On Time Dependent Entropy vis-a-vis Clausius' Inequality: Some of the Aspects Pertaining to the Global and the Local Levels of Thermodynamic Considerations

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Meixner's revelation in connection with the nonclarity about the entropy function contained in the differential form of Clausius' inequality led us to reinvestigate the foundational aspects involved therein. It is proved that the differential form of Clausius' inequality contains the entropy function for nonequilibrium states. We have also augmented the cyclic form of the Clausius' inequality to include those nonequilibrium situations wherein the system simultaneously interacts at the different positions of its bounding surface with the heat reservoirs of different temperatures. It gets once again established that no local level Clausius' inequality analogue can ever be devised if the system has a spatial nonuniformity. Contrary to Meixner's apprehension one obtains an unique time dependent entropy function from the cyclic form of Clausius' inequality.

INTRODUCTION

Meixner points out[1] in his paper of 1973 that Clausius first makes the following combined statement for reversible and irreversible processes, namely:

$$S(B) - S(A) \geq \int_{A}^{B} \frac{dQ}{T} \tag{1}$$

where A and B are the end equilibrium states, S is the entropy of an equilibrium state (very emphatically stated so by Clausius), the right hand side integration in the case of equality is taken along a reversible path between the states A and B and in the case of inequality the integration is taken along a path involving irreversibility and dQ are the differential elements of heat exchanged by the closed system with the heat reservoirs of temperature T. Obviously, in the case of reversibility T becomes identically equal to the temperature of the system. However, a few years later he (Clausius) gives the inequality in the differential, form[1], namely:

$$dS \geq \frac{dQ}{T} \tag{2}$$

Obviously, eq. (2) carries in impression that S in it is the entropy of nonequilibrium states falling within the irreversible process.

Notice that, in eq. (1) the left hand side difference in the values of entropy is totally immune to the change of paths between the equilibrium states A and B not only from one reversible to another one but also from a reversible one to those involving irreversibility.

Indeed it is true that the left hand side difference in entropy of eq. (1) is a result of a definite integral, namely,

$$S(B) - S(A) = \int_A^B dS \tag{3}$$

provided that the integration is taken along a reversible path. However, as long as one does not establish an entropy function for nonequilibrium states he simply cannot assert that the right hand side integral of eq. (3) can be equally taken for the paths involving irreversibility. Therefore, if it is argued that eq. (1) and (3) lead us to eq. (2) it would be an incorrect assertion. Since eq. (3) is true for a reversible path, eq. (1) can be expressed as (for the sake of clarity we are specifying the nature of paths by 'irr' for irreversible ones and by 'rev' for the reversible ones),

$$\int_{A \atop rev}^B dS > \int_{A \atop irr}^B \frac{dQ}{T} \tag{4}$$

$$\int_{A \atop rev}^B dS = \int_{A \atop rev}^B \frac{dQ}{T} \tag{5}$$

Since on both the sides of eq. (5) the integration can be chosen for the identically same reversible path, from it one has the Clausius entropy expression, namely:

$$dS = \frac{dQ}{T} \text{ (rev)} \tag{6}$$

However, it is necessary to state that the reversible part of the statement of the second law of thermodynamics directly gives[2] eq. (6) and the irreversible part of it gives the Clausius inequality in the cyclic integration form[2], namely:

$$\oint_{irr} \frac{dQ}{T_R} < 0 \quad \text{(closed systems)} \tag{7}$$

from where in the customary steps, which involves the use of eq. (6), one is led to eq. (1). Thus, one should not consider the steps from eq. (1) to eq. (6) as the primary derivation of eq. (6). Notice that in eq. (7) we have used the subscript R to stress that the temperature appearing therein is that of the heat reservoirs coming in thermal contact with the closed system during its cyclic operation. Also the inequality of eq. (7) pertaining only to the closed systems has been specified therein. The fact that for open systems neither such an inequality exists nor can be devised has been established earlier[3]

The type of the mathematical manipulation which gives eq. (6) from eq. (5)

as described above cannot be followed with eq. (4) because no reversible path can be coincided with an irreversible one between the same two end equilibrium states. Therefore, both the integrands of eq. (4) remain unconnected to each other. Indeed, when the equilibrium states A and B are chosen such that on a given reversible path they have the relation

$$S(B) = S(A) + dS \qquad (8)$$

then eq. (4) reads as

$$dS > \int_{\substack{A \\ irr}}^{B} \frac{dQ}{T} \qquad (9)$$

The right hand side integration of eq. (9) cannot be suppressed because as said above the two sides of this equation correspond to two different paths and also its integrand is not an exact differential (it is a result of the existence of irreversibility).

Thus it is clear that eq. (2) is not merely a differential form of eq. (1) nor was it claimed by Clausius himself. Since Clausius did not give any argument in favour of or proved the origin of eq. (2) as pointed out earlier,[1] it remains a mere speculation that in his mind he was considering that the differential change on the left hand side of it is to be taken along the same irreversible path on which the right hand side of it has been prescribed. However, this conjecture needs to be rigorously proved.

From irreversible thermodynamic point of view there are two aspects which need to be made clear. Firstly, is it possible to establish, starting from the second law of thermodynamics, a time dependent entropy function for a system in nonequilibrium and then a time and position dependent entropy function at a local level. Secondly, can one have the local level Clausius' inequality analogue for a system in nonequilibrium. In this paper we have also answered these questions which in turn provides a base for developing an irreversible thermodynamic description starting from the global level statements of the laws of thermodynamics.

The Time Dependent Entropy and Clausius' Inequality

Eu's method

Let us consider a closed system carried along an irreversible cycle and having no nonuniformity of temperature within it and across its boundaries. Hence, for the case under consideration the Clausius inequality, eq. (7), reads as:

$$\oint_{irr} \frac{dQ}{T} < 0 \qquad (10)$$

the subscript R to T is obviously redundant in this case. Since an irreversible cycle involves the time rate of exchange of energy it is better to express eq. (10) as:

$$\oint_{\text{irr}} \frac{1}{T(t)} \frac{dQ}{dt} (t) \, dt < 0 \tag{11}$$

Notice that the time t dependence of the quantities has been explicited in eq. (11). Next we proceed to follow the procedure earlier adopted by Clausius[4], Eu[5, 6] and Eu and García-Colín[7]. In this method an uncompensation function, N, is defind as,

$$N = -\oint_{\text{irr}} \frac{1}{T(t)} \frac{dQ}{dt} (t) \, dt > 0 \tag{12}$$

and as suggested by Eu[5, 7] it is then treated as an independent quantity to give

$$N = \oint_{\text{irr}} \frac{1}{T(t)} \frac{dN}{dt} (t) \, dt > 0 \tag{13}$$

Notice that the positive sign to N is guaranteed by the second law of thermodynamics which vanishes only in the case of reversibility. Further, as argued by Eu, dN has to have positive values along the irreversible segments of the cycle and should identically vanish along its reversible segments. This may also be appreciated by recalling that an irreversible process inherently has a definite arrow of time, hence there remains no reason or logic which will allow a positive sign to dN along a certain irreversible segment of the cycle and negative values to it along its rest parts of the irreversible segments. That is the second law of thermodynamics rigorously gives,

$$N \geq 0, \quad dN \geq 0 \tag{14}$$

where the validity of the equality is under the condition of reversibility.

Next on combining eqs. (12) and (13), we get

$$\oint_{\text{irr}} \left[\frac{1}{T(t)} \frac{dQ}{dt} (t) + \frac{dN}{dt} (t) \right] dt = 0 \tag{15}$$

Since the cyclic integral of eq. (15) vanishes its integrand is obtained as an exact differential. Hence, the time dependent entropy function, S(t), within an additive constant, gets identified as

$$\frac{dS(t)}{dt} = \frac{1}{T(t)} \frac{dQ}{dt} (t) + \frac{dN}{dt} (t) \tag{16}$$

In almost all previous expositions[4–7] N has been termed as the uncompensated heat but as it can be seen from the above equations its units are energy per degree and hence we have coined the term uncompensation function for it. The uncompensated heat[8] denoted by dQ' can be easily introduced as,

$$\frac{dN}{dt} (t) = \frac{1}{T(t)} \frac{dQ'}{dt} (t) > 0 \tag{17}$$

that is, the second law of thermodynamics guarantees that,

$$dQ' \geq 0 \tag{18}$$

where the equality holds in the case of reversibility. Thus on using the uncompensated heat eq. (16) reads as:

$$\frac{dS(t)}{dt} = \frac{1}{T(t)} \frac{dQ}{dt}(t) + \frac{1}{T(t)} \frac{dQ'}{dt}(t) \tag{19}$$

Notice that for developing an irreversible thermodynamic description based on the laws of thermodynamics it is required to obtain a proper expression for dQ'. Since dQ' appears only on account of irreversibility one is required to know what type of irreversibility exists and what is its origin in terms of the fundamental interactions. Moreover, from the above derivation it is clear that the time dependent entropy, $S(t)$, of eq. (16) and hence that of eq. (19) is rigorously based on the second law of thermodynamics and is obtained as a unique function. The latter assertion stems from the fact that $S(t)$ has been defined on a given particular irreversible path. Eu[5] calls it as *calortropy* but we have retained for it the name entropy because it is given by the second law of thermodynamics and none else. Further, in view of eqs. (14) and (18), both from eqs. (16) and (19) we rigorously obtain the following inequality, namely:

$$\frac{dS(t)}{dt} > \frac{1}{T(t)} \frac{dQ}{dt}(t) \tag{20}$$

which is none else than the second Clausius' inequality, namely eq. (2), but in an elaborated form. Thus we have proved on the one hand the correctness of Clausius' nonelaborated assertion which Meixner has pointed out[1] about eq. (2) and on the other hand that the inequality of eq. (2) cannot be prescribed directly even from the cyclic form of Clasius' inequality, eq. (10), whereas eq. (1) directly follows from eq. (10) because eq. (6) is independently given by the second law of thermodynamics. Therefore there remains no ambiguity that eq. (2) contains entropy, S, of nonequilibrium states and hence is a time dependent one.

If there exits a nonuniformity of temperature within the system, then instead of eq. (10) one needs to start with eq. (7) and hence instead of eq. (16) one obtains

$$\frac{dS(t)}{dt} = \frac{1}{T_R(t)} \frac{dQ}{dt}(t) + \frac{dN}{dt}(t) \tag{21}$$

Thus we see that a unique time dependent entropy, $S(t)$, is elegantly obtained in this case too. The only uncomfortable part in eq. (21) is that it contains the temperature of the heat reservoirs and hence the corresponding irreversible thermodynamic description if developed using it will have a temperature function which is foreign to the system. But the system does not have a unique single temperature because of the existence of the temperature gradient. This clearly drives us to go for a local level description instead of the global level of it which is considered so far in the above discussion. As far as the Clausius inequality is concerned we now have, instead of eq. (20), the following, namely,

$$\frac{dS(t)}{dt} > \frac{1}{T_R(t)} \frac{dQ}{dt}(t) \tag{22}$$

which is a yet another elaborated form of eq. (2) but a more general one than eq. (20). Indeed, one can introduce the uncompensated heat, dQ', in eq. (21) which gives

$$\frac{dS(t)}{dt} = \frac{1}{T_R(t)} \frac{dQ}{dt}(t) + \frac{1}{T_R(t)} \frac{dQ'}{dt}(t) \tag{23}$$

However, the problems for developing an irreversible thermodynamic description from eq. (23) remain the same which, as discussed above, are associated with eq. (21).

In the above discussion we have derived Clausius' inequality, namely eqs. (20) and (22), which has been worked out herein for the first time while the rest part of the above description is largely due to Eu[5-7]. However, in his writings Eu has not used the subscript R to T which we suppose is implied therein.

The local level description

There is an inherent difficulty in transforming eq. (21) and (22) and also eq. (23) into the corresponding local level forms because they contain the temperature of the heat reservoirs which do not make a direct thermal contact with an interior position of the system. However, the problem can be handled in two different ways. In the first choice one can easily transform eq. (16) or eq. (19) into the corresponding local level form and then see if it is possible to extract therefrom the local form of Clausius' inequality. In the second choice one first converts eq. (7) into a local form and then uses it to directly arrive at the time dependent entropy at the local level which obviously would be position dependent too. Then see if a local form of the Clausius' inequality can be arrived at therefrom. We now proceed to describe both the choices. The following discussion also confirms our earlier assertion, namely, one cannot have a local form of Clausius' inequality[3]

A.   The systems with uniform temperature

Since eq. (15) establishes the entropy function, $S(t)$, for a global system in nonequilibrium, the left hand side of eq. (19) gives

$$\frac{dS(t)}{dt} = \int_V \rho(\mathbf{r}, t) \frac{ds(\mathbf{r}, t)}{dt} dV \tag{24}$$

where s is the per unit mass entropy, V is the total volume of the closed system, **r** is the position vector and ρ is the mass density. While for the two terms on the right had side of eq. (19), we have

$$\frac{1}{T(t)} \frac{dQ}{dt}(t) = \int_A -\frac{Q(A, t)}{T(t)} d\mathbf{A} \tag{25}$$

$$\frac{1}{T(t)} \frac{dQ'}{dt}(t) = \int_V \frac{1}{T(t)} \rho(\mathbf{r}, t) \frac{dq'}{dt}(\mathbf{r}, t) dV \tag{26}$$

where A is the total bounding surface area of the closed system, $\mathbf{A}$ is the surface area coordinate on the bounding surface, $\mathbf{dA}$ is the differential element of the surface area vector, $\mathbf{Q}$ is the heat flux density vector and dq' is the per unit mass differential element of the uncompensated heat. The minus sign in eq. (25) stems from the fact that by convention the outward normal to the bounding surface is taken positive. Next on applying the Gauss theorem[9] the right hand side surface integral of eq. (25) gets converted to the corresponding volume integral and hence we have

$$\frac{1}{T(t)} \frac{dQ}{dt}(t) = \int_V - \mathrm{div}\left(\frac{\mathbf{q(r, t)}}{T(t)}\right) dV \qquad (27)$$

where $\mathbf{q}$ is the so called heat flux density vector. Notice that we have used the symbol $\mathbf{q(r, t)}$ instead of $\mathbf{Q(r, t)}$ to stress the fact that the open system features are associated with every interior position which is not the case with $\mathbf{Q}$ on the bounding surface of the closed system. Next, on substituting eqs. (24), (26) and (27) into eq. (19), we have

$$\int_V \rho(\mathbf{r}, t) \frac{ds(\mathbf{r}, t)}{dt} dV = \int_V - \mathrm{div}\left(\frac{\mathbf{q(r, t)}}{T(t)}\right) dV + \int_V \frac{1}{T(t)} \rho(\mathbf{r}, t) \frac{dq'}{dt}(\mathbf{r}, t) dV \quad (28)$$

Thus from eq. (28) we obtain the local level entropy balance equation namely:

$$\rho \frac{ds}{dt} = -\mathrm{div}\left(\frac{\mathbf{q}}{T}\right) + \frac{1}{T} \rho \frac{dq'}{dt} \qquad (29)$$

Now it is important to note that even though the uncompensated heat, dQ' is a positive quantity the same property is not inherited by its local level counterpart dq' because with the latter the irreversibility having its origin in the open system features is also associated. Hence, it is simply not possible to derive the local level analogue of eq. (20) from eq. (29). On the other hand, one may wrongly think that one can convert eq. (20) into the corresponding local form on using eqs. (24) and (27). Of course, one can use the latter two equations in the former but then one cannot suppress the integrals on both the sides of the inequality so obtained because the inequality of eq. (20) holds only for the closed systems and there is no way to guarantee that it would hold for open systems too. That is, one cannot suppress the integrals on both the sides of the following inequality, namely,

$$\int_V \rho \frac{ds}{dt} dV > \int_V - \mathrm{div}\left(\frac{\mathbf{q}}{T}\right) dV \qquad (30)$$

obtained from eq. (20). If it is done then the result would be that for a tiny open system but having no guarantee of its validity. This is in conformity with our previous demonstration[3] that no Clausius' inequality exists for open systems and cannot be ever arrived at. Notice that in the preceding two equations we have not depicted the $\mathbf{r}$ and t dependences of the physical quantities for the sake of simplicity but they are implied and remain true also in the equations described below.

In the next sub-section we are considering the most general case.

B. A most general case

If we use eq. (7) it implies that at a given instant of time during a cyclic operation the system makes a thermal contact with a single heat reservoir. This restriction gets removed by expressing eq. (7) as

$$\oint_{irr} \int_A -\frac{Q(A, t)}{T(A, t)} \cdot dA \, dt < 0 \tag{31}$$

That is, eq. (31) accommodates the situations in which at a given instant of time the closed system makes the thermal contacts with different heat reservoirs obviously at different positions on its bounding surface. Thus eq. (31) serves as the most general global level statement of the Clausius' inequality. It is also obvious that the temperature of the surface area element, dA, on the outer face of the bounding surface of the system cannot be different from that of the heat reservoir making a thermal contact with it. This is so because the temperature measurement involves a dynamic thermal equilibration of the position in question with the temperature measuring device. The time required for the thermal equilibration is of the order of nanoseconds or even less,[10, 11] Thus the temperature function is not amenable experimentally before the time required for the thermal equilibration and during this period a thermal equilibration (dynamic) would be achieved between the bounding surface of the system and the heat reservoir making a thermal contact with it. Also we have earlier described[12] how the quality of temperature remains the same in going from a heat reservoir to the bounding surface (of the system in nonequilibrium) to an interior position of a system (in nonequilibrium). This establishment imparts the required legitimacy to the temperature function appearing in eq. (31). The said legitimacy we have independently established recently by generalizing the zeroth law of thermodynamics so that the nonequilibrium states too come in its fold[13]. This in turn paves the way to apply the Gauss theorem[9] to the surface integral of eq. (31). Hence, eq. (31) transforms to,

$$\oint_{irr} \int_V -div\left(\frac{q(r, t)}{T(r, t)}\right) dV \, dt < 0 \tag{32}$$

Next we manipulate eq. (32) exactly on the same lines which gives eq. (16) from eq. (11). Thus the uncompensation function, N, is obtains as

$$N = \oint_{irr} dN = -\oint_{irr} \int_V -div\left(\frac{q}{T}\right) dV \, dt > 0 \tag{33}$$

and for dN eq. (14) holds good as described above. Now we transform N into the local uncompensation function, $\mathcal{N}(r, t)$, per unit mass, as

$$\oint_{irr} dN = \oint_{irr} \int_V \rho \frac{d\mathcal{N}}{dt} dV \, dt > 0 \tag{34}$$

Since on the right hand side of eq. (34) there are two noninterchangeable integrals[14] it is not possible to directly make any assertion about the sign of $d\mathcal{N}$. Now on substituting eq. (34) into eq. (33) and rearranging, we obtain

$$\oint_{irr} \int_V \left[-\text{div}\left(\frac{\mathbf{q}}{T}\right) + \rho\,\frac{d\mathcal{N}}{dt} \right] dV\,dt = 0 \qquad (35)$$

Since the cyclic integral of eq. (35) vanishes it is now possible to exchange the order of integration in it. Hence, we obtain

$$\oint_{irr} \left[-\text{div}\left(\frac{\mathbf{q}}{T}\right) + \rho\,\frac{d\mathcal{N}}{dt} \right] dt = 0 \qquad (36)$$

The vanishing of the cyclic integral of eq. (36) establishes that its integrand is an exact differential and hence the position and time dependent local level entropy, $s(\mathbf{r}, t)$, as a state function, is provided as

$$\rho\,\frac{ds}{dt} = -\text{div}\left(\frac{\mathbf{q}}{T}\right) + \rho\,\frac{d\mathcal{N}}{dt} \qquad (37)$$

Indeed, one can introduce the uncompensated heat, dq', as

$$d\mathcal{N} = \frac{dq'}{T} \qquad (38)$$

However, since there cannot be a definite assertion about the sign of $d\mathcal{N}$ it is not possible to assign the positive definite sign to dq'. But one, indeed, can substitute eq. (38) into eq. (37) which gives eq. (29). Notice that eqs. (33) to (38) contain the time and position dependent temperature function provided by the generalized zeroth law of thermodynamics[13].

Indeed, it is not possible to get a local level analogue of the Clausius' inequality from eq. (37) and hence from eq. (29) too. This conforms very well with our earlier demonstration[3] that no Clausius' inequality exists for open systems nor can be ever devised. However, only in those nonequilibrium situations in which each interior position of a system remains devoid of irreversibility due to the open system features, that is each interior position behaves as if it were a tiny closed system (in fact, the interior positions are the point masses from the macroscopic point of view but consist of a very large number of molecules[9]), then eqs. (29) and (37) give the following local form of the Clausius inequality, namely:

$$\rho\,\frac{ds}{dt} > -\text{div}\left(\frac{\mathbf{q}}{T}\right) \qquad (39)$$

because in this case one rigorously has

$$dq' \geq 0 \qquad (40)$$

In practice this situation is met in spatially uniform systems having irreversibility only on account of chemical reactions occurring at finite rates. But then in this

case the global level equations remain adequate for developing an irreversible thermodynamic description and hence there is no need to go for the local level description. This we are describing in a separate paper[15]. However, in a general nonequilibrium situation eq. (29) or eq. (37) can indeed be used to develop an irreversible thermodynamic description, in spite of the nonavailability of a local level analogue of Clausius' inequality. This subject matter we will discuss in a separate paper[16].

Concluding Remarks

In thermodynamic literature the Clausius' inequality is stated in three different ways, namely, eqs. (1), (2) and (7) or (10). Herein we have restressed that eq. (7) is a direct consequence of the second law of thermodynamics and hence it is a primary version of the Clausius inequality. If the Clausius inequality is expressed in the form of eq. (10) without stating that T in it is the temperature of the heat reservoirs which come in contact with the closed system during its cyclic operation, then an ambiguity creeps in about its generality. That is, one would tend to exclude the irreversibility associated with the heat exchange between the system and the heat reservoirs coming in its contact. In this paper, we have further augmented eq. (7) and the result is eq. (31). The later version of the Clausius' inequality is the most general mathematical statement because it also includes ⋅ those situations in which the closed system simultaneously interacts thermally with the heat reservoirs of different temperatures. That is, the elements of heat exchanged at different positions on the bounding surface of the closed system correspond to different temperatures at a given instant of time.

From irreversible thermodynamic point of view it is essential to know whether eqs. (1), (2) and (7) are the equivalent statements of Clausius' inequality or not and whether they contain the same physical entities. Meixner has raised a question with respect to the origin of eq. (2) because Clausius did not give its derivation. In this paper we have first elaborated that eq. (2) is not a mere differential form of eq. (1) and hence the former equation does not contain the entropy of an equilibrium state. However, to show that eq. (2) indeed contains the entropy of a nonequilibrium state one needs to first establish a time dependent entropy function. But the second law of thermodynamics does not directly provide an entropy function for nonequilibrium states. This problem we have earlier circumvented while formulating the generalized phenomenological irreversible thermodynamic theory (GPITT)[17-19], by identifying a universal inaccessibility principle (UIP) which leads directly to the time and position dependent entropy function and recently by Eu[5] wherein he begins with eq. (10) and arrives at eq. (16). As can be seen from the derivation of eq. (16), the time dependent entropy so obtained is an unique function. The same is true for the entropy function obtained through UIP which clearly dispels Meixner's apprehnsion[1] that no unique entropy function exists in nonequilibrium. The origin of eq. (2) has been established by using eqs. (16) and (21). This clearly demonstrates that eq. (2) does contain the entropy function of a nonequilibrium state. Thus eqs. (20) and (22) are obtained as the more elaborate versions of eq. (2)

ACKNOWLEDGEMENTS

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