Exergy of an open continuous medium

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Exergy is a very important thermodynamic quantity in several fields such as economy, engineering, ecology and yet it has attracted little attention in pure physics. One of the main problems of the currently used definition of exergy is its dependence on an arbitrarily chosen reference state, which is the thermodynamic state of a reservoir the system is supposedly in contact with. In this paper, starting from a very general definition of exergy, a formula is derived for the exergy balance of a general open continuous medium without any reference to an external environment. A formula is also derived for the most suitable thermodynamic parameters of the Earth atmosphere when seen as an external environment in the usual exergy applications.

I. INTRODUCTION

Exergy, a term coined by Z. Rant [1], is defined in words as "the maximum useful work possible during a process that brings the system into equilibrium with a heat reservoir, reaching maximum entropy" [2]. Indeed, the definition of such a quantity can be found, without receiving any special naming, in the renowned book of statistical physics by L. Landau [3], specifically in sections "Maximum work" and "Maximum work done by a body in an external medium" where a commonly known expression of exergy (even though not the most general, as we will see) is quoted:

\[ B = U + p_R V - T_R S \]  

(1)

where \( U, V \) and \( S \) are the internal energy, volume and entropy of the system while \( p_R \) and \( T_R \) are the constant pressure and temperature of the environment, a large thermal reservoir the system is supposedly in contact with.

Exergy, along with the expression (1), is a well known quantity in applied thermodynamics, with remarkable applications in various fields such as ecology, economics, engineering and others [4-6]. In a world where sustainability is becoming the crucial problem for the future of mankind, exergy apparently makes it possible to quantify it [7, 8]. Notwithstanding, in spite of its paramount importance, exergy has attracted little attention in pure physics, specifically in theoretical statistical mechanics and thermodynamics. Indeed, while energy is always conserved in all physical processes, exergy does not, just like entropy. However, unlike entropy, exergy always decreases in an isolated system. This is a definitely more attractive feature with respect to entropy for it just matches the characteristic of what we could properly call a resource: something that can be used for some purpose, but bound to exhaust if not replaced. Altogether, exergy is the concept of resource [9] that is actually meant in economics, politics and in the common language as well when energy is referred to. However, unlike energy and entropy, exergy is not a function of the equilibrium thermodynamic state of a system. Nor is it an intensive and additive physical quantity, with one remarkable exception, that of small systems in contact with an infinite reservoir, see Section V. In fact, exergy depends on both the thermodynamic state of the environment and the surrounding environment in a non-trivial fashion, which perhaps makes it a less attractive quantity for physicists.

Most of the quantitative applications of exergy to date are based on the equation (1) and extensions to include the chemical part. As it has been mentioned, the formula (1) requires the existence of a reservoir, with an invariably constant and uniform thermodynamic intensive quantities: temperature, pressure, chemical potentials. However, when dealing with a continuous medium which is not in contact with a heat reservoir, this is a serious limitation. For instance, in classical thermodynamics it is well known that a fluid with temperature gradients within, and yet, not in contact with a reservoir, is potentially able to perform useful work because it has not achieved full thermodynamic equilibrium. One should be able, in principle, to calculate the amount of this useful work. Another equally important question is how to calculate the intensive parameters of what can be regarded as the reservoir in most applications, i.e., the Earth atmosphere or a portion thereof. What can be taken as reference values of the atmosphere \( T_R, p_R \), given that its thermodynamic state is not constant neither uniform?

To answer these questions, a more general definition of exergy is needed, one that yields the equation (1) as a special case. Indeed, a general definition of exergy as the difference between total energy and the equilibrium energy for the actual value of entropy, appears in the aforementioned Landau’s book [3] and it has been rediscovered more recently [9] (see Section III). In this work, we extend this definition (see Section VI also reported in the Conclusions) to an open continuous medium, i.e., not necessarily isolated and we show that the special case of a system in contact with a reservoir is recovered. Besides, we will be able to provide a formula to calculate the reference thermodynamic intensive quantities for a system which is large enough to play the role of the environment.

The paper is organized as follows: in Section II we review the fundamental definition of exergy of an isolated system; in Section III we illustrate the relation between maximum work and exergy considering two finite sources at different
temperatures; in Section IV we derive the well known expressions of exergy of system and environment based on
the general definition of exergy of an isolated system; in Section VI we extend the definition of exergy to an open
continuous medium and we derive the exergy rate equation for a multi-component fluid; finally, in Section VII we
derive a formula to estimate the reference temperature and pressure of the Earth atmosphere.

Notation

In this paper we use the natural units, with $\hbar = 1$ and the Boltzmann constant $K_B = 1$, that is temperature has
the dimension of an energy.

II. EXERGY OF AN ISOLATED SYSTEM

Consider an isolated system with fixed volume $V$. Let $p_i(t)$ be the probability that the system is in a state $i$ at the
time $t$. The entropy:

$$S(t) = - \sum_i p_i(t) \log p_i(t)$$
is a function of $t$ and the second law of thermodynamics states that, after some time, it will get to its maximum value $S_{\text{eq}} = \log \Omega$ where $\Omega$ is the total number of microstates. It is common wisdom that the increase of entropy entails a degradation of the “useful” energy. This is just the exergy, which can be defined, for an isolated body \[\text{[1,2]}\], as the difference between the total, constant, energy $E_0$ and the energy that the same body would have when at equilibrium with total entropy $S(t)$ and volume $V$:

$$B(t) = E_0 - U(S(t), V)$$

(2)

It should be emphasized that $U(S(t), V)$ is not the actual total internal energy of the system, which may even coincide with $E_0$; this difference will become clear in Section III. The equation (2) has been obtained starting from an equivalent definition of exergy in ref. [9], for the case of $E_0$ only comprising internal energies (see Section III).

It is clear that exergy decreases in time because of the second law:

$$\frac{dB}{dt} = -\frac{\partial U}{\partial S} \bigg|_{V} \frac{dS}{dt} = -T_*(t) \frac{dS}{dt} \leq 0$$

(3)

where $T_*(t)$ is the temperature the system would have if thermalized at the total entropy $S(t)$. It is important to stress that $T_*(t)$ is not the physical temperature of the isolated system, which in principle does not even exists. In figure [4] $T_*(t)$ is the slope of the equilibrium function $E(S(t))$ in the point $(U(t), S)$, and becomes a physical temperature only in the equilibrium point. For a locally equilibrated system $T_*(t)$ is not easy to determine, as we will see later on in this work. However, note that the system might not even be locally equilibrated (like a non-locally thermalized kinetic system) and yet the definition (2) and the equation (3) would hold, because the entropy argument in (2) could be calculated anyway.

The above expressions can be extended to an isolated system with more conserved quantities other than volume, like momentum $P$, electric charge $Q$ etc. In the definition, one just needs to include these constants in the list of the arguments:

$$B(t) = E_0 - U(S(t), V, P, Q, \ldots)$$

A very important case is the multi-component system, comprising several chemical species $X_k$ which can give rise to chemical reactions. In this case, one should take into account that the given initial abundances $N_k(t)$ may not be at chemical equilibrium, so that the internal energy at fixed entropy value $S(t)$ should be estimated at a chemical equilibrium state, with abundances differing from the initial ones. A system of $M$ species subjected to $L$ reactions, features $M - L$ independent constants $Q_i$, which are linear functions of the $N_k$’s:

$$Q_i = \sum_{k=1}^{M} C_{ik} N_k \quad i = 1, \ldots, M - L$$

(4)

Note that the $C_{ik}$’s are also constant, depending on the stoichiometric coefficients of the reactions, but the $N_k$’s can vary in time and yet return the same $Q_i$’s because the linear system of equations is not invertible; indeed, there are $M$ $N_k$’s but only $M - L$ $Q_i$’s. The corresponding exergy expression involves the internal energy as a function of those $M - L$ independent chemical constants:

$$B(t) = E_0 - U(S(t), V, Q_1, \ldots, Q_{M-L})$$

(5)

Even though the abundances are not independent variables, as we have just discussed, it is sometimes useful to maintain them as redundant thermodynamic variables to describe the internal energy:

$$B(t) = E_0 - U(S(t), V, \overline{N}_1(t), \ldots, \overline{N}_M(t))$$

(6)

It is important to stress that the $\overline{N}_k(t)$ are not the actual abundances at the time $t$, but the equilibrium abundances, that is those the system would have if all chemical reactions were at equilibrium with a given total entropy $S(t)$. This specification is necessary because the internal energy is an equilibrium thermodynamic function, hence its arguments must be equilibrium quantities as well. Note that the equilibrium abundances $\overline{N}_k(t)$ depend on time just because $S(t)$ does. For a single chemical reaction $\sum_k \nu_k X_k = 0$, $\nu_k$ being the stoichiometric coefficients, positive for the products and negative for the reactants, the chemical equilibrium condition reads:

$$\sum_k \frac{\partial U}{\partial N_k} \bigg|_{S(t), V} \nu_k = \sum_k \mu_k(t) \nu_k = 0$$

---

1 This term includes either molecules or atoms or nuclei or subnuclear particles
where the $\mu_{ik}$ are the chemical potentials. As the internal energy can be seen as a function of the chemical constants $Q_i$ or the equilibrium abundances $N_k$, two kinds of chemical potentials can be defined. Nevertheless a relation can be derived between the chemical potentials $\mu_{iV}$ related to the $Q_i$’s and those $\mu_{k*V}$, related to the $N_k$’s:

$$\frac{\partial U}{\partial N_k} \bigg|_{S(t),V} = \mu_{k*V} = \sum_{i=1}^{M-L} \frac{\partial U}{\partial Q_i} \bigg|_{S(t),V} \frac{\partial Q_i}{\partial N_k} = \sum_{i=1}^{M-L} C_{ik} \mu_{iV}$$

(7)

which can also be interpreted by saying that the $C_{ik}$ is the “charge” of type $i$ carried by the species $k$.

It should be stressed that the exergy is not a function of the equilibrium thermodynamic state. However, according to the definitions (2) and its extension (6) in the microcanonical ensemble its value does not depend on the specific process leading to equilibrium. For most applications in engineering, the goal is in fact the reduction of the exergy destruction rate (3), hence dissipation, to a minimum, so as to maintain the resource for a longer time.

III. EXERGY OF TWO SYSTEMS

One can learn much about the nature of the exergy from the simplest case of two adjacent systems. Suppose, for further simplicity, that they are thermalized subsystems of equal size and composition at temperature $T_1$ and $T_2$ with $T_1 < T_2$ which are separated by a non-conducting wall (see figure 2). The system as a whole is obviously not at global thermodynamic equilibrium. According to the definition we can write the total exergy at the initial time $t = 0$ as:

$$B(0) = E_0 - U_{th}(S_1 + S_2)$$

where the other arguments can be omitted, assuming that the volume and number of particles do not change in time. It is important to stress that the thermalized energy $U_{th}(S_1 + S_2)$ is the total energy of the system $1 + 2$ as though it was completely thermalized with entropy $S = S_1 + S_2$ and it is not equal to $U_1 + U_2$ (see further below). As the two subsystems have equal size and composition, in a thermalized state they have the same entropy, so we can write:

$$U_{th}(S_1 + S_2) = U_1 \left( \frac{S_1 + S_2}{2} \right) + U_2 \left( \frac{S_1 + S_2}{2} \right)$$

(8)

Now, since the sum of the internal energies must be conserved in time, we can also write:

$$E_0 = U_1(S_1) + U_2(S_2)$$

so that:

$$B(0) = U_1(S_1) + U_2(S_2) - U_1 \left( \frac{S_1 + S_2}{2} \right) - U_2 \left( \frac{S_1 + S_2}{2} \right)$$

(9)

This equation can be extended to $N$ bodies in thermal contact [9]. The equation (9) demonstrates that the definition (2) is not extensive, namely that it does not allow to express the total exergy as the integral over some region of a density, unlike energy and entropy. If this was the case, the total exergy in [9] would be the sum of the exergies of the two regions in figure 2, defined according to the (2). Since the energies in the two regions are completely thermalized, we have:

$$B_i = E_i - U_{th}(S_i) = 0 \quad i = 1, 2$$

and yet $B(0)$ in eq. (9) is not vanishing, so:

$$B(0) \neq B_1 + B_2$$

Indeed, while $E_0 = E_1 + E_2$, in the equation (9) we have that:

$$U_{th}(S_1) + U_{th}(S_2) \neq U_{th}(S_1 + S_2)$$

with equality applying only if $U$ was proportional to $S$, which is generally not the case. More generally, it can be shown that if $V_1$ and $V_2$ are two adjacent non-overlapping regions, the following general inequality holds:

$$B_{V_1 \cup V_2}(t) \geq B_{V_1}(t) + B_{V_2}(t)$$

(10)
FIG. 2: Two systems in contact at temperature $T_1$ and $T_2$ can be used to extract useful work by means of an auxiliary body - depicted as circular double arrow - making infinitesimal cyclic transformations.

provided that the total energy of $V_1$ and $V_2$ can be obtained by summing the individual energies. Since $E_{V_1 \cup V_2} = E_{V_1} + E_{V_2}$, the (10) becomes:

$$U_{th}(S_1 + S_2, V_1 + V_2, Q_1 + Q_2) \leq U_{th}(S_1, V_1, Q_1) + U_{th}(S_2, V_2, Q_2)$$

which is just the thermodynamic stability condition, i.e. the convexity of the internal energy with respect to extensive quantities $[3]$. In the equation (11) $Q$ stands for the set of additive constants related to chemistry as discussed in the Section I. The inequality (10) expresses the common wisdom that exergy is not a function of a single system, but it substantially depends on both the system and its surroundings.

Altogether, this analysis shows that exergy is not an extensive quantity. While there is an energy and an entropy density, an exergy density cannot be defined, with the notable exception of systems in contact with a reservoir, see Section V. The lack of extensivity could have been realized already from the exergy destruction rate in equation (3): while the entropy is extensive, the temperature $T_*(t)$ is non-local, in that it does not belong to some finite region, but it is the temperature that the whole system would have if it was thermalized.

A. Exergy as maximum work

The example of the two systems offers the opportunity to show that the exergy defined by the equation (2) is indeed the maximum available work which can be extracted from two finite thermal sources at different temperatures. To calculate the maximum work from the system in fig. 2 in the traditional textbook approach, we need to introduce an auxiliary body which is coupled to the two systems at different temperatures (represented by the loop in figure 2) and whose purpose is to convert some internal energy into kinetic energy, through some coupling to an external device. The body is indeed the system making a Carnot cycle between the sources at different temperatures. In thermodynamics textbooks the sources are thermostats, while in our case they are finite and once some internal energy is extracted from the source at higher temperature, its temperature does not stay constant but it decreases, thus we have to consider infinitesimal Carnot cycles such that the temperatures can be considered as constant throughout them, and integrate. The work $dL$ extracted in an infinitesimal cycle reads:

$$dL = -dU_2 - dU_1$$
where \(dU_i\) are positive when internal energy of either source increases. According to the Carnot theorem, the work is maximal when the process is reversible, that is when the total entropy increase is zero:

\[
dS_{\text{tot}} = dS_1 + dS_2 = \frac{dU_2}{T_2} + \frac{dU_1}{T_1} = 0
\]

This condition allows to write the work as:

\[
dL = -\left(1 - \frac{T_2(t)}{T_1(t)}\right)dU_2 = -\eta \, dU_2
\]

where \(\eta\) is the efficiency. The total work is obtained by integrating in time the internal energy variations between the initial state and the final state:

\[
L = \int_{t_1}^{t_2} dL = -\int_{t_1}^{t_2} dU_2 + dU_1
\]

where the integration is constrained by \(S_1 + S_2 = \text{constant}\). In the initial state, the total internal energy is \(U_1(T_1(0)) + U_2(T_2(0))\) whereas in the final state, the internal energy must be that of a thermalized system at a common temperature with the same total entropy of the initial state, that is just \(U_{\text{th}}(S_1 + S_2)\). Therefore:

\[
L = U_1 + U_2 - U_{\text{th}}(S_1 + S_2)
\]

which coincides with the exergy expression (9).

### IV. A SYSTEM IN CONTACT WITH A RESERVOIR

Let us now consider a small system \(A\) embedded in a reservoir \(R\) and suppose that they are overall isolated. The system \(A\) should be viewed as a material system which is able to move around within the environment (the Lagrangian description in the mechanics of continuous media). The reservoir \(R\) is at thermodynamic equilibrium with uniform and constant intensive parameters (see figure 3) but the small system \(A\) is not at thermodynamic equilibrium with \(R\). The calculation of the exergy of \(A + R\) is made it easier by the fact that the temperature \(T_i(t)\) is, to an excellent approximation, equal to the reservoir temperature \(T_R\), so that the equation (3) is expected to become:

\[
\frac{dB}{dt} = -T_R \frac{dS_{\text{tot}}}{dt} \implies B(0) = T_R \Delta S_{\text{tot}}
\]

by using the final condition \(B(\infty) = 0\).

Since \(A + R\) is overall isolated, the total energy \(E_0\) as well as the volume \(V_A + V_R\) is constant. Suppose also that the entropy and the energy of the system and the reservoir are additive, a familiar case in classical thermodynamics, i.e. there are no long-range interactions between \(A\) and \(R\). We denote with capital letters the actual thermodynamic functions of the system and reservoir (e.g., \(S_A, V_R\)), and with overlined capital letters the values of those functions that system and reservoir had if they were in a mutual thermodynamic equilibrium state with fixed total entropy \(S_A + S_R\). We stress, for the sake of clarity, that this thermodynamic equilibrium state is virtual, so to speak, and it does not imply an actual physical equilibration process between system and reservoir, where total entropy increases. According to the general definition of exergy (6) for an isolated system, and taking into account the assumed additivity of energy, we can write the thermalized energy of the system and the reservoir as:

\[
U_{\text{th}}(S = S_A + S_R, V = V_A + V_R, \ldots) = U_A(\overline{S}_A, \overline{V}_A, \overline{N}_{kA}) + U_R(\overline{S}_R, \overline{V}_R, \overline{N}_{kR})
\]

where \(U\) is the equilibrium thermodynamic function internal energy and the dots on the left hand side stand for all other relevant constant arguments (e.g. those related to chemical reactions) as discussed in Section II. The \(N_k\) are the absolute numbers of some chemical species, with \(k = 1, 2, \ldots, M\). Note that:

\[
S_A + S_R = \overline{S}_A + \overline{S}_R \quad V_A + V_R = \overline{V}_A + \overline{V}_R
\]

for the constancy of the volume and because the internal energy must be evaluated at fixed entropy.

Now, at equilibrium, the derivatives of the internal energy with respect to entropy, volume and all the number of species are the same for system and reservoir. Besides, they are equal to the derivatives of \(U_{\text{th}}\) because of the (13) and (14):

\[
\frac{\partial U_A}{\partial S_A} = \frac{\partial U_R}{\partial S_R} = \frac{\partial U_{\text{th}}}{\partial S} \quad \frac{\partial U_A}{\partial \overline{V}_A} = \frac{\partial U_R}{\partial \overline{V}_R} = \frac{\partial U_{\text{th}}}{\partial \overline{V}} \quad \frac{\partial U_A}{\partial \overline{N}_{kA}} = \frac{\partial U_R}{\partial \overline{N}_{kR}} = \frac{\partial U_{\text{th}}}{\partial \overline{N}_k}
\]

(15)
Note that the above derivatives are calculated at the overlined equilibrium values, which differ from the actual ones. Nevertheless, for the reservoir the difference between the derivatives at the equilibrium value and those at the actual values are negligible, because the reservoir is much larger than the system. Therefore we can approximate:

$$\frac{\partial U_R}{\partial S} \simeq \frac{\partial U_R}{\partial S} = T_R$$
$$\frac{\partial U_R}{\partial V} \simeq \frac{\partial U_R}{\partial V} = -p_R$$
$$\frac{\partial U_R}{\partial N_k} \simeq \frac{\partial U_R}{\partial N_k} = \mu_{kR}$$

(16)

where $T_R$ is the temperature of the reservoir, $p_R$ its pressure and $\mu_{kR}$ its chemical potentials, all of them supposedly constant and equal to their equilibrium values.

We can now calculate the exergy rate by using the definition (6) and taking into account the eq. (16):

$$\frac{dB}{dt} = \frac{dE}{dt} - \frac{dU_{th}}{dt} = 0 - \frac{\partial U_{th}}{\partial S} \frac{dS}{dt} = -T_R \left( \frac{dS_A}{dt} + \frac{dS_R}{dt} \right)$$

(17)

which is the equation (12).

Since the reservoir is itself at thermodynamic equilibrium, the time derivative of the entropy of the reservoir can be calculated by using the known equilibrium relations of thermodynamics:

$$\frac{dS_R}{dt} = \frac{1}{T_R} \frac{dU_R}{dt} + \frac{p_R}{T_R} \frac{dV_R}{dt} - \sum_k \frac{\mu_{kR}}{T_R} \frac{dN_{kR}}{dt}$$

(18)

Taking into account the energy conservation, the volume conservation and the general chemical species balance equations:

$$\frac{dE_A}{dt} + \frac{dU_R}{dt} = 0$$
$$\frac{dV_A}{dt} + \frac{dV_R}{dt} = 0$$
$$\frac{dN_{kA}}{dt} + \frac{dN_{kR}}{dt} = R_{kA} = \nu_k R$$

(19)

where $E_A$ is the energy of the subsystem $A$ including its kinetic collective energy $K_A$ and its internal energy $U_A$; $R$ is the chemical reaction rate and $\nu_k$ the stoichiometric coefficients, negative for the reactants and positive for the
products), the (17) can be transformed into, by using the (18) and (19):

$$\frac{dB}{dt} = dE_A - T_R \frac{dS_A}{dt} + p_R \frac{dV_A}{dt} - \sum_k \mu_{kR} \left( \frac{dN_{kA}}{dt} - \nu_k R \right)$$  \hspace{1cm} (20)

The chemical reaction term indeed vanishes because the reservoir is supposedly at equilibrium:

$$\sum_k \mu_{kR} \nu_k = 0$$

and the (20) gets simplified to:

$$\frac{dB}{dt} = \frac{dK_A}{dt} + \frac{dU_A}{dt} - T_R \frac{dS_A}{dt} + p_R \frac{dV_A}{dt} - \sum_k \mu_{kR} \frac{dN_{kA}}{dt}$$  \hspace{1cm} (21)

This equation can be readily integrated over some time interval:

$$\Delta B = \Delta K_A + \Delta U_A - T_R \Delta S_A + p_R \Delta V_A - \sum_k \mu_{kR} \Delta N_{kA}$$  \hspace{1cm} (22)

The exergy decreases steadily until, at the time $t = \infty$, the system achieves full thermodynamic equilibrium with the reservoir with the same intensive quantities $T_R, p_R, \mu_{kR}$. Furthermore, the kinetic energy will vanish and the whole energy of the system will be internal, related to the other thermodynamic variables by the equilibrium thermodynamic relation with the intensive quantities $T_R, p_R, \mu_{kR}$:

$$K(\infty) = 0 \hspace{1cm} U_A(\infty) - T_R S_A(\infty) + p_R V_A(\infty) - \sum_k \mu_{kR} N_{kA}(\infty) = 0$$

Therefore, from the equation (22), we obtain the total exergy at the initial time $t = 0$:

$$B = K_A(0) + U_A(0) - T_R S_A(0) + p_R V_A(0) - \sum_k \mu_{kR} N_{kA}(0)$$  \hspace{1cm} (23)

which is just the initial exergy. The equation (23) is indeed a well known formula of the exergy of a system in contact with a reservoir and has been used extensively [5].

We note an interesting feature of the equation (23). From its general definition for an isolated system in Section II, it is obvious that $B$ is positive definite, and one may wonder if this holds for the expression (23). Indeed this does, owing to the well known thermodynamic stability condition [3] stating that any small deviations of the extensive quantities for a system in contact with a reservoir are such that:

$$\delta K_A(0) + \delta U_A(0) - T_R \delta S_A(0) + p_R \delta V_A(0) - \sum_k \mu_{kR} \delta N_{kA}(0) > 0$$

In other words, $B = 0$ is a minimum and the right hand side of the (23) is always positive.

A. System in an external field

This analysis can be extended to the case where the system $A$ (but not $R$) is subjected to an external field, like gravity acceleration. In this case, the energy of the system, defined as the sum of kinetic and internal energy\(^2\) is no longer conserved because of the injected external power $P_{ext}$. The equation (17) is replaced by:

$$\frac{dB}{dt} = \frac{dE_0}{dt} - \frac{dU_{th}}{dt} = P_{ext} - \frac{dU_{th}}{dt} = P_{ext} - T_R \left( \frac{dS_A}{dt} + \frac{dS_R}{dt} \right)$$

Likewise, the first equation (19) is replaced by:

$$\frac{dE_A}{dt} + \frac{dU_R}{dt} = P_{ext}$$

so that, eventually, the term $P_{ext}$ gets cancelled and the equations (21) and (23) hold true.

\(^2\) We follow the definition in ref. [6].
V. EXERGY OF A CONTINUOUS MEDIUM IN CONTACT WITH A RESERVOIR

The equation (23) can be extended to a collection of small systems which are all in contact with the same large reservoir. In this case, the equation (23) shows that exergy can be considered as additive, because it is the sum of additive quantities multiplied by constant intensive quantities of the reservoir. This is a common assumption when dealing with small subsystems on Earth:

\[ B = \sum_i B_i \]

This assumption is broken when the subsystems are no longer small compared to the reservoir or, tantamount, when the reservoir is not large enough so as to maintain constant and uniform thermostatic properties.

The additivity and the extensivity of all the quantities \( K, U, S, V, N \) in the equation (23) also makes it possible to define an exergy density throughout the system and the reservoir as:

\[
 b(x, t) = \frac{1}{2} \rho v^2 + u + p_R - T_R s - \sum_k \mu_k R n_k = \epsilon + p_R - T_R s - \sum_k \mu_k R n_k
\]  

(24)

where \( \rho \) is the mass density, \( u \) the internal energy density, \( \epsilon = (1/2) \rho v^2 + u \) is the total energy density, \( s \) the entropy density, \( n_k \) the number density of the species \( k \). By taking into account that in the region occupied by the reservoir \( b = 0 \), for the velocity field \( v \) vanishes the application of the basic relation \( u_R + p_R = T_R s_R + \sum_k \mu_k R n_k R \) at thermodynamic equilibrium, it can be seen that the equation (24) applies to every point in space, including the reservoir. For a finite subsystem with volume \( V \), its exergy can be obtained by integrating the (24), thus reproducing the equation (23):

\[
 B_V = \int_V dV \ b = \int_V dV \left( \frac{1}{2} \rho v^2 + u + p_R - T_R s - \sum_k \mu_k R n_k R \right) = K_V + U_V + p_R V - T_R S_V - \sum_k \mu_k R N_k V
\]

It is now possible to determine a continuity equation for the exergy density by using the continuity equations of energy, entropy and number densities:

\[
 \frac{\partial \epsilon}{\partial t} + \nabla \cdot \mathbf{j}_E = \pi \tag{25}
\]

\[
 \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{j}_S = \sigma
\]

\[
 \frac{\partial n_k}{\partial t} + \nabla \cdot \mathbf{j}_k = \nu_k r
\]

In the equation above, \( \mathbf{j} \) are the fluxes; specifically, the flux of particles of species \( k \) is \( \mathbf{j}_k = n_k \mathbf{v}_k \) where \( \mathbf{v}_k \) is the baricentric velocity of the species \( k \); \( \sigma \) is the entropy production rate within the region \( V \); \( \pi \) is the power density of external fields, which is usually written as:

\[
 \pi = \sum_k \mathbf{f}_k \cdot \mathbf{v}_k
\]

where \( \mathbf{f}_k \) is the density of force (for instance, for the gravitational field at the Earth surface \( \mathbf{f}_k = m_k n_k \mathbf{g} \)) exerting on the species \( k \); and \( r \) is the chemical reaction rate per unit volume. By taking the partial derivatives of both sides of (24) and using the (25) we get:

\[
 \frac{\partial b}{\partial t} = \frac{\partial \epsilon}{\partial t} - T_R \frac{\partial s}{\partial t} - \sum_k \mu_k R \frac{\partial n_k}{\partial t}
\]

\[
 = \pi - \nabla \cdot \mathbf{j}_E + T_R \nabla \cdot \mathbf{j}_S - T_R \sigma + \sum_k \mu_k R \nabla \cdot \mathbf{j}_k - \sum_k \mu_k R \nu_k r
\]

The last term vanishes in the reservoir which is supposedly at chemical equilibrium so that:

\[
 \sum_k \mu_k R \nu_k = 0
\]
We are thus left with:

$$\frac{\partial b}{\partial t} + \nabla \cdot \left( j_E - T_R s - \sum_k \mu_k R j_k \right) = \pi - T_R \sigma$$  \hfill (26)

The above equation can now be integrated over some region \( V \) to obtain the exergy balance equation. The equation (26) is the general form of exergy continuity equation for a multi-component continuous medium and applies to a great variety of systems. The exergy source includes a possibly positive term \( \pi \), the power supplied by the external field, and a negative term \( T_R \sigma \) due to dissipation. The energy flux \( j_E \) comprises all forms of energy inward/outward fluxes, including electromagnetic radiation or any other sort of radiation; the same applies to the entropy or the chemical species flux vectors.

A. Example: classical fluid

Among all systems for which the calculation of exergy balance equation is interesting, there is certainly a classical multi-component fluid. We refer to ref. [11] for the derivation of the expressions quoted below. Let \( \rho \) be the mass density and \( \mathbf{v} \) the hydrodynamic velocity field, defined as:

$$\rho = \sum_k m_k n_k \quad \mathbf{v} = \frac{1}{\rho} \sum_k m_k \mathbf{j}_k$$

where \( k \) is the index labeling the chemical species, with \( m_k \) its mass, \( n_k \) its number density and \( \mathbf{j}_k = n_k \mathbf{v}_k \) its flux vector. The fluxes and the entropy production rate turn out to be [11]:

$$j_E = \frac{1}{2} \rho \mathbf{v}^2 + u \mathbf{v} + \mathbf{j}_q - \mathbf{T} \cdot \mathbf{v}$$
$$j_S = s \mathbf{v} + \frac{1}{T} \mathbf{j}_q - \sum_k \mu_k \mathbf{J}_k$$
$$\sigma = \mathbf{J}_q \cdot \nabla \left( \frac{1}{T} \right) - \sum_k \mathbf{J}_k \cdot \nabla \left( \frac{\mu_k}{T} \right) + \frac{1}{T} \mathbf{n} : \nabla \mathbf{v} - \frac{1}{T} \sum_k \mu_k n_k \mathbf{v} + \frac{1}{T} \sum_k \mathbf{f}_k \cdot \mathbf{J}_k / n_k$$

where \( T = -pI + \Pi \) is the Cauchy stress tensor \([11]\) with the diagonal pressure component \(-pI\); \( \mathbf{j}_q \) is the heat flux vector and \( \mathbf{J}_k \) are the diffusion currents:

$$\mathbf{J}_k \equiv \mathbf{j}_k - n_k \mathbf{v}$$

We can now integrate the equation (26) to obtain the exergy rate of change within the region \( V \). By using the Gauss theorem:

$$\frac{\partial b}{\partial t} \bigg|_V = \frac{\partial}{\partial t} \int_V dV \ b = - \int_{\partial V} dS \ \hat{n} \cdot \left( j_E - T_R s - \sum_k \mu_k R j_k \right) - T_R \int dV \ \sigma + \int dV \ \pi$$  \hfill (28)

The total flux in the boundary term becomes, by using the eqs. (27), the decomposition of the Cauchy stress tensor and the (24):

$$j_E - T_R s - \sum_k \mu_k R j_k$$

$$= \left( \frac{1}{2} \rho \mathbf{v}^2 + u + p - T_R s - \sum_k \mu_k R n_k \right) \mathbf{v} - \sum_k \left( \mu_k R - \frac{T_R}{T} \mu_k \right) \mathbf{J}_k - \mathbf{n} \cdot \mathbf{v} + \mathbf{j}_q \left( 1 - \frac{T_R}{T} \right)$$

$$= b \mathbf{v} + (p - p_R) \mathbf{v} - \sum_k \left( \mu_k R - \frac{T_R}{T} \mu_k \right) \mathbf{J}_k - \mathbf{n} \cdot \mathbf{v} + \mathbf{j}_q \left( 1 - \frac{T_R}{T} \right)$$

\[3\] The Cauchy stress tensor is defined so as to fulfill the hydrodynamic equation of motion \( \rho d\mathbf{v}/dt = \text{div} \mathbf{T} + \mathbf{f} \) where \( \mathbf{f} \) is the external field. Thereby, the non-diagonal part of the stress-energy tensor \( \Pi \) is defined with the opposite sign with respect to ref. [11].
The first term in the last expression is the convective exergy flow, while the remaining terms make up a conductive contribution:

\[ J_B \equiv \sum_k T_R \left( \frac{\mu_k}{T} - \frac{\mu_k R}{T_R} \right) J_k + (p - p_R)v - \nabla \cdot v + j_q \left( 1 - \frac{T_R}{T} \right) \tag{30} \]

wherein a chemical, mechanical and thermal conduction terms can be recognized. Finally, plugging the eq. (29) into the (28) and by using the entropy flux expression in (27) we get:

\[ \frac{\partial}{\partial t} \int_V dV \, b = - \int_{\partial V} dS \, n \cdot (b v + J_B) - T_R \int_V dV \sigma + \int_V dV \, \pi \tag{31} \]

The expression (31) agrees with that quoted in ref. [6].

VI. EXERGY OF AN OPEN CONTINUOUS MEDIUM

The above formulae are applicable to a continuous medium, or a collection of continuous media, which are embedded in a very large reservoir with constant thermostatic properties; in this case, exergy is additive and it is possible to define an exergy density. This is especially relevant for applications to small systems on the Earth surface, where one would naturally assume the reservoir be the atmosphere, or the atmosphere along with the crust outermost shell.

Nevertheless, if the size of the systems is not much smaller than reservoir’s and if the thermostatic properties of the reservoir are not really constant and uniform, the expressions obtained in Section V become questionable. For instance, in the Earth atmosphere, temperature, pressure and, to some extent, chemical potentials are neither constant nor uniform. We may expect that constancy and uniformity lead to very good approximations when the time and space scale of the phenomenon at stake (for instance the exergy balance of a car round trip) are much smaller than those of the typical variation of the atmosphere parameters, but otherwise, these variations may play a role. Furthermore, the calculations in Section V do not provide a definite prescription for the values of the intensive parameters of the reservoir; this is a renowned and debated problem in exergy calculations [13–15] (see also ref. [5] and references therein), sometimes called reference environment problem.

Therefore, there are very good motivations to find out an expression of the exergy of an open continuous system of arbitrary size, which is not in contact with a reservoir. These expressions should, of course, reproduce those found in Section V in the limit of an infinite system with constant thermostatic parameters.

Let then \( V \) (henceforth we identify the name of the region with its volume \( V \)) be a finite region. We can define its exergy extending the equation (5), by replacing the constant energy with the total energy within the region \( E_V(t) \) at the time \( t \), the total entropy with the entropy of the region \( S_V(t) \) at the same time \( t \), that is \( S_V(t) \), and the chemical constants \( Q_i \) with those, \( Q_i(t) \) corresponding to the chemical equilibrium that would be achieved in the region \( V \) if the composition was frozen at the time \( t \):

\[ B_V(t) = E_V(t) - U_{th}(S_V(t), V, Q_1(t), \ldots, Q_M(t)) \tag{32} \]

The definition (32) is one of the main points of this work. Even though the exergy is not additive, the definition above makes it possible to answer the main questions concerning the reference environment. In the equation (32), the chemical “constants” \( Q_i(t) \) are, as has been mentioned in Section I, linearly dependent on the abundances, with coefficients \( C_{ik} \):

\[ Q_i(t) = \sum_{k=1}^{M} C_{ik} N_k(t) = \sum_{k=1}^{M} C_{ik} \overline{N}_k(t) \tag{33} \]

where \( \overline{N}_k \) are the equilibrium abundances which differ from the actual ones, as discussed in Section I. It should be pointed out that, whereas the abundances depend on time and so do the \( Q_i \’ s, the C_{ik} are still constant because they only depend on the stoichiometric coefficients of the chemical reactions. Furthermore, while the actual \( N_k(t) \’ s change in time due to chemical reactions within \( V \) and boundary fluxes as well, the \( Q_i(t) \’ s and the \( \overline{N}_k(t) \’ s only change because of boundary fluxes.\n
Let us now take the derivative of the (32):

\[ \frac{dB_V}{dt} = \frac{dE_V}{dt} - T_s V(t) \frac{dS_V}{dt} - \sum_i \mu_{si} V(t) \frac{dQ_i}{dt} \]
where \( T_V(t) \) (which has been discussed in Section II) is the temperature and \( \mu_{*iV} \) are the chemical potentials that the region \( V \) would have if at global equilibrium with the given parameters at the time \( t \). These intensive thermodynamic parameters are defined \textit{reference parameters}. By using the (33) and the (7), the above equation becomes:

\[
\frac{d B_V}{dt} = \frac{d E_V}{dt} - T_V(t) \frac{d S_V}{dt} - \sum_{ik} \mu_{*iV}(t) C_{ik} \frac{d N_k}{dt} 
\]

\[
= \frac{d E_V}{dt} - T_V(t) \frac{d S_V}{dt} - \sum_k \mu_{*kV}(t) \frac{d N_k}{dt} 
\]

Let us now introduce the densities:

\[
\frac{d B_V}{dt} = \int_V dV \left( \frac{\partial E}{\partial t} - T_V(t) \frac{\partial S}{\partial t} - \sum_k \mu_{*kV}(t) \frac{\partial n_k}{\partial t} \right) 
\]

and plug the equations (25) in the above equations to obtain the rate of change of the exergy \( B_V \) in time by using the Gauss theorem:

\[
\frac{d B_V}{dt} = - \int_{\partial V} d S \hat{\mathbf{n}} \cdot \left( \mathbf{j}_E - T_V(t) \mathbf{j}_S - \sum_k \mu_{*kV}(t) \mathbf{j}_k \right) - T_V(t) \int_V dV \sigma - \sum_k \mu_{*kV} \nu_k \int_V dV r + \int_V dV \pi \quad (35)
\]

\[
= - \int_{\partial V} d S \hat{\mathbf{n}} \cdot \left( \mathbf{j}_E - T_V(t) \mathbf{j}_S - \sum_k \mu_{*kV}(t) \mathbf{j}_k \right) - T_V(t) \int_V dV \sigma + \int_V dV \pi 
\]

taking into account that, by definition, the chemical potentials \( \mu_{*kV}(t) \) are those of chemical equilibrium at the time \( t \) within the region \( V \), so for a chemical reaction they always fulfill \( \sum_k \mu_{*kV}(t) \nu_k = 0 \). The equation (35) differs from the (28) just by the replacement of \( T_R \) with \( T_V \) and \( \mu_{kR} \) with \( \mu_{kV} \).

The equation (35) expresses the rate of change of the exergy of an open continuous medium. In principle, by integrating it in time, with known limiting condition at \( t \to \infty \), it is possible to calculate the exergy at the present time \( t \). In fact, such an integration requires the knowledge of the reference parameters as a function of time, which are highly non-trivial to calculate. These \( M + 1 \) unknowns, as we have seen, are redundant because of the \( L \) chemical equilibrium conditions:

\[
\sum_k \mu_{*kV} \nu_k = 0 
\]

for each chemical reaction; in fact, the number of independent variables is just \( M + 1 - L \). The equations which are needed to determine these independent variables include the total entropy constraint, that is:

\[
S(T_V(t), \mu_{*1V}(t), \ldots, \mu_{*MV}(t)) = \int dV s(T, \mu_1, \ldots, \mu_M) \quad (36)
\]

and the \( M - L \) equations (33):

\[
Q_i = \sum_{k=1}^M C_{ik} N_k(t) = \sum_{k=1}^M C_{ik} \bar{N}_k(t)(T_V(t), \mu_{*1V}(t), \ldots, \mu_{*MV}(t)) 
\]

which equate the chemical "constants" \( Q_i(t) \) to their expressions as a function of the equilibrium abundances. In the equation (36) the integrand function on the right hand side is the entropy density as a function of the actual temperature and chemical potentials. It is apparent that the solution of the (30) requires the knowledge of the entropy density as well as the inversion of the global equilibrium entropy function on the left hand side with respect to intensive variables at equilibrium. Such a calculation may not be easy to work out.

**A. Example: classical fluid**

To specify the eq. (35) for a classical fluid, we can go through the same steps of the derivation in the previous section. After introducing the pressure \( p_{*V} \) which is defined as the equilibrium pressure (at the time \( t \)):

\[
p_{*V}(t) \equiv p(T_V(t), \mu_{*1V}(t), \ldots, \mu_{*MV}(t)) 
\]
and using the equations \([27]\), we can turn the \([35]\) into:

\[
\frac{dB_V}{dt} = - \int_{\partial V} \frac{\partial}{\partial t} \left( b \mathbf{v} + J_B \right) - T_{sV}(t) \int dV \sigma + \int dV \pi \]

(37)

where the exergy density \(b\) in the convective flow is now defined as:

\[
b = \frac{1}{2} \rho u^2 + u + p_{sV} - T_{sV} s - \sum_k \mu_{s+kV} n_k
\]

(38)

and the exergy conductive flow is now:

\[
J_B \equiv \sum_k T_{sV} \left( \frac{\mu_k}{T} - \frac{\mu_{s+kV}}{T_{sV}} \right) J_k + (p - p_{sV}) V - \mathbf{\Pi} \cdot \mathbf{v} + J_q \left( 1 - \frac{T_{sV}}{T} \right)
\]

(39)

where both the convective and the conductive flows in the \([39]\) are obtained by replacing:

\[
T_{sV} \rightarrow T_{sV}, \quad p_{sV} \rightarrow p_{sV}, \quad \mu_{s+kV} \rightarrow \mu_{s+kV}
\]

(40)

in the equations \([24]\) and \([30]\). Although the function \(b\) in the definition \([38]\) is seemingly an exergy density, it is in fact not a proper density because the reference parameters \(T_{sV}, p_{sV}, \mu_{s+kV}\) depend, in a highly non-trivial fashion, on the whole region \(V\) and are therefore not local functions of \(x\). This is at variance with the reservoir case, where the reference parameters are permanent unchangeable constants.

By using the expression \([38]\) in the \([34]\), another interesting equation is obtained:

\[
\frac{dB_V}{dt} = \frac{\partial}{\partial t} \int_V b \mathbf{v} - \frac{dp_{sV}}{dt} V + \frac{dT_{sV}}{dt} S_V + \sum_k \frac{d\mu_{s+kV}}{dt} N_{k,V}
\]

which clearly shows that the total exergy of an open continuous medium occupying a region \(V\) is not the integral of some function over the same region. Nevertheless, by equating the above expression to the eq. \([37]\) one obtains:

\[
\frac{\partial}{\partial t} \int_V b \mathbf{v} = - \int_{\partial V} \frac{\partial}{\partial t} \left( b \mathbf{v} + J_B \right) - T_{sV}(t) \int dV \sigma + \int dV \pi + \frac{dp_{sV}}{dt} V - \frac{dT_{sV}}{dt} S_V - \sum_k \frac{d\mu_{s+kV}}{dt} N_{k,V}
\]

(41)

which has the form of a continuity equation, like in the case of a region in contact with a reservoir eq. \([31]\), with additional source terms. Indeed, the formula \([41]\) extends the \([31]\) to the case of a general open continuous medium which is not in contact with a reservoir with known and constant reference parameters and it is one of the main results of this work. If \(b\) is interpreted as an exergy density that the system had if the reference parameters \(p_{sV}, T_{sV}, \mu_{s+kV}\) were those of a reservoir, the equation \([41]\) states that the exergy varies in time because of entropy production, external power and because of the variation of the reference parameters. This equation is especially useful for the calculation of chemical exergy resources on Earth: their exergetic value is affected by the change of the reference parameters, including temperature, pressure and chemical potentials.

VII. THE REFERENCE PRESSURE AND TEMPERATURE OF THE ATMOSPHERE

We now present an explicit calculation of the parameters \(T_s, p_s\) and \(\mu_{s,k}\) by solving the \([36]\) for the Earth atmosphere, considered as an open continuous system. Needless to say, this is an important calculation, as the atmosphere is usually seen as the reservoir for most exergy applications and it is thus crucial to have well-founded values for those parameters. We will present here a calculation with the assumption of no chemical reactions between the chemical species in the atmosphere. This assumption entails a very accurate approximation as long as the time scale in the possible applications is much shorter than the composition-changing chemical reactions time. With no chemical reactions, the atmosphere is thus in chemical equilibrium and the number of independent thermodynamic variables is equal to the number of species in the atmosphere, plus of course the temperature. By fixing the relative fractions \(x_i = n_i/n\) of each gas species, the number of independent variables boils down to two: temperature \(T\) and density \(n\), or, tantamount, the temperature \(T\) and the pressure \(p\).

The atmosphere is described as a continuous system having its lower boundary at the Earth surface and with no upper boundary (see figure \(3\)). Indeed, the gases making the atmosphere are subjected to a gravitational field and their density decreases exponentially for increasing height, hence there is no need of setting an upper boundary.
FIG. 4: The reference frame for the atmosphere. The coordinate $z$ is the height, the plane $z = 0$ being the Earth surface is the lower boundary.

Even though the Earth surface is spherical, it is a very good approximation to describe it as a flat plane with a vertical coordinate $z$ like in fig. 4, because the effective thickness of the atmosphere is much smaller than the scale of variation of the gravitational field; in other words, the gravity acceleration can be considered as constant throughout the atmosphere. Furthermore, the intensive parameters are a function of the point, even at global equilibrium. Therefore, the equations to be solved to determine the two independent thermodynamic variables should be then written in principle as:

$$\int_V dV \ s(T_*(x), p_*(x)) = \int_V dV \ s(T(x), p(x))$$

$$(42)$$

$$\int_V dV \ n(T_*(x), p_*(x)) = \int_V dV \ n(T(x), p(x))$$

where the first corresponds to the (36) and the second to the constraint of given number of molecules; the integration region $V$ corresponds to $z > 0$ in figure 4. In fact, the constraint of global equilibrium in the atmosphere demands $T_*$ to be uniform and the pressure $p_*$ to be a function of the vertical coordinate $z$ (see figure 4) through:

$$p_*(x) = p_0 \exp[-\langle m \rangle gz/T_*]$$

$$(43)$$

where $p_0$ is a constant and $\langle m \rangle$ is the average mass:

$$\langle m \rangle = \sum_k \frac{m_k n_k}{n} = \sum_k m_k x_k$$

$m_k$ being the mass of the molecular species $k$.

The most convenient method to solve the first equation (42) is to make use of the so-called $TdS$ equation:

$$TdS = C_p dT - T \frac{\partial V}{\partial T} \bigg|_p dp$$

which, in this form, just applies to a thermodynamic system with fixed chemical composition. For point-dependent functions should use the corresponding $TdS$ equation involving mass densities instead:

$$Td\bar{s} = \bar{c}_p dT - T \frac{\partial \bar{v}}{\partial T} dp$$

$$(44)$$
where the mass densities $\bar{w}$ are related to the proper densities $w$ through the relation:

$$w = \rho \bar{w}$$

In the eq. (44) $c_p$ is the heat capacity per unit mass at constant pressure (specific heat) and, obviously, $\bar{v} = 1/\rho$. We can now write down the local equation of state in terms of the usual densities:

$$p = nT = \sum_k n_k T$$

Taking into account that $\rho = \sum_k m_k n_k$ we have:

$$\frac{p}{\rho} = \bar{v} = \frac{\sum_k n_k T}{\sum_k m_k n_k} = \sum_k \bar{\chi}_k T$$

where $\bar{\chi}_k$ are the concentrations per unit mass, as it appears from the above equation. Hence:

$$\frac{\partial \bar{v}}{\partial T} = \sum_k \bar{\chi}_k$$

(45)

Also, from the known expression of internal energy of an ideal gas:

$$u = \sum_k f_k n_k T \Rightarrow \bar{u} = \sum_k \frac{f_k}{2} \bar{\chi}_k T$$

where $f_k$ is the number of microscopic degrees of freedom of the $k$-th molecular species, we can readily find, by using the equation of state:

$$\bar{c}_p = \frac{\partial}{\partial T} (\bar{u} + p \bar{v}) \bigg|_p = \sum_k \left( \frac{f_k}{2} + 1 \right) \bar{\chi}_k$$

(46)

Therefore, by using the (45) and the (46), the (44) becomes:

$$d\bar{s} = \sum_k \left( \frac{f_k}{2} + 1 \right) \bar{\chi}_k \frac{dT}{T} - \sum_k \bar{\chi}_k \frac{dp}{p}$$

(47)

which can be integrated to give:

$$\bar{s} = \sum_k \left( \frac{f_k}{2} + 1 \right) \bar{\chi}_k \log T - \sum_k \bar{\chi}_k \log p + \bar{s}_0$$

taking into account that $\bar{\chi}_k$ are fixed. After multiplication by $\rho$, and using the equation of state one obtains the entropy density:

$$s = \sum_k \left( \frac{f_k}{2} + 1 \right) n_k \log T - n \log p + s_0 = \sum_k \left( \frac{f_k}{2} + 1 \right) x_k n \log T - n \log p + s_0$$

$$= \kappa n \log T - n \log p + s_0$$

(48)

where $\kappa$ is constant. The (48) can be finally used in the equation (42). The $s_0$ depends on some standard thermodynamic state, which can be chosen to be the exactly $T_\ast$ and $p_\ast$ - at the same point $x$ where we the entropy density is calculated - as in the left hand side of the first equation in eq. (42). Therefore, this constant will cancel out in the first of the equations (42) and we are left with:

$$\int_V dV \frac{p_\ast(x)}{T_\ast} (\kappa \log T_\ast - \log p_\ast(x)) = \int_V dV \frac{p(x)}{T(x)} (\kappa \log T(x) - \log p(x))$$

(49)

to be solved along with the second of the equations (42) which becomes, by using the equation of state:

$$\int_V dV \frac{p_\ast(x)}{T_\ast} = \int dV \frac{p(x)}{T(x)} = N$$

(50)
with \( N \) the total number of molecules in the atmosphere. Note that, in spite of the appearance, these two equations are independent of the units chosen for the pressure and the temperature.

By using the eq. (43), and approximating \( dV = dSdz \) we obtain from the (50):

\[
p_0 = \frac{N(m)g}{A}
\]

where \( A \) is the Earth surface. The parameter \( p_0 \) is then independent of the \( T_\ast \) and it is just the atmospheric pressure at sea level. We can also use the (43) in the equation (49) to obtain, after integration in \( z \) with \( N \) are independent of the units chosen for the pressure and the temperature.

We can now approximate the integration with a discrete sum over sufficiently small cells and we have:

\[
\Delta T \simeq \exp \left[ \frac{1}{N} \sum_i \Delta V_i \log \left( \frac{T_i}{p_i^{1/\kappa}} \right) \right]
\]

whence we can determine \( T_\ast \):

\[
T_\ast = \left( \frac{p_0}{e} \right)^{1/\kappa} \exp \left[ \frac{1}{N} \sum_i \Delta V_i \log \left( \frac{T_i}{p_i^{1/\kappa}} \right) \right] = \left( \frac{p_0}{e} \right)^{1/\kappa} \exp \left[ \int V dV \log \left( \frac{T(x)}{p(x)^{1/\kappa}} \right)^{n(x)/N} \right]
\]

This is the final formula for the reference temperature of the atmosphere. To calculate it, we have to integrate the temperature and pressure over the whole atmosphere volume, i.e. \( z > 0 \) in figure [4]. Since \( p(x)/T(x) = n(x) \) one can see that, expectedly, the region near \( z = 0 \) with higher density weigh more in the integral in the eq. (51) than those at lower density located at high \( z \). The constant \( \kappa \):

\[
\kappa = \sum_k \left( \frac{f_k}{2} + 1 \right) x_k
\]

can be readily calculated from the composition of the atmosphere and its approximate value is \( \simeq 3.55 \). Even if not manifestly, it can be checked that the formula (51) turns out to be independent of the chosen temperature and pressure units.

A more suggestive form of the (51) can be found by reintroducing the density \( n \):

\[
T_\ast = \left( \frac{p_0}{e} \right)^{1/\kappa} \exp \left[ \frac{1}{N} \int V dV n(x) \log \left( \frac{T(x)}{p(x)^{1/\kappa}} \right) \right] = \left( \frac{p_0}{e} \right)^{1/\kappa} \exp \left[ \int V dV \log \left( \frac{T(x)}{p(x)^{1/\kappa}} \right)^{n(x)/N} \right]
\]

We can now approximate the integration with a discrete sum over sufficiently small cells and we have:

\[
T_\ast \simeq \left( \frac{p_0}{e} \right)^{1/\kappa} \exp \left[ \sum_i \Delta V_i \log \left( \frac{T_i}{p_i^{1/\kappa}} \right)^{n_i/N} \right] = \left( \frac{p_0}{e} \right)^{1/\kappa} \exp \left[ \sum_i \log \left( \frac{T_i}{p_i^{1/\kappa}} \right)^{n_i/\Delta V_i/N} \right]
\]

whence

\[
T_\ast = \left( \frac{p_0}{e} \right)^{1/\kappa} \prod_i \left( \frac{T_i}{p_i^{1/\kappa}} \right)^{N_i/N}
\]

(52)

where \( N_i = n_i \Delta V \) is the number of molecules in the \( i \)-th cell. The equation (52) tells us that, surprisingly, the exergy reference temperature of the atmosphere is to be calculated with a modified weighted geometric mean, and not with a weighted linear mean as one would have naively guessed. This result is in agreement with calculations of the reference temperature in ref. [3] for a collections of ideal gas cells at different temperatures and constant densities.

The numerical computation of the right hand side of the eq. (52) requires the analysis of the recorded temperatures and pressures at different locations and altitudes. We can take the logarithm of both sides of (52) and write:

\[
\log T_\ast = \frac{1}{\kappa} \sum_i \frac{N_i}{N} \log T_i - \frac{1}{\kappa} \frac{N_i}{N} \log \left( \frac{p_i}{p_0} \right)
\]

(53)

Let now be \( \bar{T} \) the average temperature calculated with a weighted arithmetic mean:

\[
\bar{T} = \frac{1}{N} \sum_i \frac{N_i}{N} T_i
\]
with:

\[ T_i = \bar{T} + \delta T_i \]

which is just a definition of \( \delta T_i \). Similarly, we can define a pressure fluctuation \( \delta p_i \) with respect to a most probable value as expressed by the equation \([43]\):

\[ p_i = p_{\ast i} + \delta p_i = p_0 \exp[-(m)gz/T_s] + \delta p_i \]

By plugging the above definitions in the equation \([53]\) we obtain:

\[ \log T_s = \sum_i N_i/N \log(\bar{T} + \delta T_i) - \frac{1}{\kappa} \left[ \sum_i N_i/N \left( -\frac{(m)gz}{T_s} \right) + \log \left( 1 + \frac{\delta p_i}{p_{\ast i}} \right) + 1 \right] \]

It can now be checked, by turning the sum into an integration and using the equation of state, as well as the equation \([43]\) and the value of \( p_0 \), that the first term within the square brackets on the right hand side yields \(-1\). We are then left with:

\[ \log T_s = \sum_i N_i/N \log(\bar{T} + \delta T_i) - \frac{1}{\kappa} \left[ \sum_i N_i/N \log \left( 1 + \frac{\delta p_i}{p_{\ast i}} \right) \right] \]

The \( \delta T_i \) and \( \delta p_i \) are supposedly small compared to the central values, so we can expand to second order in the \( \delta T_i, \delta p_i \):

\[ \log T_s \simeq \log \bar{T} - \frac{1}{2} \sum_i N_i/N \left( \frac{\delta T_i}{T} \right)^2 + \frac{1}{2\kappa} \left[ \sum_i N_i/N \left( \frac{\delta p_i}{p_{\ast i}} \right)^2 \right] \]

From this equation we can obtain an approximation of the reference temperature as:

\[ T_s \simeq \bar{T} \exp \left[ -\frac{1}{2} \sum_i N_i/N \left( \frac{\delta T_i}{T} \right)^2 + \frac{1}{2\kappa} \sum_i N_i/N \left( \frac{\delta p_i}{p_{\ast i}} \right)^2 \right] \]

Hence, after defining the temperature and pressure variance as:

\[ \sigma_T^2 = \sum_i N_i/N \left( \frac{\delta T_i}{T} \right)^2 \quad \sigma_p^2 = \sum_i N_i/N \left( \frac{\delta p_i}{p_{\ast i}} \right)^2 \]

we have:

\[ T_s \simeq \bar{T} \left( 1 - \frac{1}{2} \sigma_T^2 + \frac{\bar{T}}{2\kappa} \sigma_p^2 \right) \]

\[ \text{(54)} \]

The deviation of the reference temperature from the weighted aritmetic mean over atmospheric cells is therefore small, as \( \sigma_T \) and \( \sigma_p \) are expectedly much smaller than 1.

\section*{VIII. SUMMARY AND CONCLUSIONS}

We have reviewed the concept of exergy from the point of view of non-equilibrium thermodynamics and provided a general compact definition:

\[ B_V(t) = E_V(t) - U_{th}(S_V(t), V, Q_1(t), \ldots, Q_M(t)) \]

(see Section \([VI]\) as the difference between the energy and the thermalized energy within a region \( V \). This definition applies to an arbitrary open continuous system, not necessarily in contact with an equilibrium reservoir or an environment with fixed intensive thermodynamic parameters. Such definition leads to general continuity equations \([35], [41]\) which extend known expressions \([9]\) of continuous media in contact with a reservoir. Besides, the general definition makes it possible to calculate the reference thermodynamic parameters for a system which is large enough to be considered as an environment in many applications. As an example, we have derived the equations to calculate the reference parameters of the Earth atmosphere in a general non-equilibrium state for the pressure \([43]\) and the temperature \([52]\).
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