the following:

First of all, we can affirm that our expression of \mathbf{S} in Eq. (29) is exact. Whereas, Boltzmann’s entropy expression $S = k \ln(\Omega)$, is, as known, limited by the validity of the classical Boltzmann distribution.

As it so happens, the Boltzmann distribution constitutes only an approximation.

Henceforth, as a result of our quantum thermodynamics derivations, we are now entitled to jot down the corrected Boltzmann entropy formula:

$$S = k \ln(\overline{n^2}); \tag{33}$$

at which point, we can just as well write (cf. Eq. (32))

$$S = k \ln\left(\frac{1}{N} \sum_{i=1}^N n_i^2\right), \tag{34}$$

which represents the “exact Boltzmann equation” derived out of the present approach.

Discussion

Among known works in the area of quantum thermodynamics one can cite [11,12], where few tens of papers on the subject had been encapsulated. Nevertheless, it was seen that none of these studies appear to have achieved anything similar to what we have presented herein; i.d., the disclosing of the quantum mechanical roots of the second law of thermodynamics.

In this way, using the laws of gases, we first derived Eq. (21), where we introduced a dimensionless quantity named “sentropy” in the form of $\mathbf{S} = S/k$, which turned out to be nailed to $PV^{5/3}$ (Eq. (24)). This is the constant quantity (C) coming along with an adiabatic transformation; where we have deployed C in quantum mechanical terms (Eqs. (25a) and (25b)). Henceforth, entropy S and thereby the second law of thermodynamics becomes straightly grounded in QM [3].

We emphasize that, in the derivation of Eq. (25a), we applied the Schrödinger equation to each particle of gas confined in a closed container of a macroscopic scale; assuming that, in the ideal gas, the interaction between molecules of the gas can be neglected [1–4]. The known solution of the Schrödinger equation yields a set of discrete energy levels E_n for each particle confined in the container and characterized by a set of quantum numbers n_x, n_y , and n_z associated with the spatial directions x, y and z correspondingly; i.e.

$$E_n = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2} \right) = \frac{\hbar^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2}. \tag{35}$$

Based on Eqs. (24) and (25d), we obtain

$$PV^{5/3} = N_A \frac{\hbar^2}{12m} \overline{n^2}. \tag{36}$$

Let us hence work out the square root of $n^2 = \overline{n^2}$ in the above equation for 1 mol of H_2 , which delineates the pressure of 10^5 Pascal (1 atmosphere) in a volume of 1 m^3 . We thus get

$$n \cong \sqrt{\frac{10^5 \times 12 \times 2 \times 1839 \times 0.9 \times 10^{-30}}{6.023 \times 10^{23} \times 6.62^2 \times 10^{-68}}} \approx 1.2 \times 10^{11}. \tag{37}$$

As indicated in Ref. [3], our approach can be naturally extended from an ideal gas to a real gas via introducing into the Schrödinger equation a perturbation term, describing an interaction between molecules. In this case, we would obtain, in general, another set of

principal quantum numbers than for the ideal gas. However, this does not affect the validity of Eq. (25a) and subsequent equations derived on this basis; which thus have the general character and are applicable to any kind of gas, where the interaction between molecules, excepting their collision, can be considered small.

Assuming that \mathbf{S} takes the value of *null* at the lowest state, the above relationships – given that the average of squared quantum numbers at the given state is unity – finally leads to Eq. (29).

To formulate this latter equation, we did not even have to bother with what kind of energy distribution governs the system under scrutiny, nor did we need to take into account which quantum numbers the constituents of the system actually exhibit. When everything is taken into consideration, it may just as well be a question of a classical Boltzmann distribution, or a Maxwellian distribution, etc. Whatever the case, Eq. (29) would still remain valid – although, its calculation will certainly yield different results based on a given particular distribution.

We have moreover shown that the exact expression of entropy (34) formally coincides with the classical Boltzmann formula for entropy (30) at $\overline{n^2} = \Omega$ (see Eq. (32)), where Ω is the number of Boltzmann microstates the system assumes. We point out that the equality (32) is only an approximate one, given that the classical Boltzmann formula $\mathbf{S} = k \ln \Omega$, which is ultimately based on the classical Boltzmann distribution, constitutes an approximation too.

Thereby, we have, in effect, a new and exact formulation of entropy rooted in quantum mechanics (see Eqs. (33) and (36))

$$S = k \ln\left(\frac{4mPV^{5/3}}{N_A \hbar^2}\right), \tag{38}$$

written for one mole of gas.

We are, at this stage, ready to lay down the foundation for a quantum thermodynamics involving no temperatures, but energies and quantum numbers instead, and no Boltzmann constant, but just the Planck constant as delineated by Eq. (36). Recall that this latter equation becomes a universal gas equation rooted in QM, with its rhs remaining constant only in the case of adiabatic transformations.

Finally, it is important to enumerate the approximations we made. Our first assumption was that we overlooked any irreversibility, which would lead to the Clausius inequality instead of Eq. (15) [13]. We have worked with just one kind of constituent. With respect to an adiabatic transformation, we considered the formula $PV^{5/3} = \text{Constant}$, assuming that C_p/C_v (i.e., the ratio of specific heat under constant pressure to the specific heat under constant volume) is 5/3.

At the same time, we emphasize that the key relationship (25d) is of a universal character, and can further be straightforwardly recast into fully relativistic cases. At any rate, we were able to demonstrate herein the foundational steps for a natural symbiosis of the second law of thermodynamics with quantum mechanics.

Last but not the least, the present work can be extended readily to the case of irreversibility, allowing us to tap a complete second law of thermodynamics rooted in QM. But this topic is left for a future work.

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