**An ideal gas adiabatic process in thermodynamics and quantum mechanics**

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**Abstract:**

 An adiabatic process is considered from the perspective of thermodynamics (a process with no heat transfer) and quantum mechanics (a process in which the population of the different energy levels remains unchanged), and it is applied to the expansion of an ideal gas. This article shows that the population of the energy levels does not change if the expansion is quasi-static, although the particles in a certain energy level are rearranged among the different degenerate states. Also, the energy change of the system is calculated following the microscopic model (as a set of quantum particles in an infinite potential well) and a well-known thermodynamic result is recovered.

**Key words:** adiabatic process, particles in a box, energy level population

**1. Introduction**

 Thermodynamics and quantum mechanics are two very distinct subjects in the academic curriculum of a physicist. Thermodynamics is the quintessential phenomenological and macroscopic science, while quantum mechanics seeks to explain nature at an atomic and molecular level. Although it may seem strange to find them associated with one problem, that is the intention of this article. The goal here is to study what happens at a microscopic level when an ideal gas goes through an adiabatic process, and to recover known results of thermodynamics.

Regarding the structure of this article, it is organized in five sections. The rest of this introductory section is devoted to a careful analysis of the meaning of the term “adiabatic”. Section 2 will serve to review some knowledge of thermodynamics, statistical mechanics and quantum mechanics. As this article is meant to be educational, it is convenient to refresh the concepts needed to understand it. Then, sections 3 and 4 contain the analysis of an ideal gas that undergoes an adiabatic process. Finally, in section 5 the results are summarized.

 Adiabatic comes from a Greek word meaning “impassable”. In the case of thermodynamics, it means that there is no heat transfer between the system and the environment. However, authors do not completely agree on the use of the term. Landau and Lifschitz [1] define it thus: “*Let us suppose that a body is thermally isolated, and is subject to external conditions which vary* ***sufficiently slowly****. Such a process is said to be* adiabatic” (p. 39). For Huang [2]: “*Any transformation the system can undergo in thermal isolation is said to take place adiabatically*” (p. 5). And Callen uses the term adiabatic in the sense that there is no heat flow [Ref. 3, p. 17], the same as Swendsen [Ref. 4, p. 63]. Note that only Landau mentions the speed of the process.

 On the contrary, in quantum mechanics “adiabatic” means that there is no transfer among the different eigenstates of the Hamiltonian. In fact, the Hamiltonian changes so slowly over time that the system is always in an eigenstate. The assumption is that the probability of a state transitioning into another is very low and it becomes negligible. The concept was introduced in 1928 by Born and Fock, and in their own words: “*A physical system remains in its instantaneous* [*eigenstate*](https://en.wikipedia.org/wiki/Eigenstate) *if a given* [*perturbation*](https://en.wikipedia.org/wiki/Perturbation_theory_%28quantum_mechanics%29) *is acting on it slowly enough and if there is a gap between the* [*eigenvalue*](https://en.wikipedia.org/wiki/Eigenvalue) *and the rest of the* [*Hamiltonian*](https://en.wikipedia.org/wiki/Hamiltonian_%28quantum_mechanics%29)*’s* [*spectrum*](https://en.wikipedia.org/wiki/Spectrum_of_an_operator).” [5]

 Maybe the term “adiabatic” in quantum mechanics is closer to the term “quasi-static” used in thermodynamics. In this article, when we speak of adiabatic we are thinking of a process where there is no heat transfer, and which occurs in a quasi-static manner so that it is also isentropic, that is to say, we are adopting Landau and Lifshitz’s definition. However, a quick look into the literature is enough to notice that a process with no heat flow between the system and the environment is not necessarily reversible and isentropic [6].

 In short, it is necessary to distinguish between the usual sense of the term “adiabatic” in thermodynamics (with no heat transfer) and in quantum mechanics (sufficiently slow for the particles to remain in the same state), and to remember that in this article the term means both: without heat transfer and sufficiently slow.

 More formally, the energy *E* of a system can be expressed in terms of the occupation number *Ni* of the level *i* characterized by a degeneration *gi* and an energy *εi* as follows:

(1.1)

 The energy change can be written as:

(1.2)

 An adiabatic change in the strict sense used in this article means that:

(1.3)

 The energy change is due exclusively to the change in the energy of the levels. When we get to section 4 and consider the adiabatic expansion or compression of an ideal gas, we will see that the work carried out by or on the system is translated as a shift in the energy levels that does not affect the occupation number.

**2. A brief review of well known results**

 The ideal gas is a common topic in any thermodynamics course [3, 7]. In this article, we are mainly interested in the adiabatic processes. So, we will assume that the gas undergoes an adiabatic expansion and a simple exercise [3, 7] would show that, during an adiabatic process, if *V* represents the volume of the gas and *T* the temperature, it holds that:

(2.1)

*γ* is the quotient of specific heats at a constant pressure *Cp* and volume *Cv*. It is worth remembering that *γ = 5/3* for an monoatomic ideal gas in 3-D.

 The microscopic quantum model associated with an ideal gas is that of a particle in a box (infinite potential well). Let us remember that if the particle has a mass *m* and the box has dimensions *Lx*, *Ly*, *Lz*, then the energy levels are given by [8, 9]:

(2.2)

 For the purpose of simplifying the notation, we are introducing a characteristic longitude *L0* in terms of which we can rewrite the dimensions of the box, and we are introducing a reference energy *E0* that will allow us to work with a dimensionless energy *εijk*:

;

(2.3)

 For later use, it is convenient to also introduce a reduced (dimensionless) temperature given by: *t = kB T / E0*.

 Now, in the field of statistical mechanics it is necessary to remember that the partition function *Z* is defined as [1-4]:

(2.4a)

The summation includes all the energy levels indicated with a generic index *i*. If we use reduced variables, the expression of the partition function *z* is:

(2.4b)

 An ideal gas is, in microscopic terms, a set of free particles in a box. So, with this microscopic model it is simple to obtain the partition function *Z* of a particle in a box of a volume *V* at a temperature *T* [1-4]:

(2.5a)

In terms of reduced variables, the partition function is:

(2.5b)

 If the ideal gas contains *N* particles, the number of particles *Nijk* in the quantum state (*i,j,k*) can be easily calculated [1-4]. It is convenient to normalize *Nijk* by dividing it by *N* to obtain the occupation probability of the state *pijk = Nijk / N*. Statistical mechanics courses [1-4] show that:

(2.6)

 And for later use, it is important to note that, in terms of the reduced pressure *p* and the reduced volume *v*, the equation of state of an ideal gas for *N* particles is:

(2.7)

**3. Adiabatic expansion of an ideal gas**

 Here, we will consider an adiabatic expansion of a 3-D ideal gas, as shown in Figure 1. We have seen that in an adiabatic process there must be no change in the occupation number of the different quantum levels. Naturally, dividing the number of particles in the quantum state by the total number of particles gives us the occupation probability *pijk* and from (1.3) we can write:

(3.1)

 Is it necessary to keep in mind that *pijk* depends on *εijk* and on *z* that is a function of the volume and the temperature, so that:

(3.2)

 Assuming that the expansion takes place in the direction *x*, then *dly =* *dlz = 0* and we get:

(3.3)

 In Eq. (3.3), when deriving *t* in relation to *x* we indicate that the process is adiabatic, hence the subscript *s* in the last derivative. And from (2.1) we immediately obtain its value. The other derivatives result from working with (2.6) taking into account (2.5b) and (2.3). Thus:

(3.4a)

 The superscript (*x*) added to the differential serves to indicate that this is the change of the occupation probability when the expansion takes place in the direction *x*. Note that the change of the occupation probability is not zero. This means that the typical situation described in Figure 1 implies a rearrangement in the population of the quantum states and, therefore, the condition required by quantum mechanics is not fulfilled in a strict sense. Later, we will see that a rearrangement takes place among quantum states within the same energy level, but before that we will consider a special case.

 Let us assume that the adiabatic expansion takes place simultaneously in the three directions, so that we will have a change associated with the expansion in the direction *y* and another change associated with the expansion in the direction *z*. From (3.4a) it can be inferred that those changes can be calculated as:

(3.4b)

(3.4c)

 It is interesting to note that the sum of (3.4a) + (3.4b) + (3.4c) gives zero only when verifying that:

(3.5)

 In other words, for the occupation probability of the quantum states to not change during an adiabatic process, the expansion should keep the relative size of the box. The typical classroom example shown in Figure 1 leads to a change in the populations of the quantum states. However, we will see next that when the problem is tackled using spherical coordinates, things turn out differently.

 Let us define a spherical coordinates system (*r, θ, φ*) given by:

(3.6)

 With this change of coordinates, the energy of the state (*i, j, k*) is simply:

(3.7)

We can see that the degenerate energy states are on the surface of a sphere in the space of reduced quantum numbers (*i / lx, j / ly, z / lz*). Note that plotting this in terms of the quantum numbers without normalizing (*i, j, k*), would result in an ellipsoid.

 Now, let us return to the typical example of an adiabatic expansion in a single direction. We have seen that the occupation of the state (*i, j, k*) does not remain constant. However, we are going to calculate the change in the occupation probability of all the states with the same energy *εijk*. For this, we will rewrite Eq. (3.4a) in terms of the new coordinates and integrate over both angular variables.

(3.8)

 Note that *pijk* depends on the energy *εijk* which is a function only of *r*. Now, integrating over the entire surface of the sphere gives:

(3.9)

 This is a very interesting result. Although the occupation of a particular quantum state (*i,j,k*) does not remain constant, a redistribution occurs among other states with equal energy. And the total population of the states with energy *εijk* remains constant. Thus, the microscopic condition for a process to be adiabatic is fulfilled: the occupation of an energy level is constant even though there is a redistribution of the particles among the different degenerate states.

 At this point it seems convenient to rewrite Eq. (3.4a). For this, remember the expression of the energy given by (2.3), so that:

(3.10)

 This equation provides a better understanding of what is happening. The box is expanding in the direction *x*, and we are observing what happens with the occupation probability of a quantum state (*i, j, k*). Eq. (3.10) shows that the population of the quantum state increases for values of *i > (εijk / 3 )1/2lx* and decreases if *i* is smaller than that value. But the redistribution is such that when integrating in all the directions of the quantum numbers space, the net result is zero according to (3.9). There is a transfer among quantum states of equal energy. So, the process can be said to be adiabatic in a quantum mechanics sense because the condition (1.3) is fulfilled.

 It can be concluded that the quasi-static expansion of an ideal gas in which no heat transfer to or from the exterior occurs, is an adiabatic process from the point of view of both thermodynamics and quantum mechanics.

**4. Work done by the system**

 From equation (1.2) it is inferred that, when the adiabatic expansion occurs, if there is no change in the occupation number of the levels, any change in the energy of the system is the result of a modification of the quantum levels. And from the macroscopic point of view, the energy change is the result of the work *dw* done by/on the system. We will calculate it explicitly.

(4.1)

 The expression (4.1) is a compact form of the complete expression implying three summations on the three indexes *i, j, k* but, to avoid complicating the notation, only one is indicated. In other words, in this section “*i*” is used as the abbreviated version of “*ijk*”. And we will assume a change in *lx*. So, from (2.5) we get:

(4.2)

And considering that from (2.6), this gives:

(4.3)

 Eq. (2.5b) enables to calculate *∂z/∂lx* and this leads to the conclusion that (4.3) can be rewritten as:

(4.4)

Finding the derivative of this equation is immediate from (2.5b) which leads to conclude that *(∂*ln *z / ∂lx) = ( lx)-1*. And as the reduced volume is *v = lx ly lz* it is clear that *dlx / lx = dv / v*. So, keeping in mind the reduced equation of state (2.7), it turns out that the work done in the adiabatic expansion is:

(4.5)

 And our journey ends here. We have recovered a very well-known result of thermodynamics [3, 7], *dE = -p dv = dw* for an adiabatic expansion, but note that our point of departure was the microscopic description of a gas as quantum particles in a box.

**5. Final remarks**

 In this article we solved a well-known problem of thermodynamics: the adiabatic expansion of an ideal gas, but we did this from a microscopic point of view. That is why we first analyzed the meaning of “adiabatic process” in thermodynamics and in quantum mechanics. As seen, in one case adiabatic means with no heat transfer, while in the other it means that the population of the energy levels suffers no change during the process. Thus, in the case of the expansion of an ideal gas, there must be no heat transfer and the expansion should be quasi-static for the process to be adiabatic in both senses.

 In section 3 we considered the ideal gas model as a group of quantum particles in an infinite potential well, and we demonstrated that the expansion with no heat transfer and quasi-static retains the number of particles in each energy level. However, something interesting happens: the particles are rearranged among the states with equal energy. This means that the population of each degenerate state with a certain energy does change, but in such way that the number of particles in that energy level remains the same. And that is the condition for the process to be considered adiabatic from the quantum mechanics point of view. Finally, in section 4 we calculated the energy change of the system and we recovered the old thermodynamic result: *dE = -p dv*, but note that we did this by observing the microscopic behavior of the system. In other words, starting from a quantum description and making use of statistical mechanics we recovered an expression known since the beginnings of thermodynamics. Certainly, this is not a novel result. Rather, we reach a known destination through an original road. And this is interesting from an educational perspective, hence the value of this exercise.

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**Figure**



**Figure 1:** This is the well-known problem studied in this article: an ideal gas is enclosed in an adiabatic vessel and the piston is slowly moving from an initial position (Lx\_initial) to a final one (Lx\_final). The piston moves in a quasi-statically. In this way, the populations of the energy levels remain unchanged and the process is adiabatic both from the point of view of thermodynamicas and quantum mechanics.