

Article

A New Perspective on Classical Ideal Gases

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Abstract: The ideal-gas barometric and pressure laws are derived from the Democritian concept of independent corpuscles moving in vacuum, plus a principle of simplicity, namely that these laws are independent of the kinetic part of the Hamiltonian. A single corpuscle in contact with a heat bath in a cylinder and submitted to a constant force (weight) is considered. The paper importantly supplements a previously published paper: First, the stability of ideal gases is established. Second, we show that when walls separate the cylinder into parts and are later removed, the entropy is unaffected. We obtain full agreement with Landsberg's and others' (1994) classical thermodynamic result for the entropy of a column of gas submitted to gravity.

Keywords: ideal gas law; corpuscular concepts; classical gas theory; canonical single-corpuscle thermodynamics; gas stability; Gibbs paradox

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1. Introduction

The paper gives an alternative derivation of the classical barometric and ideal gas laws. Our results coincide with those obtained from the Bohr-Sommerfeld (BS) quasi-classical approximation of Quantum Mechanics and the Boltzmann factor, but our method is more straightforward. Initially, we obtained the average force, $\langle F \rangle$, exerted by a corpuscle on a piston from the BS theory. The corpuscle action (area in

the position-momentum, z - p , phase-space, where z denotes the corpuscle altitude and the momentum, $p = -wt$, where $-w$ is the force applied to the corpuscle, e.g., its weight, and t is time) is discrete and evenly spaced in units of the Planck constant, $2\pi\hbar$. Because our model is not a harmonic oscillator, the discrete corpuscle energies are unevenly spaced. Thus, going to the continuous limit converting sums into integrals, we must introduce an energy distribution, $\omega(E)$, where E denotes the energy, in the form given later. After going through these semi-classical considerations, we discovered that it was sufficient to postulate the simplicity principle, according to which the barometric law must not depend on the equations of motion. This concept, unlike quantum theory, could have been understood at the time of ancient Greece. Furthermore, we show that if the entropy is taken as the negative average value of the logarithms of the microstate probabilities, accounting for a possible uncertainty concerning the presence or not of a corpuscle, introduction and removal of separations in the cylinder containing the corpuscle does not affect the entropy.

By *ideal gas*, we mean a collection of non-interacting corpuscles. We may, therefore, restrict ourselves to a single corpuscle. If there is more than one corpuscle, the corpuscles are classical and, thus, distinguishable. We first suppose that we know with certainty whether a corpuscle is present or not in the cylinder, then relax this assumption. Only motion along the vertical z -axis is considered, but generalization of the barometric and ideal-gas law to three dimensions is straightforward. As said above, the corpuscle considered is submitted to an external force, $-w$, perhaps of electrical origin, w being called the corpuscle “weight”, or equivalently to a potential, $\mathcal{P}(z) = wz$. Because the presence of a corpuscle affects the potential negligibly, the latter is viewed as an *external* potential. We call a *perfect gas* an ideal gas with no external force acting on the corpuscle, except at the boundaries and with the non-relativistic approximation being made.

According to our definition, ideal gas constant-volume heat capacities depend on temperature, θ , and volume, h . The free expansion of an ideal gas may, therefore, entail temperature changes, while this is not the case for a perfect gas. There is full agreement between our general results and the first and second laws of thermodynamics as they are spelled out in textbooks and the usual perfect-gas laws derived by Bernoulli in the limit considered. The role of a constant force acting on the corpuscle and special-relativity have been discussed, for example, by Landsberg [1] and Louis-Martinez [2].

The present paper is a generalization of our previous papers [3,4], where our motivation is explained in more detail than here. Presently, we calculate the average forces exerted on both ends of a vertical cylinder; they are different when the corpuscle has weight. We prove the gas stability from the fact that the corpuscle round-trip time is a non-decreasing function of the energy. We show that the entropy does not vary when separating walls are introduced and removed. The entropy is not postulated to be additive or extensive: it is defined as the negative average value of the logarithms of the microstate probabilities, thereby accounting for a possible uncertainty concerning the presence or not of a corpuscle, through the concept of conditional probabilities. Our conclusion agrees with an expression for the entropy given by Landsberg and others [1], involving an integration over the cylinder height of $\rho(z) \ln(1/\rho(z))$, where $\rho(z)$ is the probability density that the corpuscle be at z (or the corpuscle density for a large number of corpuscles). The difference between Landsberg’s approach and our approach is that we conceptually divide the total system into subsystems and Landsberg does not. Both approaches yield the same result. Related concepts were introduced by Peters [5,6].

We first consider the round-trip time, $\tau(z_m)$, needed for a corpuscle thrown upward from the ground level, $z = 0$, with energy, $E = w z_m$, to reach a maximum altitude, z_m , and come back to the ground level. If the corpuscle bounces elastically on the ground, $\tau(z_m)$ represents the oscillation period. Since we consider only round-trip times, that is, time delays measured at some altitude, no problem of clock synchronization arises. The time during which the corpuscle is located above some altitude, $z \leq z_m$, during a period is $\tau(z_m - z)$, since, under our assumption of a constant weight, the τ -function does not depend on the initial altitude or initial time. For brevity, we set $w = 1$ in most of the present paper. The weight is easily restored from dimensional considerations. For example, the result, $\exp(-\beta z)$, should read, $\exp(-\beta w z)$, in view of the fact that β has the dimension of an energy reciprocal.

We consider only thermal-equilibrium situations: If we wait a sufficiently long period of time, an isolated system ceases to evolve. We take it as an empirical result that, leaving aside general-relativity effects (According to *general relativity*, thermal energy has weight, but this (so-called Tolman) effect that entails a temperature variation at equilibrium, $\theta(z) = \theta(0)/(1 + 2z g/c^2)$, where g denotes the gravity acceleration and c , the speed of light, is entirely negligible; see, for example, Equation (1) of [7]. This paper gives the following interpretation of equilibrium: an (adapted) quote is: “The temperature θ is essentially equal to $\hbar$ divided by the time required by the system to move from one state to the next”. This interpretation leads to the condition of temperature uniformity for weak gravity, since, in that case, time intervals do not depend significantly on altitude.), two bodies left in contact for a sufficient period of time with energy being allowed to flow from one to the other reach an equilibrium state corresponding to equal temperatures, as one can judge by our senses. Energy may flow spontaneously (*i.e.*, without work expenditure) from a hot body to a colder one, but the converse never occurs: the process is non-reversible (zeroth law of thermodynamics). Our θ notation for the temperature is the one employed by Gibbs. We quote [8]: “Gibbs, writing before the introduction of Boltzmann’s constant, k_B , uses θ with the dimensions of energy for what we should today call $k_B T$; consequently, his thermodynamic analog of entropy is what we should today call S/k_B and is dimensionless. In this respect Gibbs’ notation is really neater formally and more cogent physically than ours”. In our discussion, the temperature, θ , enters solely on the basis of dimensional considerations. However, we later show that our expressions for the gas internal energy and force (or pressure) derive from the partial derivatives of the Helmholtz potential (or free energy), $A(\theta, h)$. The heat delivered by the gas in reversible processes is $\delta Q = \theta dS$, an expression for the entropy, $S(\theta, h)$, being given. This result enables us to prove that the formally-introduced temperature, θ , is a thermodynamic temperature.

To conclude, the purpose of the present paper is to show that the thermodynamics of ideal gases and, particularly, the barometric and ideal-gas laws, may be obtained solely on the basis of the Democritus model, according to which nature consists of corpuscles moving in a vacuum, plus a principle of simplicity: namely that these fundamental laws are *independent* of the law of corpuscle motion. To wit, writing the corpuscle Hamiltonian (see Appendix A) as $\mathcal{K}(p) + z$, the barometric and ideal-gas laws *do not depend* on the $\mathcal{K}(p)$ function, but the internal kinetic energy, K , does. Thus, the Hamiltonian equations recalled in the Appendix are unnecessary, as far as the barometric and ideal-gas laws are concerned, but they are needed (in the form of a round-trip function) for the internal energy and other quantities relevant to classical thermodynamics.

As said earlier, we consider a single corpuscle. Because of the slight thermal motion of the container wall, there is an exchange of energy between the corpuscle and the heat bath, so that the corpuscle energy slowly varies in the course of time. We are looking for averages over arbitrary, long time intervals.

2. The Barometric Law

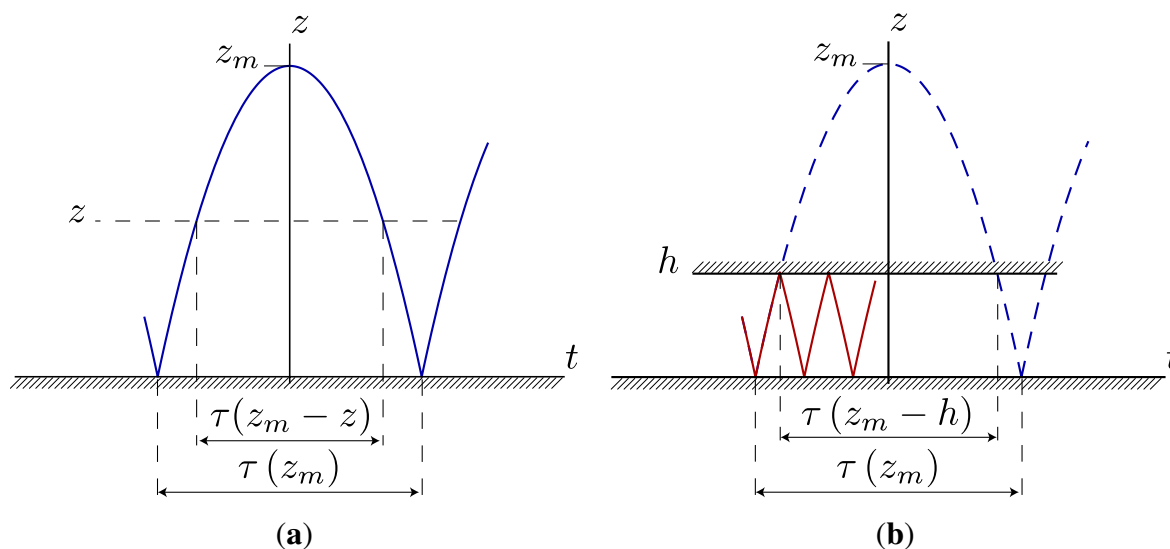
We consider a single corpuscle moving only along the vertical z coordinate and submitted to a constant force, -1 . If the corpuscle energy is E , the maximum altitude reached is $z_m = E$. The round-trip time, $\tau(z_m)$, is the motion period, and the time per period during which the corpuscle is above z is (see Figure 1a) $\tau(z_m - z)$. It follows that the fraction of time during which the corpuscle is above z is $\tau(z_m - z)/\tau(z_m)$. Because of thermal fluctuations, the corpuscle energy is not fixed, but must be described by a probability distribution. By invoking the simplicity principle, *i.e.*, by demanding independency of the τ -function, one obtains an energy distribution proportional to $\omega(z_m) = \exp(-\beta z_m)\tau(z_m)$, yielding the average fraction of time during which the corpuscle is above z as:

$$\langle \text{above } z \rangle = \frac{\int_z^\infty dz_m \omega(z_m) \tau(z_m - z) / \tau(z_m)}{\int_0^\infty dz_m \omega(z_m)} \quad (1)$$

The result obtained for the distribution, $\omega(z_m) = \exp(-\beta z_m)\tau(z_m)$, is indeed:

$$\langle \text{above } z \rangle = \frac{\int_z^\infty dz_m \exp(-\beta z_m) \tau(z_m - z)}{\int_0^\infty dz_m \exp(-\beta z_m) \tau(z_m)} = \exp(-\beta z) \quad (2)$$

Figure 1. Space-time (z, t) trajectory of a unit-weight corpuscle bouncing off the ground at $z=0$. In (a), the maximum altitude reached by the corpuscle is $z_m = E$, where E denotes the energy. The motion is periodic, with period $\tau(z_m)$, where $\tau(\zeta)$ denotes the corpuscle round-trip time at a distance, ζ , from the top of the trajectory. The time during which the corpuscle is located above z , divided by the period, is evidently $\tau(z_m - z)/\tau(z_m)$. This expression holds, even if the motion is not symmetric in time. In (b), the maximum altitude is restricted to h by a piston. The motion period becomes $\tau(z_m) - \tau(z_m - h)$.



In the integrals going from z to ∞ , we have replaced $\exp(-\beta z_m)$ by $\exp(-\beta z) \exp(-\beta(z_m - z))$. Here, $\beta \equiv 1/\theta$; the energy, θ , will later on prove to be a thermodynamic temperature. In terms of the variable, $z_m - z$, all the integrals go from zero to infinity and cancel out. Even though there are integral signs, no integration has been performed. We simply consider an integral as a sum of terms and employ the rule of addition associativity. We have also employed the fact that $f(x) = \exp(x)$ is the only function, such that $f(a + b) = f(a)f(b)$. Note that our “desired result” does not refer to a specific barometric law that would be known before hand, but to the fact (simplicity principle) that this law, whatever it is, does not depend on the equations of motion. It is postulated on the basis of common experiences that in a state of equilibrium, there exists a unique temperature. Thus, a general form of the barometric law has been obtained without invoking the Boltzmann distribution, which is presently viewed as a *consequence* of the simplicity principle. For a three-dimensional configuration corresponding to real atmospheres, the same result holds: the $\tau(\cdot)$ -function is modified; however, the barometric law does not depend on that function, and therefore, the result in Equation (2) is unaffected. The more complicated case, where the weight, w , depends on z , is treated in [4]. The result amounts to replacing z in the above expression by a potential, $\mathcal{P}(z)$. This known result is obtained here most simply.

2.1. Reflecting Plane at $z = h$

We now suppose that there is a reflecting plane located at h , and the corpuscle is located between zero and h . When $z_m \leq h$, the plane at $z = h$ is immaterial, and the fraction of time spent by the corpuscle above z is as before: $\frac{\tau(z_m - z)}{\tau(z_m)}$. When $z_m \geq h$, the fraction of time spent by the corpuscle above z is $\frac{\tau(z_m - z) - \tau(z_m - h)}{\tau(z_m) - \tau(z_m - h)}$; see Figure 1b. It follows that if $\omega(z_m)$ denotes the energy distribution, the average fraction of time spent by the corpuscle above z ($0 \leq z \leq h$) is:

$$\langle \text{above } z \rangle = \frac{\int_z^h dz_m \omega(z_m) \frac{\tau(z_m - z)}{\tau(z_m)} + \int_h^\infty dz_m \omega(z_m) \frac{\tau(z_m - z) - \tau(z_m - h)}{\tau(z_m) - \tau(z_m - h)}}{\int_0^h dz_m \omega(z_m) + \int_h^\infty dz_m \omega(z_m)} \quad (3)$$

This expression is independent of the $\tau(\cdot)$ function, according to our simplicity principle, if and only if $\omega(z_m)$ is selected as follows:

$$\begin{cases} \omega(z_m) = \exp(-\beta z_m) \tau(z_m) & z_m \leq h \\ \omega(z_m) = \exp(-\beta z_m) (\tau(z_m) - \tau(z_m - h)) & z_m > h \end{cases} \quad (4)$$

Using the elementary transformations given in [4], we obtain, employing only the associativity of addition and the fact that $\exp(x)$ is the only function, such that $\exp(a + b) = \exp(a) \exp(b)$:

$$\langle \text{above } z \rangle = \frac{\exp(-\beta z) - \exp(-\beta h)}{1 - \exp(-\beta h)} \quad (5)$$

The same result is obtained if we suppose that the barometric law applies also in the presence of a reflecting plate at h and evaluate the ratio of the integral of $\exp(-\beta z)$ from z to h and the integral of $\exp(-\beta z)$ from zero to h .

Similarly, supposing that the corpuscle is located between zero and $2h$, we obtain the probability, P_A , that the corpuscle be in the lower half and the probability, P_B , that the corpuscle be in the upper half in the form:

$$P_A = \frac{1}{1 + \exp(-\alpha)}, \quad P_B = \frac{1}{1 + \exp(\alpha)}, \quad \alpha \equiv \beta h, \quad P_A + P_B = 1 \quad (6)$$

These expressions will be needed later on.

When the corpuscle is submitted to an arbitrary potential, $\mathcal{P}(z)$, the barometric law reads:

$$\rho(z) \propto \exp(-\beta \mathcal{P}(z)) \quad (7)$$

where $\rho(z)$ denotes the corpuscle density at z . The details can be found in [4]. The result is the well-known generalized Boltzmann factor that reduces to the previous one when $\mathcal{P}(z) = z$. However, it is obtained here from the simplicity principle alone.

3. Average Force Exerted by a Corpuscle on Pistons

We consider a unit-area cylinder with a vertical z -axis at some temperature. There is a lower piston at altitude h_o and an upper piston at altitude $h_1 = h_o + h$. The cylinder contains a single corpuscle located between h_o and h_1 , submitted to a force, -1 . We evaluate the average force, $\langle F_o \rangle$, exerted by the corpuscle on the lower piston and the average force, $\langle F \rangle$, exerted by the corpuscle on the upper piston. The following relation necessarily holds: $\langle F_o \rangle + \langle F \rangle + 1 = 0$.

3.1. Mechanical Average

The word “average” enters in this paper as a mechanical average and as a thermal average. Physically, it is supposed that the pistons have so much inertia that they do not respond to individual collisions. Let the corpuscle energy be denoted E . The maximum altitude, z_m , that the corpuscle would reach in the absence of the piston is $E = z_m$. The mechanical average force exerted by the corpuscle on the lower piston is twice the corpuscle momentum, p , when it collides with the plane, times the number of collisions per unit time, $1/\tau$, where τ denotes the motion period, as was well understood by Bernoulli centuries ago. When the corpuscle does not reach the piston, $z_m \leq h$, we have $\tau = \tau(z_m)$. That is, $F_o = 2p/\tau$. If we set $t = 0$ when $p = 0$, that is, at the top of the corpuscle trajectory, the corpuscle momentum is at time t : $p = -t$, and the collision time is $t = \tau(z_m)/2$ (see Figure 1). Thus, $F_o = -(2\tau(z_m)/2)(1/\tau(z_m)) = -1$. When the corpuscle possesses enough energy to reach the upper piston, the motion period becomes $\tau(z_m) - \tau(z_m - h)$. Then, the force, F_o , experienced by the lower piston is:

$$\begin{cases} F_o(z_m) = -1 & z_m \leq h \\ F_o(z_m) = -\frac{\tau(z_m)}{\tau(z_m) - \tau(z_m - h)} & z_m > h \end{cases} \quad (8)$$

The force, F , experienced by the upper piston when the corpuscle energy is z_m is likewise:

$$\begin{cases} F(z_m) = 0 & z_m \leq h \\ F(z_m) = \frac{\tau(z_m - h)}{\tau(z_m) - \tau(z_m - h)} & z_m > h \end{cases} \quad (9)$$

so that, irrespectively of z_m , we have: $F_o + F = -1$. This means that the cylinder, considered as a rigid object of negligible weight, has an effective weight precisely equal to one, a most intuitive result. By linearity, the same conclusion must hold for average forces: $\langle F_o + F \rangle = -1$.

3.2. Thermal Average

Because the cylinder is in contact with a bath, it suffers a slight thermal motion, and the corpuscle energy, z_m , slowly varies in the course of time. We are considering an arbitrary, large number of samples, each of them containing a single corpuscle.

Accordingly, the average force, $\langle F_o \rangle$, experienced by the bottom of the cylinder and the average force, $\langle F \rangle$, experienced by the piston are, respectively, from Equations (8) and (9), if $\omega(z_m)$ denotes the energy distribution:

$$\langle F_o \rangle = \frac{\int_0^\infty dz_m \omega(z_m) F_o(z_m)}{\int_0^\infty dz_m \omega(z_m)} = - \frac{\int_0^h dz_m \omega(z_m) + \int_h^\infty dz_m \omega(z_m) \frac{\tau(z_m)}{\tau(z_m) - \tau(z_m - h)}}{\int_0^h dz_m \omega(z_m) + \int_h^\infty dz_m \omega(z_m)} \quad (10)$$

$$\langle F \rangle = \frac{\int_0^\infty dz_m \omega(z_m) F(z_m)}{\int_0^\infty dz_m \omega(z_m)} = \frac{\int_h^\infty dz_m \omega(z_m) \frac{\tau(z_m - h)}{\tau(z_m) - \tau(z_m - h)}}{\int_0^h dz_m \omega(z_m) + \int_h^\infty dz_m \omega(z_m)} \quad (11)$$

According to our simplicity principle, the average forces must be *independent* of the corpuscle equation of motion and, thus, of the $\tau(\cdot)$ -function. This condition is obtained from Equations (10) and (11), if one selects the distribution previously given in Equation (4). The average forces become, using Equations (4), (10) and (11):

$$\begin{aligned} \langle F_o \rangle &= - \frac{\int_0^\infty dz_m \exp(-\beta z_m) \tau(z_m)}{\int_0^h dz_m \exp(-\beta z_m) \tau(z_m) + \int_h^\infty dz_m \exp(-\beta z_m) (\tau(z_m) - \tau(z_m - h))} \\ &= \frac{1}{\exp(-\beta h) - 1} \rightarrow \begin{cases} -\frac{\theta}{h} & h \ll \theta \\ -1 & h \gg \theta \end{cases} \\ \langle F \rangle &= \frac{\int_h^\infty dz_m \exp(-\beta z_m) \tau(z_m - h)}{\int_0^h dz_m \exp(-\beta z_m) \tau(z_m) + \int_h^\infty dz_m \exp(-\beta z_m) (\tau(z_m) - \tau(z_m - h))} \\ &= \frac{1}{\exp(\beta h) - 1} \rightarrow \begin{cases} \frac{\theta}{h} & h \ll \theta \\ 0 & h \gg 1 \end{cases} \end{aligned} \quad (12)$$

with $\langle F_o \rangle + \langle F \rangle = -1$, since $1/(\exp(-x) - 1) + 1/(\exp(x) - 1) + 1 = 0$, proceeding as in the previous section.

For a collection of N independent (classical, distinguishable) corpuscles having a unit weight, the force is a sum of N terms of the form given above. In the case of zero weights ($w_i=0$ or, more precisely, $\beta w_i h \ll 1$), the above expression would give $\langle F \rangle h = \theta$. Thus, we have obtained the perfect-gas law: $\langle F \rangle h = N \theta$. It does not depend on the nature of the corpuscles.

For an arbitrary potential, $\mathcal{P}(z)$, the force, $\langle F \rangle$, follows from the barometric distribution in Equation (7), according to:

$$\langle F \rangle = \frac{\int_h^\infty dz \exp(-\beta \mathcal{P}(z))}{\int_0^h dz \exp(-\beta \mathcal{P}(z))} \quad (13)$$

where the limits on the denominator are consequences of the fact that the corpuscle is located between zero and h . This result coincides with the previous one in Equation (12) when $\mathcal{P}(z) = z$.

3.3. Average Force for a Three-Dimensional Space

We suppose that the cylinder radius is very large compared with h , and we do not consider the force exerted by the corpuscle on the cylinder wall. The motion of the corpuscle along directions perpendicular to z *does* affects the round-trip time function, $\tau(\cdot)$. However, since the average force does not depend on this function, the ideal-gas law is unaffected. This is so for any physical system involving a single corpuscle, provided that the physical laws are invariant under a z -translation (besides being static).

The internal energy, to be discussed in the following section, though, is incremented. One can prove that in the non-relativistic approximation and in the absence of gravity, the internal energy is multiplied by three. It would be increased further by corpuscle rotation or vibration, which is not considered here. Using conventional methods, Landsberg [1] and Louis-Martinez [2] obtain exactly the same result as given above (except for the factor, three, in the expression for the internal energy, relating to the number of space dimensions considered).

4. Internal Energy

The gas internal energy, U , is the average value of $E \equiv z_m$, the gravitational energy being accounted for. First, assume that the cylinder rests on the ground level: $h_o = 0$. The expression for U is, using the energy distribution given in Equation (4):

$$U = \frac{\int_0^\infty dE E \exp(-\beta E) \tau(E)}{\int_0^\infty dE \exp(-\beta E) \tau(E)} - \frac{h}{\exp(\beta h) - 1} \quad (14)$$

where the method employed before has been used. The mathematical details can be found in [3]. The first term minus θ corresponds to the kinetic energy, K , while the second term plus θ corresponds to the potential energy, P . In the non-relativistic limit, the first term, minus θ , gives the well-known expression, $K = \theta/2 \equiv k_B T/2$. Without any force acting on the corpuscle, we have, of course, $P = 0$. The internal energy, $U(\theta, h)$, thus is the sum of a term, K , the function of θ , but not of h , and a term, P , obtained in analytical form, that tends to zero when $h \ll \theta$. To evaluate the first term, we need to know the round-trip time, $\tau(z_m)$, to within an arbitrary proportionality factor, and an integration must be performed in that case.

The expressions given earlier for the average force, $\langle F \rangle$, in Equation (12) and the internal energy, U , in Equation (14) may be written, with $\beta \equiv 1/\theta$:

$$\begin{aligned} \langle F \rangle &= \frac{\partial \ln(Z)}{\beta \partial h} & U &= -\frac{\partial \ln(Z)}{\partial \beta} \\ Z(\beta, h) &= (1 - \exp(-\beta h)) \frac{1}{2\pi\hbar} \int_0^\infty dz_m \exp(-\beta z_m) \tau(z_m) \end{aligned} \quad (15)$$

Z is a form of the (Gibbs) phase integral of $\exp(-\beta\mathcal{H})$, where $\mathcal{H}$ is the Hamiltonian given in the Appendix [9]. The Planck constant, $2\pi\hbar$, introduced to make Z dimensionless plays no physical role in this paper (remember that z should read wz). All the physical results may be derived from the above expression of $Z(\beta, h)$.

As said above, the internal energy, U , may be written as the sum of a potential energy, P , and a kinetic energy, K . The potential energy with $h_o = 0$ may be written as the ratio of the integral of $z \exp(-\beta z)$ from zero to h and the integral of $\exp(-\beta z)$ from zero to h . In general, P must be incremented by h_o .

The temperature, θ , introduced above only on dimensional grounds is defined to within an arbitrary constant. We may convene that $\theta = 1$, exactly as the hydrogen triple-point temperature (HTP). The value of θ at the water triple-point (WTP), for example, would then be obtained experimentally by measuring the efficiency of reversible heat engines operating with WTP as a hot bath and HTP as a cold bath. The known value is $\theta_{WTP} = 19.737\dots$

5. Stability

Solutions obtained for the force, $\langle F \rangle$, and the energy, U , imply stable equilibria, provided that two conditions be satisfied. Firstly, the isothermal compressibility, $\kappa_T \equiv -(1/h)\partial h/\partial \langle F \rangle$, must be positive. This is readily verified, since the derivative of the force, $\langle F \rangle$, given in Equation (12), with respect to h is negative. Secondly, one must verify that the isochoric heat capacity, C_V , is positive. This problem is solved below. Given that C_V and κ_T are positive, it follows that the isobaric heat capacity, $C_P > C_V$, is positive, and the isentropic compressibility, $\kappa_s = \kappa_T C_V/C_P$, is positive, also. Thus, let us show that C_V is positive. The internal energy is the sum of the potential energy, P , which is easily seen to be an increasing function of θ and the kinetic energy, K .

The former may be written, according to Equation (14):

$$P = \theta - \frac{h}{\exp(\beta h) - 1} = \theta \left(1 - \frac{\alpha}{\exp(\alpha) - 1} \right) \quad \alpha \equiv \beta h$$

$$\frac{\partial P(\theta, h)}{\partial \theta} = 1 - \left(\frac{\alpha/2}{\sinh(\alpha/2)} \right)^2 > 0 \quad (16)$$

The latter may be written as:

$$K = -\theta + \frac{\int_0^\infty dE E \exp(-\beta E) \tau(E)}{\int_0^\infty dE \exp(-\beta E) \tau(E)} = -\frac{\phi'}{\phi}, \quad \phi(\beta) \equiv \int_0^\infty dE \exp(-\beta E) \tau'(E) \quad (17)$$

integrating by parts, where primes indicate derivatives with respect to the argument. In order to get $C_V > 0$, it thus suffices to show that $\phi''\phi \geq \phi'^2$, that is, letting $f(\beta, E) \equiv \exp(-\beta E)\tau'(E)$, for short:

$$\left(\int_0^\infty dE E^2 f(\beta, E) \right) \left(\int_0^\infty dE f(\beta, E) \right) \geq \left(\int_0^\infty dE E f(\beta, E) \right)^2 \quad (18)$$

Since τ is a non-decreasing function of E , f is non-negative and Equation (18) is the classical inequality regarding the moments on order of zero, one and two of the measure μ defined by: $d\mu = f(\beta, E)dE$.

Thus, $C_V = \frac{\partial U}{\partial \theta} \geq 0$, and the expressions obtained from our simplicity principle imply the stability of the equilibria.

6. The Helmholtz Fundamental Relation

It is convenient to introduce the Helmholtz fundamental relation: $A(\theta, h) \equiv -\theta \ln(Z(\theta, h))$. The letter A originates from the German “Arbeit”, or work, but this letter may also stand for (constant temperature) “Available work”. Indeed, the work performed at a constant temperature is the difference between the final and initial A values.

The force, $\langle F_o \rangle$, that the corpuscle exerts on the lower piston, the force, $\langle F \rangle$, that the corpuscle exerts on the upper piston and the internal energy result from the Helmholtz fundamental relation depending separately on h_o and $h_1 = h_o + h$. We thus consider a cylinder whose base has been raised from $z = 0$ to $z = h_o$. The previous relations for $\langle F_o \rangle$, $\langle F \rangle$ in Equation (12) and for U in Equation (14) may be written as:

$$\begin{aligned} \langle F_o \rangle &= \frac{1}{\exp(-\beta h) - 1} = -\frac{\partial A}{\partial h_o}, & \langle F \rangle &= \frac{1}{\exp(\beta h) - 1} = -\frac{\partial A}{\partial h_1} \\ U &= A - \theta \frac{\partial A}{\partial \theta} = \frac{\partial(\beta A)}{\partial \beta} \\ A(\theta, h_o, h_1) &= -\theta \left(\ln(1 - \exp(-\beta h)) + \ln \left(\frac{1}{2\pi\hbar} \int_0^\infty dz_m \exp(-\beta z_m) \tau(z_m) \right) \right) + h_o \end{aligned} \quad (19)$$

with $h \equiv h_1 - h_o$. Thus, if the cylinder bottom is raised to an altitude, h_o , A and U are both incremented by h_o . From now on, we set $h_o = 0$ for simplicity, unless specified otherwise.

We have obtained an expression for the Helmholtz fundamental relation, $A(\theta, h)$, for the special case of a single corpuscle submitted to a constant force in the canonical ensemble. This fundamental relation has the same mathematical and physical content as the often-used energy fundamental relation, $U = U(S, h)$, and the entropy fundamental relation, $S = S(U, h)$; see [10]. The following expressions therefore coincide with the conventional ones applicable to any working substance. Indeed, the fundamental entropy relation is obtained in parametric form from the expressions for $U(\theta, h)$ and $S(\theta, h)$, with θ as a parameter. Even though we cannot explicitly obtain $S = S(U, h)$, it is easy to verify that $\frac{\partial S}{\partial U} = \beta$.

We have indeed:

$$\frac{\partial S(U, h)}{\partial U} = \frac{\partial S(\theta, h)/\partial \theta}{\partial U(\theta, h)/\partial \theta} = \beta, \quad S(\theta, h) = -\frac{\partial A(\theta, h)}{\partial \theta}, \quad U(\theta, h) = A(\theta, h) - \theta \frac{\partial A(\theta, h)}{\partial \theta} \quad (20)$$

Likewise, we obtain the well-known relation, $\frac{\partial S(U, h)}{\partial h} = \beta \langle F \rangle$, if we enforce the condition, $dU = 0$. The Helmholtz fundamental relation will suffice for our purposes.

At a given temperature, the corpuscles are independent. Accordingly, for N corpuscles, $\langle F \rangle$ and U are simply multiplied by N . A is multiplied by N , plus a function of N that we do not specify further. It follows that if $S(U, h)$ denotes the fundamental entropy relation for a single corpuscle, the fundamental entropy relation for N corpuscles reads $N S(\frac{U}{N}, h)$, to within an additional arbitrary function of N . For

a perfect gas, this function may be selected, such that the entropy is extensive in h . The entropy is, in general, not extensive, but there is no reason why it should be. Let us quote Jaynes [8]: “The question of extensivity cannot have any universally valid answer; for there are systems, for example systems with electric charge or gravitational forces, for which the scaling law does not hold because of long range interactions”.

6.1. The Energy, θ , is a Thermodynamic Temperature

We prove in this section that θ , introduced in previous sections on dimensional grounds only, is a thermodynamic temperature. We do this by showing that the efficiency of a reversible thermal cycle employing ideal gases is, $1 - \theta_c/\theta_h$, where θ_c is the cold-bath temperature and θ_h , the hot bath temperature: this is the accepted Kelvin definition of absolute temperatures.

From the law of conservation of energy, the heat released by the gas is from Equation (19):

$$-\delta Q \equiv dU + \langle F \rangle dh = dA - \frac{\partial A}{\partial \theta} d\theta - \frac{\partial A}{\partial h} dh - \theta d\left(\frac{\partial A}{\partial \theta}\right) \equiv \theta dS, \quad S = -\frac{\partial A}{\partial \theta} \quad (21)$$

For any function, $f(\theta, h)$, such as U , A , S , $df \equiv \frac{\partial f}{\partial \theta} d\theta + \frac{\partial f}{\partial h} dh$. We employ only two independent variables, namely, θ and h , so-that partial derivatives are unambiguous. If the gas is in contact with a thermal bath ($\theta=\text{constant}$), δQ is the heat gained by the bath. The quantity, S , defined above, is called “entropy”. In particular, if heat cannot go through the gas container wall (adiabatic transformation), we have $\delta Q = 0$, that is, according to the above result, $dS = 0$. Thus, reversible adiabatic transformations are isentropic. Note that S , here defined as the ratio of two energies, is dimensionless. It may therefore be written as the logarithm of a dimensionless quantity. The fact that S , defined above, is a state function suffices to prove that θ is a thermodynamic temperature.

7. Expressions for the Entropy

In Equation (21), we have expressed the state function, S , in terms of the Helmholtz potential, A :

$$S = -\frac{\partial A}{\partial \theta} = \frac{\partial (\theta \ln(Z))}{\partial \theta} = \beta U + \ln(Z(\beta, h)) \equiv g(\beta) - \frac{\alpha}{\exp(\alpha) - 1} + \ln(1 - \exp(-\alpha)) \quad (22)$$

where $\alpha = \beta h$, using for U the expression given in Equation (19), where g is some function.

7.1. Perfect Gases

For a perfect gas ($w \rightarrow \text{zero}$, non-relativistic approximation), the expression for Z in Equation (22) may be written as:

$$Z(\beta, h) \propto h \theta^{1/2}, \quad \ln(Z(\beta, h)) = \ln(h \theta^{1/2}) = -\beta A(\beta, h) \\ \langle F \rangle = -\frac{\partial A}{\partial h} = -\frac{1}{\beta} \frac{\partial(\beta A)}{\partial h} = \frac{\theta}{h} \quad U = \frac{\partial(\beta A)}{\partial \beta} = \frac{\theta}{2} \quad (23)$$

These are the usual expressions for the equation of state and the internal energy of a perfect gas.

According to Equations (22) and (23), the entropy is, omitting an additional factor of $1/2$:

$$S = -\frac{\partial A}{\partial \theta} = \frac{\partial (\theta \ln(h \theta^{1/2}))}{\partial \theta} = \ln(h \theta^{1/2}) \quad (24)$$

Since $U = \theta/2$, the fundamental entropy relation reads:

$$S(U, h) = \ln(h \sqrt{2U}) \quad (25)$$

We recover from this expression, again, $\frac{1}{\theta} = \frac{\partial S}{\partial U} = \frac{1}{2U}$ and $\frac{\langle F \rangle}{\theta} = \frac{\partial S}{\partial h} = \frac{1}{h}$, that is, $\langle F \rangle h = \theta$

7.2. Another Form of the Entropy

Recall from Equation (22) that:

$$S \equiv -\frac{\partial A(\beta, h)}{\partial \theta} = -\beta \frac{\partial \ln(Z(\beta, h))}{\partial \beta} + \ln(Z(\beta, h)) \quad (26)$$

The successive trajectory actions are discretized with spacings equal to the Planck constant, and thus, the corresponding energies are correspondingly discretized with subscripts, k ; we suppose that different k values correspond to different energies. In the present classical paper, the Planck constant is allowed at the end to assume arbitrarily small values.

Let the $Z(\beta, h)$ function be written as a sum of terms, $\exp(-\beta \varepsilon_k(h))$, instead of an integral. Then, the entropy, S , may be written as:

$$S = -\sum_{k=0}^{\infty} p_k(\beta, h) \ln(p_k(\beta, h)), \quad p_k(\beta, h) = \frac{\exp(-\beta \varepsilon_k(h))}{Z(\beta, h)}, \quad Z(\beta, h) = \sum_{k=0}^{\infty} \exp(-\beta \varepsilon_k(h)) \quad (27)$$

as one readily verifies by substituting the expression for p_k into the expression of S . The above is a simple mathematical transformation. However, when there is some uncertainty concerning the presence of a corpuscle in the cylinder, it is useful to interpret the p_k as independent probabilities. The entropy may not decrease when constraints are removed or restored inside a thermally isolated body [11].

Let us consider now two boxes labeled “A” and “B” and a single corpuscle. If the corpuscle is in box “A”, the probability that the level, kA , be occupied is denoted p_{kA} with $\sum_{k=0}^{\infty} p_{kA} = 1$. If the corpuscle is in box “B”, the probability that the level, kB , be occupied is denoted p_{kB} with $\sum_{k=0}^{\infty} p_{kB} = 1$. When the corpuscle is in box A with independent probability, P_A , and in box B with probability $P_B = 1 - P_A$, the p_{kA} should be multiplied by P_A , and the p_{kB} should be multiplied by P_B . We therefore have for the entropy, in that case:

$$S = -\sum_{k=0}^{\infty} p_{kA} P_A \ln(p_{kA} P_A) - \sum_{k=0}^{\infty} p_{kB} P_B \ln(p_{kB} P_B) = S_A P_A + S_B P_B + \Delta S$$

$$S_A = -\sum_{k=0}^{\infty} p_{kA} \ln(p_{kA}), \quad S_B = -\sum_{k=0}^{\infty} p_{kB} \ln(p_{kB}), \quad \Delta S = P_A \ln(1/P_A) + P_B \ln(1/P_B) \quad (28)$$

where S_A is the conditional entropy of A and, likewise, for B. The additional term, ΔS , accounts for the fact that it is not known with certainty whether the corpuscle is in box A or in box B. When the two boxes are identical ($S_A = S_B$), the entropy is $S_A + \Delta S$.

8. Change in Entropy Upon Introduction and Removal of a Separation

The process presently discussed is often considered in relation with the so-called “Gibbs’s paradox”; see, for example, [8,12]. We consider a thermally-isolated vertical cylinder of height $2h$ (from $z = 0$ to $z = 2h$), which may be separated by an impermeable wall at altitude h . The lower part of the cylinder is labeled “A” and the upper part is labeled “B”. We will show that when a separation is introduced or removed, the entropy remains the same.

8.1. Change in Temperature

The internal energy, U , is constant, since the cylinder is adiabatic and no work is performed. We will show that this entails the temperature being constant. This is non-obvious, since, for ideal gases, U depends on both θ and h . The general form of the internal energy, U , of a cylinder of height h whose bottom is located at $z = h_o$ reads:

$$\beta U(\beta, h, h_o) = \beta K(\beta) + 1 - \frac{\alpha}{\exp(\alpha) - 1} + \beta h_o, \quad \alpha \equiv \beta h \quad (29)$$

Before the separation is introduced, the internal energy is given by the above expression with h changed to $2h$ and $h_o = 0$, that is:

$$\beta U_{before} = \beta K(\beta) + 1 - \frac{2\alpha}{\exp(2\alpha) - 1}, \quad \alpha \equiv \beta h \quad (30)$$

Once the separation is introduced at $z = h$, the probability that the corpuscle be in the lower part is P_A , and the probability that the corpuscle be in the higher part is P_B with:

$$P_A = \frac{1}{1 + \exp(-\alpha)}, \quad P_B = \frac{1}{1 + \exp(\alpha)} \quad (31)$$

as we have seen in Equation (6). Thus, the internal energy becomes:

$$\begin{aligned} \beta U_{after} &= \beta U_A P_A + \beta U_B P_B \\ \beta U_A &= \beta K(\beta) + 1 - \frac{\alpha}{\exp(\alpha) - 1} \\ \beta U_B &= \beta K(\beta) + 1 - \frac{\alpha}{\exp(\alpha) - 1} + \alpha, \quad \alpha \equiv \beta h, \end{aligned} \quad (32)$$

since in the latter case, $h_o = h$. It follows that $U_{after} = U_{before}$ implies that the α factors are the same before and after, since:

$$1 - \frac{2\alpha}{\exp(2\alpha) - 1} = 1 - \frac{\alpha}{\exp(\alpha) - 1} + \frac{\alpha}{\exp(\alpha) + 1} \quad (33)$$

This is admitted below.

8.2. Change in Entropy

Let us now evaluate the changes of entropy. Without the separation, we have a cylinder height $2h$ and no uncertainty that the corpuscle is there. Then, the entropy is given by Equation (26) with α changed to 2α :

$$S_{before} = g(\beta) - \frac{2\alpha}{\exp(2\alpha) - 1} + \ln(1 - \exp(-2\alpha)), \quad \alpha \equiv \beta h \quad (34)$$

where we have introduced, for brevity, a function of β only, $g(\beta)$, which will cancel out later on.

When the separation is put in place, the two boxes being identical, they have the same entropy, but one must take into account the fact that there is a probability, P_A , that the corpuscle be in box “A” and a probability, P_B , that the corpuscle be in box “B” and employ Equation (28). Thus:

$$S_{after} = g(\beta) - \frac{\alpha}{\exp(\alpha) - 1} + \ln(1 - \exp(-\alpha)) + \Delta S$$

$$\Delta S = -P_A \ln(P_A) - P_B \ln(P_B) = \ln(1 + \exp(\alpha)) - \frac{\alpha}{1 + \exp(-\alpha)} \quad (35)$$

We have, therefore:

$$S_{after} - S_{before} = -\frac{\alpha}{\exp(\alpha) - 1} + \ln(1 - \exp(-\alpha)) + \ln(1 + \exp(\alpha)) - \frac{\alpha}{1 + \exp(-\alpha)} + \frac{2\alpha}{\exp(2\alpha) - 1} - \ln(1 - \exp(-2\alpha)) = 0 \quad (36)$$

Thus, the entropy remains unchanged when the separation is restored.

To summarize, if we consider an adiabatic cylinder of height $2h$, the entropy for the corpuscle is given by the standard formulas, with h being replaced by $2h$. When a separation is introduced half-way, the standard formula applies, but one must add the quantity denoted above, ΔS , that accounts for the fact that we do not know with certainty whether the corpuscle is in the lower or upper box. Then, we find that the entropy is unchanged. If the separation is removed, the entropy again remains the same.

This result obtains for any (infinitely thin) separations. If we thus consider a cylinder of height h in the limit of a large number, $n \equiv h/dz$, of separations whose distances are dz , the term, ΔS , in Equation (28) becomes the integral from zero to h of $-\rho(z) \ln(\rho(z))$, where $\rho(z) \propto \exp(-\beta z)$ is the probability of having a corpuscle between z and $z + dz$ (or the corpuscle density for a large number of corpuscles). All the slices of height dz being identical, they have the same entropy. Adding ΔS enables one to recover the expression for the entropy of a cylinder of height h , employing only the barometric law and the expression of the entropy for a vanishingly small value of h , that is, with a negligible weight acting on the corpuscle. This view-point generalizes the one considered in [1], which was restricted to the non-relativistic approximation and did not make reference to the Gibbs paradox. This entropy result is readily generalized to any potential, $\mathcal{P}(z)$, since the barometric law is known. Thus, the term, ΔS , is not an addition to the conventional classical thermodynamic expression of entropy, which would be involved when cylinders are split into parts. Without it, *classical* thermodynamics would be inconsistent.

Finally, consider a thermally insulated perfect gas (no weight, non-relativistic, single corpuscle) expanding freely. Because the internal energy depends only on temperature and no work is performed in free expansion, the temperature remains a constant, and we may set, for simplicity, $\theta = 1$. When

the corpuscle, initially in box A, is allowed to move freely in A + B by removing a separation, the entropy is increased by $\delta S = \ln(2h) - \ln(h) = \ln(2)$, because at constant temperature, the entropy may be taken to be $\ln(h)$ when the corpuscle is in box A and $\ln(2h)$ when the corpuscle is in box A + B. Next, the corpuscle is forced to return to its initial location (box A) by a piston. In the isothermal regime (the cylinder being now in contact with a heat bath at $\theta = 1$), the work performed by the piston is $\delta W = \delta Q = \delta S = \ln(2)$, as we have seen before in Equation (21). In a Carnot cycle, for example, this work would entail a cycle efficiency lower than the Carnot efficiency: this the cost that has to be paid for having allowed a free expansion. This in effect means that the cycle is no longer reversible.

However, when, on the other hand, the corpuscle is in box A with probability 1/2 and in box B with probability 1/2 and the separation is removed, the initial situation may be recovered simply by restoring the separation. In that case, there is no change in entropy, as expected intuitively. Indeed, in the initial configuration, we must account for the uncertainty entropy, $\Delta S = \ln(2)$, defined in Equation (28). Thus, the initial entropy is $\ln(h) + \ln(2)$. The final entropy, $\ln(2h)$, is, therefore, the same as initially, that is, the Carnot efficiency is now unaffected: the cycle just described is reversible.

9. Conclusions

Let us recall the concepts introduced in the present paper. One can imagine that after having introduced the notion of corpuscles moving in vacuum, Democritus observed the elastic bounces of a unit weight on a balance and defined the weight “impulse” from the motion period. Not knowing the nature of the motion, he may have thought of introducing an energy distribution, such that the average force, $\langle F \rangle$, *does not depend* on the law of motion. This, as we have seen, may be done. This distribution involves, for dimensional reasons, a quantity, θ , having the dimension of energy. Considering a thermal engine operating between two baths at temperatures θ_c , θ_h , one finds, on the basis of the principles just stated, without any further assumptions, that the maximum efficiency is $1 - \theta_c/\theta_h$. This allows us to call θ the thermodynamic temperature, defined only up to a constant factor. The latter may be fixed by conceding, for example, that $\theta = 1$ at the hydrogen triple point.

The present paper provides a first-principle proof of the barometric and ideal-gas laws, including a possible effect of a corpuscle weight, w , with no knowledge of the round-trip time function, $\tau(\cdot)$, being required. Explicit expressions of the kinetic part of the internal energy may be obtained, however, only when the round-trip time function is known to within an arbitrary constant factor or, equivalently, when the kinetic part of the corpuscle Hamiltonian is known. The ideal-gas internal kinetic energy depends only on temperature, while the ideal-gas internal potential energy, divided by θ , is a simple analytic function of h/θ . Since the theory presented is strictly classical, the universal constant, $\hbar$, is needed only to make the results dimensionless. We have proven the stability of the gas from the equations obtained for the force, $\langle F \rangle$, and the internal energy, U . We have also shown that, at least for ideal gases, the energy and the entropy are unchanged when a separation is introduced and considered the case of free expansion. The case of non-constant weights has been treated, based on the same concepts, in [4], with results that agree with the Gibbs phase integral.

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Conflicts of Interest

The authors declare no conflict of interest.

Appendix

A. The Hamilton Formalism

We consider a Hamiltonian of the form

$$\mathcal{H}(p, z) = \mathcal{K}(p) + \mathcal{P}(z) \quad (37)$$

whose value can be considered as the corpuscle energy: $E = \mathcal{K}(p_o) + \mathcal{P}(z_o)$ for some initial values of p and z . $\mathcal{P} = w z$ is the potential energy, with $-w$ the force exerted on the corpuscle.

The equations of motion are:

$$v \equiv \frac{dz}{dt} = \frac{d\mathcal{K}}{dp} \quad \frac{dp}{dt} = -\frac{d\mathcal{P}}{dz} = -w \quad (38)$$

They are best understood in wave optics terms, see for example [13], with $E = \hbar\omega$, $p = \hbar k$. The quantity analogous to energy is the wave angular frequency $\omega \equiv 2\pi$ divided by the time period, and the quantity analogous to momentum p is the wave number (2π divided by the space period), that is: $\hbar\omega = \mathcal{K}(\hbar k) + \mathcal{P}(z)$. The first relation in Equation (38) says that the group velocity v is the derivative of $\omega(k)$ with respect to k , as one can easily see graphically by tracing two arrays of parallel lines on a plane with slightly different time and space periods.

The solution of the second equation in Equation (38) is: $p = p_o - w t$. Provided $w \neq 0$ we may select a time origin such that this relation reads: $p = -w t$. This is assumed henceforth.

Through a second-order expansion we take $\mathcal{K}(p)$ to be of the form: $a_o + a_1 p + a_2 p^2$ where a_o, a_1, a_2 are constants, and obtain:

$$\frac{dz}{dt} = a_1 + 2a_2 p = a_1 - 2a_2 w t, \quad z = z_o + a_1 t - a_2 w t^2 \quad (39)$$

with z_o a constant. The energy is equal to $w z_m$ where z_m is the maximum altitude reached by the corpuscle at time $t_m = \frac{a_1}{2a_2 w}$, hence $z_m = z_o + \frac{a_1^2}{4a_2 w}$. The round-trip time $\tau = t_2 - t_1$ is the difference of the successive times at which $z = 0$, that is $t_{1,2}$ are the two solutions of: $a_2 w t^2 - a_1 t + \frac{a_1^2}{4a_2 w} - z_m = 0$. For $a_1 = 0$ we obtain: $\tau = 2\sqrt{\frac{z_m}{a_2 w}} = 2\sqrt{\frac{2m z_m}{w}}$ if we set: $a_2 \equiv \frac{1}{2m}$. The same result is obtained for any value of a_1 . The non-relativistic approximation is thus a straightforward application of the second-order expansion of any $\mathcal{K}(p)$ function.

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