



HAL
open science

On Classical Ideal Gases

Jacques Arnaud, Laurent Chusseau, Fabrice Philippe

► **To cite this version:**

Jacques Arnaud, Laurent Chusseau, Fabrice Philippe. On Classical Ideal Gases. 2011. hal-00615244v1

HAL Id: hal-00615244

<https://hal.science/hal-00615244v1>

Preprint submitted on 18 Aug 2011 (v1), last revised 19 Apr 2013 (v5)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

On Classical Ideal Gases

Jacques ARNAUD *, Laurent CHUSSEAU †, Fabrice PHILIPPE ‡

August 18, 2011

Abstract

The air density on earth decays as a function of altitude z approximately according to an $\exp(-wz/\theta)$ -law, where w denotes the weight of a nitrogen molecule and $\theta = k_B T$ where k_B is a constant and T is the thermodynamic temperature. To derive this law one usually invokes the Boltzmann factor, itself derived from statistical considerations. We show that this (barometric) law may be derived solely from the democritian concept of corpuscles moving in vacuum. We employ a principle of simplicity, namely that this law is *independent* of the law of corpuscle motion. This view-point puts aside restrictive assumptions that are source of confusion. Similar observations apply to the ideal-gas law. In the absence of gravity, when a cylinder terminated by a piston, containing a single corpuscle and with height h has temperature θ , the average force that the corpuscle exerts on the piston is: $\langle F \rangle = \theta/h$. This law is valid at any temperature, except at very low temperatures when quantum effects are significant and at very high temperatures when the corpuscle may split into smaller parts. It is usually derived under the assumption that the temperature is proportional to the corpuscle average kinetic energy, or else, from a form of the quantum theory. In contradistinction, we show that it follows solely from the postulate that the ideal-gas law is independent of the law of corpuscle motion. On the physical side we employ only the concept of potential energy. A consistent picture is offered leading to the barometric law when $wh \gg \theta$, and to the usual ideal-gas law when $wh \ll \theta$. Most of the end results are known, but the method appears to be novel. The mathematics being elementary (no integration is needed), the present paper should facilitate the understanding of the physical meaning of the barometric and ideal-gas laws.

*Mas Liron, F30440 Saint Martial, France

†Institut d'Électronique du Sud, UMR n°5214 au CNRS, Université Montpellier II, F34095 Montpellier, France

‡LIRMM, UMR n°5506 au CNRS, 161 rue Ada, F34392 Montpellier, France

1 Introduction

The purpose of this paper is to show that the barometric and ideal (or perfect)-gas laws may be obtained on the sole basis of the democritian 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 (non-relativistic, relativistic, or otherwise: see Appendix A). The temperature θ enters into these laws solely for dimensional reasons. We show from the general expressions of the gas internal energy and of the force (or pressure) that the heat delivered by the gas is θdS , an expression of the entropy S being given. This result enables us to prove that the formally-introduced temperature θ is a thermodynamic temperature. Indeed, we recover for ideal gases the general Carnot result asserting that the maximum efficiency of thermal engines is: $1 - \theta_l/\theta_h$, where θ_l denotes the cold bath temperature and θ_h the hot bath temperature. An alternative derivation of the Carnot result, also based on the concept of potential energy, may be found in [1, 2].

The reader may feel that our statement that the above invariance principle *implies* the barometric and ideal-gas laws, without anything else, is surprising. Yet, we hope that we can convince him/her that this is indeed the case. On the other hand, a quick reading of standard books on Thermodynamics may lead other readers to believe that this is a well-known fact. Indeed, Callen [3] writes on p. 239: “The essence of the ideal-gas law is that molecules of the gas do not interact. This simple fact *implies* (see Sec. 16.10), that $PV \propto NT$ ”. However, when one looks at that section of the book, on p. 372, one finds that the author, in order to reach this conclusion, needs postulate the Newtonian law of motion, quantum theory, and the Boltzmann factor. The claim that corpuscle independence entails the ideal-gas law (without anything else) therefore does not appear to have been justified in such books.

Let us emphasize that our goal is to derive the barometric and ideal-gas laws from first principles, only conservation of potential energy being assumed. We do not use the concept of kinetic energy, nor do we postulate any law of corpuscle motion. Accordingly, a given potential $\phi(z) = wz$ for a weight w does not imply any specific law of motion $z(t)$. Because the presence of corpuscles affects negligibly the gravitational potential, one may consider the latter as an *external* potential. In contradistinction, the electrical field due to charged corpuscles may not be negligible compared to the external electrical field.

To our knowledge, the concept presented in this paper has not been considered before. However, the final expressions relating to the ideal-gas law in the presence of gravity are known, see for example Landsberg [4].

Concepts relating to heat since the antiquity: From Boyle’s time (*circa* 1660) to Carnot’s time (*circa* 1824), the most popular theory, usually referred to as the “caloric theory of heat”, considered heat as a kind of fluid consisting of weightless mutually repelling particles, attracted by matter. This fluid could flow from hotter to colder matter, see Levermore [5]. This hypothesis, however, did not explain Rumford’s experiments showing that friction alone generates heat. Doubts about the validity of the caloric theory were expressed in Carnot’s notes, published after his early death. As a matter of fact, the alternative model of heat as a form of *matter* motion (without any additional fluid) had already been enunciated in the antiquity.

Democritus, who lived about 300 years B.C., described nature as a collection of corpuscles that cannot be split, moving in vacuum. These corpuscles differ from one-another in form, position and weight. In the case of a gas, interaction between corpuscles may often be neglected, but they collide with the container’s walls. Platon [6] ascribed heat to corpuscular motion: “Heat and fire are generated by impact and friction, but that’s motion”. Much later, Francis Bacon (1561-1626) wrote: “The very nature of heat is motion, and nothing else”. This view-point is

more explicit in Daniel Bernoulli writing (1738): “Gas atoms are moving randomly, and pressure is nothing else but the impact of the atoms on their container walls”. Lastly, Carnot introduced energy considerations *circa* 1830: “Heat is nothing but motive power, or rather another form of motion. When motive power is destroyed, heat is generated precisely in proportion of the motive power destroyed. Likewise, when heat is destroyed, motive power is generated”.

In the present paper, we employ the law of conservation of potential energy, well known since the antiquity from cords and pulleys experiments, rather than the concept of kinetic energy introduced by Leibniz (1646-1716). The Leibniz form is now recognized as being valid at small temperatures only ($\theta \equiv k_B T \ll mc^2$, where mc^2 denotes the corpuscle rest energy). It should be recalled that the thermodynamic temperature is generally *not* proportional to the average kinetic energy.

Experimental results relating to air: The first accurate experiments relating to gases relied on the invention of the thermometer by Galileo and of the barometer by his assistant Torricelli. Then, to Pascal experiments on atmospheric pressure. Pascal ascribed the diminution of the height of a mercury column as a function of altitude to the reduction of the weight of the air above the barometer. It was later shown that the pressure decays exponentially (or more precisely as the sum of two exponentials, one relating to nitrogen, and one relating to oxygen).

Let us recall the crucial experiments performed in the seventeenth century concerning the properties of air. Air, consisting mostly of di-atomic nitrogen, may be viewed as an ideal gas. When a tight box contains some amount of air, the volume-pressure product is a constant at room temperature, a law enunciated for the first time by Boyle in 1660: “Pressure and expansion are in reciprocal proportions”. Boyle employed a J-shaped glass tube, with the sealed small side full of air, and the other full of mercury. The left-side height was a measure of volume and the right-side height a measure of pressure. Subsequent experiments have shown that this law is applicable at any constant temperature, for example at various liquid boiling temperatures, within some experimental range. We call “generalized Boyle law” the expression: $V(P, \theta) = f(\theta)/P$, where P represents pressure, V volume, and $f(\theta)$ some temperature measure.

From an experimental standpoint we could define temperature as the pressure relating to some given amount of matter contained within some fixed volume. As the temperature gets higher the pressure increases. This pressure may be used to define θ . Of course, different temperature scales would be obtained for different substances, but such thermometers may be calibrated one against another because temperatures tend to equalize in equilibrium. Rarefied helium may be described with great accuracy as a collection of independent corpuscles, except perhaps at very low temperatures when quantum effects become significant and at very high temperatures when the helium atoms may get ionized. The theory presented in this paper shows on the basis of the corpuscular model that θ , initially introduced formally from dimensional considerations, coincides with the thermodynamic temperature. This is the temperature that enters in the expression of thermal-engine efficiencies.

Gay-Lussac has shown in 1802 that, at atmospheric pressure, the volume increment of various gases from freezing to boiling water temperatures is 37.5, see for example Holbrow [7]. Appropriate gas thermometers enabled experimentalists to establish the proportionality of volume and temperature at constant pressure. This measurement was subsequently made at various pressures, for example at various altitudes. The generalized Gay-Lussac law may be enunciated as follows: The two-variable function $V(P, \theta) = \theta g(P)$, where $g(P)$ is some unknown function of pressure. Comparison of the generalized Boyle and Gay-Lussac laws shows that: $PV = \theta h(N)$, where $h(N)$ defines the amount of gas considered.

The empirical Gay-Lussac law makes sense only if one specifies which thermometer is being employed. One may employ a gas thermometer from a selected gas such as helium in two

ways. One method consists of defining the temperature as the cylinder height (or volume) at a fixed pressure, for example at the standard atmospheric pressure. In the following, we assume that a second method is being employed instead: the temperature is defined as the force that must be exerted on the piston to maintain the height at a fixed value, for example one meter. If the Gay-Lussac experiment were applied to a gas identical to the gas employed in the thermometer (helium in our example) the fact that pressure is proportional to temperature would be obvious. The importance of the Gay-Lussac experiment is that the proportionality law is found to be approximately valid for any gas. It was subsequently discovered that the Gay-Lussac law is reasonably accurate only at very small pressures. The theoretical reason that explains this observation is that, at low pressures, the molecules of the tested gas and those of the thermometer gas may both be considered as independent non-interacting corpuscles.

In 1803, Dalton, on the basis of his studies of chemical compounds and gaseous mixtures suggested that matter consists of atoms of different masses that combine in simple ratios. He discovered the partial-pressure law according to which the total pressure exerted by a gas mixture is equal to the sum of the pressure that each one of the gases would exert if it occupied the full volume alone. Finally, in 1811, Avogadro concluded that equal volumes of gases at the same temperature and pressure contain the same number of molecules (or corpuscles). This entails that PV/θ is proportional to N , now interpreted as the number of corpuscles.

On empirical grounds, the ideal-gas law may therefore be written as:

$$PV = N\theta \tag{1}$$

where V denotes the volume, P the pressure, N the number of corpuscles, and $\theta \equiv k_B T$ the temperature.

The ideal-gas law has been partly explained on the basis of a kinetic theory by Waterston [8] in 1843, the kinetic theory being based itself on non-relativistic mechanics. The next important theoretical discovery is due to Boltzmann. Let us now recall the basic assumptions on which rest the usual proofs of the barometric and ideal-gas laws, and then present our model.

Usual kinetic and statistical theories A recent reference by Miller [9] lists the assumptions on which the gas kinetic theory is supposed to rest. Some of them express the democritian hypothesis and are indeed essential. The usefulness of the others, listed below, however, may be questioned:

1. Gases consist in corpuscles having non-zero mass.
2. The corpuscles are quickly moving.
3. They are perfectly spherical and elastic.
4. The average kinetic energy depends only on the system temperature.
5. Relativistic effects are negligible.
6. Motion laws are time reversible.
7. The number of molecules is so large that a statistical treatment is appropriate.

Comment: As we shall show, none of the above assumptions are needed. It suffices that the (perhaps unique) corpuscle be in thermal contact with the ground. Besides, item 4 (The average kinetic energy *depends* only on the system temperature) is insufficient to establish the ideal-gas law because the temperature remains undefined. In the non-relativistic approximation the

appropriate assumption should read: “The average kinetic energy is *proportional* to the system temperature”. But at arbitrary temperatures this assumption is false.

Let us sketch the most usual derivations of the barometric and ideal-gas laws to remind the readers of the underlying assumptions. Note that the barometric law may be obtained from the ideal-gas law, and conversely, if one postulates that weightless infinitely-thin plates may be introduced or removed at will in the gas at various altitudes. However, this postulate is at best plausible. Norton [10] derived the ideal-gas law from the barometric equation. But the latter involves the Boltzmann factor that requires other physical considerations (see below), while in the present paper this factor comes in naturally, that is, for purely mathematical reasons.

The barometric law is usually viewed as a straightforward consequence of the Boltzmann factor: the probability that a corpuscle has energy E is proportional to: $\exp(-E/\theta)$ where $\theta = k_B T$ and the energy $E = w z$, where w denotes the corpuscle weight (e.g., the weight of a di-atomic nitrogen molecule) and z the altitude. Hence the exponential decay.

The derivation of the Boltzmann factor itself is based on a quantization of the energy¹, and the postulated equi-probability of the micro-states. Let the discrete (non-degenerate) energy levels be denoted by $\varepsilon_1, \varepsilon_2, \dots$. If distinguishable corpuscles are distributed among the energy levels, with n_1 corpuscles in level 1, n_2 corpuscles in level 2, and so on, the number of ways of doing that is inversely proportional to: $n_1! n_2! \dots$. It is postulated that this number reaches its maximum value at equilibrium under the constraint that $n_1 + n_2 + \dots = N$, the total number of corpuscles, and $n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots = E$, the total energy. In the limit of large N values, one finds that: $n_i \propto \exp(-\varepsilon_i/\theta)$, for some θ -value that depends on N and E . Even though physicists are now-a-day very familiar with that procedure, it is not so easy to explain it to students. Besides, it rests on a number of assumptions.

The traditional derivation of the ideal-gas law, on the other hand, is based on non-relativistic mechanics. For a one-dimensional model, one considers a corpuscle moving back and forth between two plates separated by a distance h , one of them playing the role of a piston. If v denotes the speed of a corpuscle, an impact on a plate delivers to it an impulse $2 m v$ where m denotes the corpuscle mass, and this occurs every $2h/v$ time units. It is concluded that the force F exerted on the piston is: $2 m v / (2h/v) = m v^2 / h$, that is: $F h = 2 K$, where $K = \frac{1}{2} m v^2$ denotes the kinetic energy. It is recognised that there may be a distribution of kinetic energies. Postulating that the temperature θ is proportional to the average kinetic energy one obtains for the average force the ideal-gas law: $\langle F \rangle h \propto \theta$. Alternatively, one may quantize the corpuscle wave-function and employ the Boltzmann factor.

The procedure described above has been generalized to relativistic motion ($k_B T \sim m c^2$), where $m c^2$ denotes the corpuscle rest energy, but the relation of v to p is different, and averaging requires a generalized Boltzmann factor. The same ideal-gas law is valid at any temperature (within the corpuscular model). Our thesis is that the ideal-gas law has simply nothing to do with the law of corpuscle motion, and that it is therefore not surprising that it holds for both the Galileo and Einstein laws of motion. The assumption that temperature is proportional to the average kinetic energy cannot possibly be derived from first principles since it is only an approximation acceptable when $k_B T \ll m c^2$. These are some of the reasons why we feel that the traditional proofs are unsatisfactory. An alternative is offered below. We will consider in succession the barometric law, the ideal-gas law, and the internal energy. We finally show that the formally introduced temperature θ is the thermodynamic temperature. Expressions for the round-trip time of a corpuscle from and back to the ground $z=0$ level, denoted by τ , is derived in Appendix A. The case of non-linear potentials was treated by the same method in [12].

¹This concept was introduced by Boltzmann who, however, considered only the limit in which the difference between successive energies is arbitrarily small.

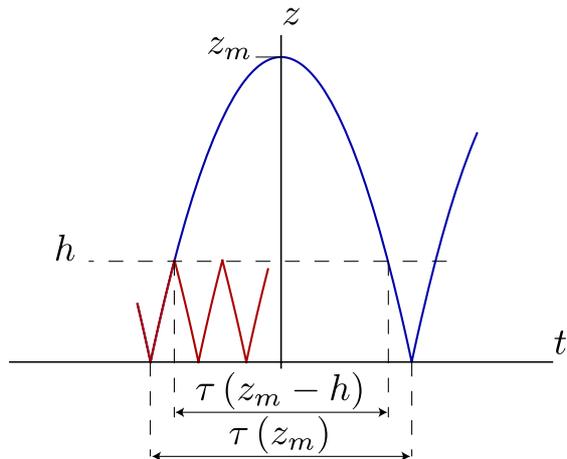


Figure 1: Space-time (z, t) trajectory of a corpuscle of unit weight ($w = 1$) bouncing off the ground ($z = 0$). The maximum altitude reached by the corpuscle is $z_m = E$, where E denotes the energy. The motion is periodic with period $\tau(z_m)$, where $\tau(Z)$ denotes the corpuscle round-trip time at a distance Z from the top of the trajectory. When the altitude is restricted to h by a plate (dashed horizontal line) the motion remains periodic with a period evidently equal to: $\tau(z_m) - \tau(z_m - h)$.

2 The barometric law

We are considering an unit-area cylinder with vertical axis in uniform gravity, resting on the ground ($z = 0$) at some temperature. We consider only motion along the vertical z -axis, denoted in general by $z = z(t; E)$, where t denotes time. The corpuscle energy is defined as: $E \equiv w z_m$ where w is the corpuscle weight and z_m the maximum altitude. In the following, some regularity of the $z(t)$ -function is assumed, but no specific law is presumed, except in examples. We set for convenience $t = 0$ at the top of the trajectory, that is: $z(0) = z_m$, $z'(0) = 0$, where a prime denotes a derivative with respect to t .

Consider a single period of corpuscle motion as shown in Fig. 1. Let the corpuscle distance from the top of its trajectory be denoted by $Z \equiv z_m - z \geq 0$, at times t_1 and $t_2 \geq t_1$. We call²: “round-trip time” $\tau(Z) \equiv t_2 - t_1$. Because gravity is static and uniform (that is, independent of altitude and time) this τ -function depends only on Z . As an example, for non-relativistic motion: $Z(t) = \frac{1}{2}gt^2$, with $w \equiv mg$ where m denotes the corpuscle mass and g the gravitational acceleration. In that example: $\tau(Z) = 2\sqrt{2Z/g} \propto \sqrt{Z}$, g being a constant.

The period of motion of a corpuscle bouncing off the ground ($z = 0$) without any loss of energy (rigid walls and negligible gas friction), and having energy $E \equiv w z_m$, is according to the above definitions: $\tau(z_m)$. The time spent by the corpuscle above some z -level is obviously zero

²We do not assume that $z(t) = z(-t)$ or $t_2 + t_1 = 0$. Asymmetric laws of motion occur if one employs clock synchronisation rules different from the one proposed by Einstein. For example, if a light pulse emitted from $z = 0$ at $t = 0$ propagating upward is employed to synchronise clocks located at different altitudes, the apparent upward speed of light is, by this convention, infinite. The downward speed of light is then $c/2$ if c denotes the Einstein speed of light, so that the two-way speed of light remains equal to c , in agreement with very precise experiments. The anisotropy mentioned in the present note refers to a change of formalism, not of physics. It is of some importance that the laws discussed in this paper do not depend on such conventional changes.

if $z > z_m$. The fraction of time during which the corpuscle is above z is:

$$\text{fraction of time above } z = \frac{\tau(z_m - z)}{\tau(z_m)}, \quad (2)$$

if $z \leq z_m$, as suggested on Fig. 1.

We now suppose that the ground on which the corpuscle is bouncing off has been heated to some temperature (the concept of temperature will be precisely defined later on). This means that the ground level ($z=0$) is not perfectly static as assumed above, but instead is quivering. Concretely, the ground level could be moving up and down according to some zero-mean fluctuation of small amplitude so that, upon impacting on the ground, the corpuscle may lose energy (when the ground level is moving downward), or gain energy (when the ground level is moving upward). We will not need the explicit form of this fluctuation. We only assume that the amplitude of that fluctuation is so small that the corpuscle energy does not vary significantly over many periods. Yet it may evolve slowly. The energy distribution $\omega(E)$ refers to averages over arbitrarily long times, and is presently unknown; it will be determined by enforcing the condition that the law of interest (presently the barometric law) does not depend on the corpuscle law of motion.

On the average, the fraction of time \mathcal{A} during which the corpuscle is above some z -level is, according to (2), and remembering that $z_m = E/w$ where w is a constant:

$$\mathcal{A}(z) = \frac{\int_{wz}^{\infty} dE \omega(E) \tau(E/w - z)/\tau(E/w)}{\int_0^{\infty} dE \omega(E)}. \quad (3)$$

The lower limit of the integral in the numerator is wz since the fractional time is equal to zero when $E \leq wz$.

We now argue that $\omega(E)$ must be: $\exp(-E/\theta)\tau(E/w)$, where θ is a constant having the dimension of energy as is required by the fact that the argument of an exponential is dimensionless. First, let us introduce this distribution law in (3). We obtain:

$$\begin{aligned} \mathcal{A}(z) &= \frac{\int_{wz}^{\infty} dE \exp(-E/\theta)\tau(E/w - z)}{\int_0^{\infty} dE \exp(-E/\theta)\tau(E/w)} \\ &= \frac{\exp(-wz/\theta) \int_{wz}^{\infty} dE \exp(-(E - wz)/\theta)\tau(E/w - z)}{\int_0^{\infty} dE \exp(-E/\theta)\tau(E/w)} \\ &= \frac{\exp(-wz/\theta) \int_0^{\infty} dE' \exp(-E'/\theta)\tau(E'/w)}{\int_0^{\infty} dE \exp(-E/\theta)\tau(E/w)} \\ &= \exp(-wz/\theta). \end{aligned} \quad (4)$$

On the third line, we have used as an integration variable $E' \equiv E - wz$ instead of E . The last line follows from the fact that E, E' are dummy variables, so that we may replace E' by E . Note that, even though we have introduced integral signs, no integration has been performed.

The distribution $\omega(E)$ introduced above is the one that leads to a result (last line of (4)) independent of the particular form of the $\tau(Z)$ -function, and therefore of the law of motion. For a purely mathematical reason, the term: $\tau(E/w)$ must be there to cancel a similar term in the denominator of the expression of the fractional time. On the other hand, the only function of $u \equiv E/\theta$ that may cause the integral in the numerator to go from 0 to infinity and cancel out with the integral in the denominator is: $\exp(-u)$, the argument being defined only to within a constant factor. In order to obtain the energy distribution $\omega(E)$, one would need to know the function $\tau(Z)$. But, remarkably, the energy distribution is not needed explicitly.

From a physical standpoint, the energy distribution may be written as $\exp(-E(f)/\theta)$, where f denotes the action, equal to the $z(t)$ motion area for one period, and $df/dE = \tau(E/w)$. In quantum mechanics the action f is set equal to an integer (1,2,..., ignoring a small constant) times the reduced Planck constant \hbar . The term $\exp(-E/\theta)$, usually referred to as the “Boltzmann factor”, enters here solely by mathematical necessity [2].

The gas density, defined as the probability that the corpuscle be located between z and $z+dz$, divided by dz , is: $\rho(z) = -d\mathcal{A}(z)/dz = (w/\theta) \exp(-wz/\theta)$. This is the barometric law. Since w and θ are constant, the density decays exponentially as a function of altitude z . In the earth atmosphere the density of di-atomic oxygen decays faster than the density of di-atomic nitrogen because the weight of an oxygen atom exceeds that of a nitrogen atom in the ratio $\approx 16/14$.

3 Average force exerted by a corpuscle on a piston

We now treat the ideal-gas law by similar methods. We are considering again a unit-area cylinder with vertical axis in uniform gravity, resting on the ground ($z = 0$) at some temperature. A tight piston can move in the vertical z direction. The cylinder height is denoted by h and contains a single corpuscle of weight w . In our one-dimensional model, the pressure P corresponds to the average force $\langle F \rangle$, the volume V to the height h , and $N = 1$. Our result provides the ideal-gas law in a generalized form, taking into account gravity. In that case, the pressure varies as a function of altitude. More precisely, the force exerted by the corpuscle on the lower end of the cylinder exceeds the force exerted on the upper end (or piston) by the corpuscle weight. But in the absence of gravity, the forces exerted on both ends are the same.

We are introducing (static and uniform) gravity, not so much for the sake of generality, but because this helps clarify the concept of corpuscle energy: the corpuscle energy is defined as the maximum altitude that the corpuscle would reach in the absence of the piston, multiplied by the corpuscle weight. Precisely, the maximum height reached by a corpuscle of weight w and energy E in the absence of a piston is: $z_m \equiv E/w$, the corpuscle bouncing elastically from the ground, that is, without any loss or gain of energy.

Consider first the case where h is infinite, that is, in the absence of a piston. The time period is denoted as before by $\tau(Z)$ with $Z = z_m$. The average force exerted on the ground, equal to the corpuscle weight w , is the product of the impulse i and the number of impulses per unit time. Thus $w = i/\tau(z_m)$, and $i = w\tau(z_m)$. In other words, the impulse transmitted to a piston when the corpuscle impacts on it is the product of the corpuscle weight and the motion period.

If the plate is located at $z = h$ the impulse is: $i_h = w\tau(z_m - h)$. When the corpuscle is moving back and forth between the planes at $z = 0$ and $z = h$ (instead of being located above h) the impulse is just opposite to i_h . It is therefore in absolute value equal to $w\tau(z_m - h)$.

Next, we introduce a rigid thin plate at $z = h$, viewed as a piston, and consider a corpuscle bouncing on the $z = 0$ and $z = h$ plates alternately. The time period becomes: $\tau(z_m) - \tau(z_m - h)$, as one can see from inspection of the figure. We call F the force exerted on the $z = h$ plate, averaged over a time period. It follows from the previous expressions that:

$$\begin{aligned}
 F &= 0 & z_m &\leq h \\
 F &= \frac{i_h}{\tau(z_m) - \tau(z_m - h)} = w \frac{\tau(z_m - h)}{\tau(z_m) - \tau(z_m - h)} & z_m &> h.
 \end{aligned}
 \tag{5}$$

As a consequence of the slight quivering of the cylinder lower end (thermal motion), the corpuscle energy E slowly varies in the course of time. The force F just defined must be weighed by some energy distribution $\omega(E)$ in such a way that the average force $\langle F \rangle$ be *independent* of the corpuscle equation of motion, and thus of the $\tau(\cdot)$ -function. In the limit where $wh \ll \theta$, a

condition that amounts to ignoring gravity, we obtain the ideal-gas law in the form: $\langle F \rangle = \theta/h$. We later on prove that θ is the thermodynamic temperature.

The above condition obtains from (5) if one selects the following energy distribution:

$$\begin{aligned}\omega(E) &= \exp(-E/\theta)\tau(E/w) & E \leq wh \\ \omega(E) &= \exp(-E/\theta)(\tau(E/w) - \tau(E/w - h)) & E > wh,\end{aligned}\quad (6)$$

where θ has the dimension of an energy. For the case where $E \leq wh$, the $\omega(E)$ -distribution is of course the same as in Section 2. The average force becomes, using (5) and (6):

$$\begin{aligned}\langle F \rangle &= w \frac{\int_{wh}^{\infty} dE \exp(-E/\theta)\tau(E/w - h)}{\int_0^{wh} dE \exp(-E/\theta)\tau(E/w) + \int_{wh}^{\infty} dE \exp(-E/\theta)(\tau(E/w) - \tau(E/w - h))} \\ &= \frac{w}{\exp(wh/\theta) - 1}.\end{aligned}\quad (7)$$

In the above integrals going from wh to ∞ we have replaced $\exp(-E/\theta)$ by $\exp(-wh/\theta)\exp(-(E-wh)/\theta)$ and introduced the variable $E' \equiv E-wh$, so that all the integrals go from zero to infinity and cancel out. Note that no integration has been performed.

For a collection of N independent corpuscles having weights w_i , $i = 1, \dots, N$ respectively, the force is a sum of N terms of the form given in 7. In the case of zero gravity ($w=0$ or more precisely: $wh \ll \theta$), the above expression gives: $\langle F \rangle h = \theta$. Thus we have obtained the ideal-gas law: $\langle F \rangle h = N\theta$.

The average force from the barometric law: We show in the present paragraph that the expression in (7) of the average force may be obtained alternatively from the barometric law established in Section 2: $\rho(z) = C \exp(-wz/\theta)$, where C is a constant, if one uses the concept that plates may be added or removed at some altitude $z = h$.

Indeed, the gas weight above the plate is the integral of $w\rho(z)$ from $z = h$ to $z = \infty$. Since we consider a single corpuscle located between 0 and h the integral of $\rho(z)$ from 0 to h must be unity, a condition that determines C . Thus, from that view point, the average force may be written as:

$$\langle F \rangle = w \frac{\int_h^{\infty} dz \exp(-wz/\theta)}{\int_0^h dz \exp(-wz/\theta)} = \frac{w}{\exp(wh/\theta) - 1}, \quad (8)$$

that coincides with our previous result in (7).

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. Motion of the corpuscle along directions perpendicular to z does affect the round-trip time $\tau(Z)$. However, since the average force does not depend on this quantity, the ideal-gas law is unaffected.

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 3. It would be incremented further by corpuscle rotation or vibration, not considered here. Using conventional methods, Landsberg [4] in Eq. (2.6), and Louis-Martinez [14] in Eq. (68), obtain exactly the same result as given above (except for the factor 3 in the expression of 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 , if only motion along the z -axis is considered (note that the gravitational energy is accounted for in U). The expression of U is, using the energy distribution given in (6):

$$\begin{aligned}
 U &= \frac{\int_0^{wh} dE E \exp(-E/\theta) \tau(E/w) + \int_{wh}^{\infty} dE E \exp(-E/\theta) (\tau(E/w) - \tau(E/w - h))}{\int_0^{wh} dE \exp(-E/\theta) \tau(E/w) + \int_{wh}^{\infty} dE \exp(-E/\theta) (\tau(E/w) - \tau(E/w - h))} \\
 &= \frac{\int_0^{\infty} dE E \exp(-E/\theta) \tau(E/w)}{\int_0^{\infty} dE \exp(-E/\theta) \tau(E/w)} - \frac{wh}{\exp(wh/\theta) - 1}.
 \end{aligned} \tag{9}$$

The internal energy divided by the temperature: $U(\theta, h)/\theta$, thus is the sum of two terms. The second one is an explicit function of the dimensionless quantity wh/θ , which tends to -1 when $h \rightarrow 0$. The first term is a function of θ but not of h . To evaluate this first term we need to know the round-trip time $\tau(Z)$ to within an arbitrary proportionality factor, and an integration must be performed in that case.

In order to write the above expression in terms of dimensionless quantities, we must introduced a universal constant, c , having the dimension of speed. Defining: $x \equiv E/\theta$, $\theta' \equiv \theta/mc^2$, $h' \equiv h/(c^2/g)$, (9) becomes, remembering that $w = mg$:

$$\frac{U}{\theta} = \frac{\int_0^{\infty} dx x \exp(-x) f(\theta' x)}{\int_0^{\infty} dx \exp(-x) f(\theta' x)} - \frac{h'/\theta'}{\exp(h'/\theta') - 1}, \tag{10}$$

where the function $f(y)$ depends on the round-trip time.

In the special case of non-relativistic motion $y \ll 1$, we have $f(y) \propto \sqrt{y}$, see the appendix. The first term in (10) is then equal to $3/2$ (note that: $2 \int_0^{\infty} dx x \exp(-x) \sqrt{x} = 3 \int_0^{\infty} dx \exp(-x) \sqrt{x}$), so that in the absence of gravity the internal energy U is equal to $3\theta/2 - \theta = \theta/2$, a well-known result.³

5 The energy θ is the thermodynamic temperature

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

The expressions given earlier for the average force $\langle F \rangle$ in (7) and the internal energy U in (9) may be written, setting $\beta \equiv 1/\theta$, as:

$$\begin{aligned}
 \langle F \rangle &= \frac{\partial \ln(Z)}{\beta \partial h} & U &= -\frac{\partial \ln(Z)}{\partial \beta} \\
 Z(\beta, h) &= (\exp(-\beta wh) - 1) \int_0^{\infty} dE \exp(-\beta E) \tau(E/w).
 \end{aligned} \tag{11}$$

Z is essentially the quantity called in statistical mechanics the partition function. It becomes dimensionless if it is divided by the reduced Planck constant \hbar , which however plays here no

³A plot of U from low to high temperatures in the case of an external force much larger than gravity (e.g., an electrical force) can be seen in [1,2]. A three-dimensional expression of U in terms of Bessel functions can be found, for example, in Greiner, p. 234. [19]

physical role. The continuous energy E in the integral may be replaced by closely-spaced discrete energies ε_i , $i = 1, 2, \dots$, the spacing between adjacent energies accounting for the τ -function. This procedure is the one employed in the numerical evaluation of integrals; it does not in itself imply quantization. The factor preceding the integral in (11) entails that the energies ε_i , $i = 1, 2, \dots$ are multiplied by some function of h .

If we introduce the Helmholtz free-energy (the letter A is from the German “Arbeit” or work): $A(\theta, h) \equiv -\theta \ln(Z(\theta, h))$ the expressions in (11) are conveniently written⁴:

$$\langle F \rangle = -\frac{\partial A}{\partial h} \quad U = A - \theta \frac{\partial A}{\partial \theta}. \quad (12)$$

From (12) we obtain:

$$-\delta Q \equiv dU + \langle F \rangle dh = dA - \frac{\partial A}{\partial \theta} d\theta - \frac{\partial A}{\partial h} dh - \theta d\left(\frac{\partial A}{\partial \theta}\right) = \theta dS \quad S \equiv -\frac{\partial A}{\partial \theta}, \quad (13)$$

where δQ represents the heat released by the gas, from the law of conservation of energy. For any function $f(\theta, h)$ such as U , A , S : $df \equiv \frac{\partial f}{\partial \theta} d\theta + \frac{\partial f}{\partial h} dh$. Note that we employ only two independent variables, namely θ and h , so-that partial derivatives are un-ambiguous. If the gas is in contact with a thermal bath (θ =constant), δQ is the heat gained by the bath. The quantity S defined above is called the “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 adiabatic transformations are isentropic.

The Carnot cycle: A Carnot cycle consists of two isothermal transformations at temperatures θ_l and θ_h , and two intermediate adiabatic transformations ($dS = 0$). After a complete cycle, the entropy recovers its original value and therefore $dS_l + dS_h = 0$. According to (13): $-\delta Q_l = \theta_l dS_l$, $-\delta Q_h = \theta_h dS_h$ and therefore $\delta Q_l/\theta_l + \delta Q_h/\theta_h = 0$. Energy conservation gives the work δW performed over a cycle from: $\delta W + \delta Q_l + \delta Q_h = 0$. The cycle efficiency is defined as the ratio of δW and the heating $-\delta Q_h$ supplied by the hot bath. We have therefore: $\eta \equiv \frac{\delta W}{-\delta Q_h} = \frac{\delta Q_l + \delta Q_h}{\delta Q_h} = 1 - \frac{\theta_l}{\theta_h}$, from which we conclude that θ is the “thermodynamic temperature”.

We have implicitly assumed in the above discussion that the working medium (presently an ideal gas) has reached the bath temperature before being contacted with it. Otherwise, there would be at that time a jump in entropy, and the cycle would no longer be reversible. Given initial θ , h values, the temperature change $d\theta$ for an increment dh in the isentropic regime ($dS = 0$) follows from the relation: $d\theta = -\left(\frac{\partial S/\partial h}{\partial S/\partial \theta}\right)dh$, where $S(\theta, h)$ may be expressed in terms of $Z(\theta, h)$, (11), from the above expressions. The details will be omitted. It suffices to know that θ may be varied by varying h , in a calculable manner, in an adiabatic transformation.

Practical units: The energy $\theta = \langle F \rangle h$ has been defined so far only to within a multiplicative factor, from dimensional considerations. This factor is fixed by agreeing that $\theta = 273.16 k_B$ exactly when the cylinder is in thermal equilibrium with water at its triple point. Here $k_B = 1.38066... \cdot 10^{-23}$ joules, is considered as an energy unit (akin to the calorie = 4.182... joules). This manner of defining θ is equivalent to the usual one, though expressed differently. The dimensionless quantity $T \equiv \theta/k_B$ is the usual unit of thermodynamic temperature, expressed in kelvin.

⁴Note incidentally that: $\frac{\partial U}{\partial h} = \theta \frac{\partial \langle F \rangle}{\partial \theta} - \langle F \rangle$. It follows that, given $\langle F \rangle$, we may obtain $U(\theta, h)$ by an integration over h , provided an unknown function of θ be added. This relation is in fact applicable to any working medium, as one can show by considering a Carnot cycle with small temperature differences (see for example Kubo [20], p. 81).

Next, measurements have shown that the number of atoms in 0.012 kg of carbon 12 is: $N_A \approx 6.0221367 \cdot 10^{23}$. For this quantity of matter (called a mole), the ideal-gas law therefore reads: $\langle F \rangle h = N_A \theta$, or: $PV = RT$, with the ideal-gas constant: $R \equiv N_A k_B \approx 8.31451$ joules per kelvin per mole.

6 Conclusion

Let us briefly recall the concepts introduced in the present paper. One can imagine that after having introduced the corpuscular concept, 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 (parabolic? hyperbolic?), he may have thought of introducing a weight factor 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 weight factor involves for dimensional reasons a quantity θ having the dimension of energy. Considering a thermal engine operating between two baths at temperatures θ_l, θ_h one finds on the basis of the principles just stated that the maximum efficiency is: $1 - \theta_l/\theta_h$. This allows us to call θ the thermodynamic temperature. To be sure, the present paper does not provide explicit expressions of gases internal energy if the round-trip time function $\tau(Z)$ remains unknown. It does provide, however, a first-principle proof of the ideal-gas law, including a possible effect of uniform gravity, and of the barometric equation. We have recovered the usual thermodynamical and semi-classical statistical-mechanical expressions for the special case of ideal gases submitted to gravity.

William of Ockham (1287-1347) set as a matter of principle that one should not employ more concepts than those that are strictly necessary to explain the observed phenomena. (Some authors consider that the Ockham philosophy predates the advent of modern science by insisting on facts and the kind of reasoning employed rather than on speculations about essences). Accordingly, it seems important to elucidate the assumptions on which rest, in particular, the barometric and ideal-gas laws that play an essential role in theoretical physics and many applications. Our thesis is that these laws may be obtained on the sole basis of the Democritus model of corpuscles and vacuum. It is indeed unnecessary to specify the laws of motion. One can further show that the ideal-gas internal energy depends only on temperature (in the absence of gravity). To evaluate explicitly this energy it is, however, necessary to know the round-trip corpuscle time. From a pedagogical standpoint and in application of Ockham’s concept one should not postulate principles which, without being erroneous, are unnecessary. In a text-book presentation of Physics, it seems to us that it would be appropriate to give first considerations similar to those presented in this paper, since the explicit laws of motion are not needed.

A General equations of motion

Laws of motion are conveniently written in the Hamiltonian form. If $H(z, p)$ denotes the Hamilton function of coordinate z and momentum p , we have:

$$v(t) \equiv \frac{dz(t)}{dt} = \frac{\partial H(z, p)}{\partial p} \quad \frac{dp(t)}{dt} = -\frac{\partial H(z, p)}{\partial z}. \quad (14)$$

Because the Hamilton function does not depend explicitly on t , the energy of a corpuscle is the constant: $E = H(z, p)$ for some initial z, p values.

Non-relativistic approximation for a constant weight: In that approximation, $H(z, p) = \frac{p^2}{2m} + wz$ for a weight (or force) $w \equiv mg$. It follows that $v = p/m$ and $dp/dt = -w$. With the

initial conditions: $z(0) = 0$ and $p(0) = 0$, the corpuscle motion is described by: $z(t) = -\frac{1}{2}gt^2$. Hence, $\tau(Z) \equiv 2t(-z) = 2\sqrt{2Z/g} \propto \sqrt{Z}$. For consistency with subsequent expressions one may add to $H(z, p)$ the constant mc^2 .

Relativistic expression for constant electrical forces: We presently have for a weightless corpuscle with electrical charge e and submitted to a constant electrical field \mathcal{E} , setting $w \equiv e\mathcal{E}$, (see Landau [17], p.115, for the relativistic form without gravity in three dimensions):

$$H(z, p) = mc^2\sqrt{1 + (p/mc)^2} + wz \rightarrow p = -wt, \\ \frac{dz(t)}{dt} = \frac{\partial H(z, p)}{\partial p} = c\frac{p'}{\sqrt{1 + p'^2}} \quad p' \equiv \frac{p}{mc}. \quad (15)$$

From these expressions we may obtain the equation of motion with $z(0) = z_m$, and the round-trip time as a function of $z_m - z$.

The traditional methods of calculating $\langle F \rangle$ and U in the absence of gravity consist instead in calculating the average values of pv and $H(p)$, respectively, using as a weight the Boltzmann factor: $\exp(-H(p)/\theta)$.

Uniform acceleration g : The Hamilton equations of motion in one space dimension (z) derive from a hamiltonian function of z and p (see Louis-Martinez [14], Eq(5) with $N = 1$):

$$H(z, p) = (mc^2 + mgz)\sqrt{1 + (p/mc)^2} \quad (16)$$

$$v(t) \equiv \frac{dz(t)}{dt} = \frac{\partial H(z, p)}{\partial p} = c\left(1 + \frac{z}{z_g}\right)\frac{p'}{\sqrt{1 + p'^2}} \quad p' \equiv \frac{p}{mc} \quad z_g \equiv \frac{c^2}{g} \quad (17)$$

$$\frac{dp(t)}{dt} = -\frac{\partial H(z, p)}{\partial z} = -mg\sqrt{1 + p'^2} \quad \rightarrow \frac{dp'(t)}{dt} = -\frac{g}{c}\sqrt{1 + p'^2}. \quad (18)$$

We take the time origin such that: $p(0) = 0$. Note that the term $mc^2 + mgz_m \equiv mc^2(1 + z_m/z_g)$, where the maximum altitude z_m represents the corpuscle energy. The round-trip time is now a function of $\zeta_m - \zeta$, where $\zeta = \log(1 + z/z_g)$. The non-relativistic expressions are recovered when $z, ct \ll z_g$. An Hamiltonian function that would account for Quantum Gravity has been proposed by Chandra [18].

References

- [1] J. Arnaud, L. Chusseau, and F. Philippe, "A simple model for Carnot heat engines," *Am. J. Phys.*, vol. 78, no. 1, pp. 106–110, 2010. [Online]. Available: <http://arxiv.org/abs/0812.2757>
- [2] J. Arnaud, L. Chusseau, and F. Philippe, "Démocrite et la puissance motrice du feu (Democritus and the motive power of fire)," 2011, 79 pages. [Online]. Available: <http://arxiv.org/abs/1104.0836>
- [3] H. C. Callen, *Thermodynamics and a introduction to thermo-statistics*, 2nd ed. New-York: Wiley and Sons, 1985.
- [4] P. T. Landsberg, J. Dunning-Davies, and D. Pollard, "Entropy of a column of gas under gravitation," *Am. J. Phys.*, vol. 62, no. 8, pp. 712–717, 1994.
- [5] D. Levermore, "Early theories of gases," <http://www2.math.umd.edu/~lvrmr/History/EarlyTheories.html>.

- [6] E. Hecht, *Physique*. de Boeck University, 2003, see § 14.8.
- [7] C. H. Hollbrow and J. C. Amato, “What Gay-Lussac didn’t tell us,” *Am. J. Phys.*, vol. 79, pp. 17–24, 2011.
- [8] J. Waterston, “On the physics of media that are composed of free and perfectly elastic molecules in a state of motion,” *Philosophical Transactions of the Royal Society of London A*, vol. 183, pp. 1–79, 1892, this article, submitted to that journal in 1843, was initially rejected.
- [9] F. P. Miller, A. F. Vandome, and J. McBrewster, Eds., *Ideal gas law*. Mauricius: Alphascript Publishing, 2009, this booklet reproduces Wikipedia articles relating to the ideal-gas law. Numerous references to Physics textbooks are listed there. See also: http://en.wikipedia.org/wiki/Kinetic_theory.
- [10] J. D. Norton, “Atoms, entropy, quanta: Einstein’s miraculous argument of 1905,” *Studies in History and Philosophy of Modern Physics*, vol. 37, pp. 71–100, 2006. [Online]. Available: <http://www.pitt.edu/~jd/papers/miraculous.pdf>
- [11] This concept was introduced by Boltzmann who, however, considered only the limit in which the difference between successive energies is arbitrarily small.
- [12] J. Arnaud, L. Chusseau, and F. Philippe, “On the ideal gas law,” arXiv 1105.2643 v2, May 2011. [Online]. Available: <http://arxiv.org/abs/1105.2643>
- [13] We do not assume that $z(t) = z(-t)$ or $t_2 + t_1 = 0$. Asymmetric laws of motion occur if one employs clock synchronisation rules different from the one proposed by Einstein. For example, if a light pulse emitted from $z = 0$ at $t = 0$ propagating upward is employed to synchronise clocks located at different altitudes, the apparent upward speed of light is, by this convention, infinite. The downward speed of light is then $c/2$ if c denotes the Einstein speed of light, so that the two-way speed of light remains equal to c , in agreement with very precise experiments. The anisotropy mentioned in the present note refers to a change of formalism, not of physics. It is of some importance that the laws discussed in this paper do not depend on such conventional changes.
- [14] D. J. Louis-Martinez, “Classical relativistic ideal gas in thermodynamic equilibrium in a uniformly accelerated reference frame,” arXiv 1012.3063, Dec. 2010. [Online]. Available: <http://arxiv.org/abs/1012.3063>
- [15] A plot of U from low to high temperatures in the case of an external force much larger than gravity (e.g., an electrical force) can be seen in [1, 2]. A three-dimensional expression of U in terms of Bessel functions can be found, for example, in Greiner, p. 234. [19].
- [16] Note incidentally that: $\frac{\partial U}{\partial h} = \theta \frac{\partial \langle F \rangle}{\partial \theta} - \langle F \rangle$. It follows that, given $\langle F \rangle$, we may obtain $U(\theta, h)$ by an integration over h , provided an unknown function of θ be added. This relation is in fact applicable to any working medium, as one can show by considering a Carnot cycle with small temperature differences (see for example Kubo [20], p. 81).
- [17] L. D. Landau and E. M. Lifshitz, *Statistical Physics*. Oxford: Pergamon Press, 1980, vol. 5, Part I.
- [18] N. Chandra and S. Chatterjee, “Thermodynamics of ideal gas in double special relativity,” arXiv 1108.0896, Aug. 2011. [Online]. Available: <http://arxiv.org/abs/1108.0896>

- [19] W. Greiner, L. Neise, and H. Stöcker, *Thermodynamics and Statistical Mechanics*. New-York: Springer-Verlag, 1997.
- [20] R. Kubo, *Thermodynamics*. Amsterdam: North-Holland, 1968.