On the Need to Insert the Concept of Relativity in Thermodynamics Courses

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Abstract

Contrary to the first law of thermodynamics which is generally considered as easily understandable, the second law is often felt as raising conceptual difficulties. It can be noted that their usual presentation is not homogeneous, since the expressions referring to the first law are generally energy equations, while those referring to the second law are entropy equations. If we give to the second law the form of an energy equation, it seems that we are led to extend the significance of the first law. The reason is that, doing so, the change in internal energy corresponding to a given process appears to be different as we are in conditions of irreversibility or of reversibility. In thermodynamic language, this is a way to say that the equality $dU_{irr} = dU_{rev}$ classically interpreted as the formulation of the first law must be substituted by the inequality $dU_{irr} > dU_{rev}$. Writing this last expression under the form $dU_{irr} = dU_{rev} + dU_{add}$, the question asked concerns the origin of the additional energy noted dU_{add} . The suggested answer is that dU_{add} is a consequence of the Einstein mass-energy relation $E = mc^2$. This would mean that the laws of thermodynamics are closely linked to the concept of relativity and that the difference $dU_{irr} - dU_{rev}$ can also be formulated $dU_{irr} = dU_{rev} - c^2 dm$. Such an interpretation was evidently impossible for the creators of the thermodynamic theory, since relativity was unknown at that time. The aim of the present paper is to detail the reasons which lead to this hypothesis, with the hope that it can be felt as a clarification and extension of the theory.

Keywords: Thermodynamics, reversibility, irreversibility, energy, entropy, relativity, Einstein's relation

1. Location of an Ambiguity in the Usual Understanding of the Thermodynamic Theory

1.1 Preliminary Remark

One of the postulates closely linked to the first law of thermodynamics lies on the idea that when a system evolves from an initial state (noted 1) to a final state (noted 2), its change in internal energy is independent of the level of irreversibility of the process. Using the symbol "*irr*" for reversibility, the symbol "*rev*" for reversibility, and the symbol U for the internal energy, this is a way to say that the change in internal energy always obeys the relation:

$$\left[\Delta U_{irr}\right]^2 = \left[\Delta U_{rev}\right]^2 \tag{1}$$

which means that U is considered as a state function.

Translated in differential form, eq. 1 becomes:

$$dU_{irr} = dU_{rev} \tag{2}$$

which shows more directly that dU is an exact differential.

When the exchanges of energy between the system and its surroundings are limited to work (noted W) and heat (noted Q) - condition corresponding to the numerical example that will be examined in section 2.3 - the expression for dU is:

$$dU = dw + dq \tag{3}$$

In eq. 3, the use of the minuscule letters w and q is the classical convention to recall that, contrary to what is admitted for dU, the terms dw and dq are not necessarily exact differentials.

A first consequence of the combination of eq. 2 and 3 is that if dw obeys the relation:

$$dw_{irr} > dw_{rev} \tag{4}$$

the corresponding relation for dq is necessarily:

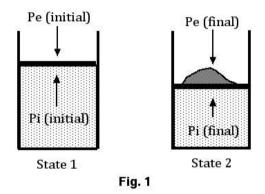
$$dq_{irr} < dq_{rev} \tag{5}$$

and conversely.

Before examining the consequence of this preliminary remark, let us come back to the concepts of reversibility and irreversibility when they are applied to work and to heat.

1. 2 The Concepts of Reversibility and Irreversibility Applied to Work

Referring to Fig.1, we consider a gas (clear grey) contained in a cylinder which is made of a diathermic material and equipped with a mobile frictionless piston (black). When the piston is at equilibrium (state 1), it is the sign that the external pressure P_e is equal to the internal pressure P_i . If the external pressure increases to a new value P_e , for example by placing a given amount of sand (dark grey) on the piston, this last one will move downwards until the internal pressure P_i becomes equal to the new external pressure P_e (state 2). We suppose that, both in the initial state and the final state, the gas is at the temperature T of the surroundings. This condition is facilitated by the fact that the walls of the system are permeable to heat, being supposed to be made of a diathermic material.



The sand can be put on the piston very rapidly or very slowly. In the first case, the external pressure reaches immediately the new value P_e , which is different from the internal pressure P_i at each moment of the process. It is only at the end of the process that both pressures become equal.

In such condition, we know that the process is said to be **irreversible** and that the work done on the gas is given by the relation:

$$dw_{irr} = -P_e dV \tag{6}$$

where dV is the change in volume of the gas.

If, on the contrary, the sand is deposited very progressively, we can admit that, at each moment of the process, the external pressure P_e and the internal pressure P_i are nearly equal. In such condition, the process is said to be reversible and eq. 1 takes the particular form:

$$dw_{rev} = -P_i dV \tag{7}$$

The consequence of this situation is that, for a determined value of dV, the difference between dw_{irr} and dw_{rev} can be written:

$$dw_{irr} - dw_{rev} = dV(P_i - P_e) \tag{8}$$

where P_i and P_e are the respective average values of both pressures at the moment taken in consideration.

Observing, from fig.1, that dV is positive when $P_i > P_e$ and negative when $P_i < P_e$, we see that the product $dV(P_i - P_e)$ is always positive. Therefore another possible writing of eq. 8 is:

$$dw_{irr} = dw_{rev} + dw_{add} \tag{9}$$

where dw_{add} represents the additional work $dV(P_i - P_e)$ whose value is positive.

This is a way to say that the terms dw_{irr} and dw_{rev} are always linked together by the relation:

$$dw_{irr} > dw_{rev} \tag{10}$$

It can be noted that the relation $dw_{irr} > dw_{rev}$ previously presented as a possible hypothesis (eq. 4) now appears as being always verified (eq. 10). The consequence of this observation is that, if the postulate $dU_{irr} = dU_{rev}$ recalled by eq. 2 is exact, the relation $dq_{irr} < dq_{rev}$ given by eq. 5 must be always verified too.

Before examining in the next section what is the proposal classically admitted for the relation between dq_{irr} and dq_{rev} it can be recalled that the energy designated dw_{add} in eq. 9 does not appear under the form of work, but generally under the form of heat, coupled with a reduction of the time required by the system to pass from the initial state 1 to the final state 2.

Another important remark is that the relation proposed between dw_{irr} and dw_{rev} sometimes appears as $dw_{rev} > dw_{irr}$ and not $dw_{irr} > dw_{rev}$. As explained in a previous paper (Tane 2007), this inversion comes from the fact that instead of giving a positive value to the work reveived by the system (convention of thermodynamicians defining the work as $dw_{irr} = -P_e$ dV, as done in eq. 6), some authors attribute the positive value to the work done by the system (convention of engineers defining the work as $dw_{irr} = P_e dV$). In thermodynamics textbooks, the convention of thermodynamicians is almost systematically adopted in the writing of equations, but the convention of engineers remain frequently in use in the way of drawing the diagrams. Indeed, the curves *PV* representing the difference between reversible and irreversible work generally appear in the right upper part of the diagrams (instead of the right lower part), giving the the impression that the adequate relation is $dw_{rev} > dw_{irr}$. Such a proposal is true referring to the convention of engineers, but not to the convention of thermodynamicians. The present paper is exclusively written according to this last convention.

1.3 The Concepts of Reversibility and Irreversibility Applied to Heat

In physics textbooks, this question is closely linked to the concept of entropy and introduced in the chapters dealing with the second law of thermodynamics. The problem is often presented in the following condensed way.

In conditions of reversibility, the change in entropy is linked to the change in heat and the absolute temperature *T* by the relation:

$$dS = dq / T \tag{11}$$

In condition of irreversibility, the corresponding equation becomes:

$$dS > dq / T \tag{12}$$

Through the numerical examples which are generally proposed to illustrate the use of these equations, it can be understood that the precise meaning of eq. 11 is:

$$dS = dq_{rev} / T_i \tag{13}$$

and that the precise meaning of eq. 13 is

$$dS = dq_{rev} / T_e + ds_i \tag{14}$$

where ds_i is designated as the internal component of the entropy.

The consequence of this observation is that the relation between dq_{irr} and dq_{rev} is not accessible from a direct reading of these expressions. A complementary step is needed which consists in converting eq. 13 and 14, which have the dimension of entropy, in equations having the dimension of energy.

If we focus attention on the entropy eq. 14, which corresponds to the more general case, we see that multiplying each term by T_e leads to the energy equation:

$$T_e dS = dq_{rev} + T_e ds_i \tag{15}$$

whose significance is:

$$dq_{irr} = dq_{rev} + T_e ds_i \tag{16}$$

Knowing that the term ds_i is always positive (fundamental information associated to the second law) and the term T_e is too (absolute temperature), it appears that the product $T_e ds_i$ is itself always positive.

Therefore, the terms dq_{irr} and dq_{rev} are linked together by the general relation

$$dq_{irr} > dq_{rev} \tag{17}$$

(23)

which can also be written:

$$dq_{irr} = dq_{rev} + dq_{add} \tag{18}$$

where dq_{add} has a positive value.

As can be seen, there is a similarity between eq. 18 which concerns heat and eq. 9 which concerns work, expressing the difference between dw_{irr} and dw_{rev} .

An extension of this similarity is possible, because observing the correspondance between the different terms of eq. 15 and eq. 16 (and remembering the information given by eq. 13), we see that the general definitions of dq_{irr} and dq_{rev} can be directly given by the relations:

$$dq_{irr} = T_e dS \tag{19}$$

$$dq_{rev} = T_i dS \tag{20}$$

The entropy being a state function, the terms dS of eq. 19 and 20 have the same value for a determined process. In such conditions, the difference between dq_{irr} and dq_{rev} takes the form:

$$dq_{irr} - dq_{rev} = dS(T_e - T_i)$$
⁽²¹⁾

It can be noted from eq. 19 and 20 that the sign of dS is always the same as the sign of dq. Having dq > 0 when $T_e > T_i$ and dq < 0 when $T_e < T_i$, the same is true for dS. Therefore, the term $dS(T_e - T_i)$ of eq. 21 appears to be always positive,

 $dq_{irr} = dq_{ray} + dq_{add}$

confirming the relation $dq_{irr} > dq_{rev}$ already suggested by eq. 17.

Writing eq. 21 under the form:

$$dq_{irr} = dq_{rev} + dS(T_e - T_i)$$
⁽²²⁾

or

we see that this last expression is equivalent to the one already given by eq. 18.

2. Theoretical Consequences of This Analysis

2.1 The Reason Explaining the Need of Relativity in Thermodynamics

Taking into account that the respective definitions of dU_{irr} and dU_{rev} are:

$$dU_{irr} = dq_{irr} + dw_{irr} \tag{24}$$

$$dU_{rev} = dq_{rev} + dw_{rev} \tag{25}$$

we see that having simultaneously $dq_{irr} > dq_{rev}$ (eq. 17) and $dw_{irr} > dw_{rev}$ (eq. 10), the equality $dU_{irr} = dU_{rev}$ becomes impossible and need to be substituded by the inequality:

$$dU_{irr} > dU_{rev} \tag{26}$$

Writing this last expression under the form:

$$dU_{irr} = dU_{rev} + dU_{add} \tag{27}$$

the question asked is the origin of the energy noted dU_{add} . The fact that we are really confronted to a problem appears more clearly if we consider an isolated system divided in two parts having a mutual exchange of energy. Indeed, the application of eq. 26 and 27 to both parts leads to the idea that the internal energy of the global system goes increasing, although this system is isolated. The numerical example examined in section 2.3 is an illustration of this situation.

The hypothesis suggested in previous papers (Tane, 2005; Krasnoholovets and Tane, 2006) is that the additional energy could be explained by the Einstein mass-energy relation $E = mc^2$, whose derivative takes the initial form $dE = c^2 dm$ knowing that c, the speed of light, is constant. It is a way to say that each irreversible process generates - inside the system to which it refers - an energy due to a correlative disintegration of matter. Although the change in mass, in most cases, is too small to be detectable, the corresponding increase in energy appears as a general feature, giving to the term dU_{add} the significance:

$$dU_{add} = -c^2 dm \tag{28}$$

and to eq. 27 the significance:

$$dU_{irr} = dU_{rev} - c^2 dm \tag{29}$$

In eq. 28 and 29, the minus sign placed in front of the term $c^2 dm$ is inspired by the the fact, often observed in nuclear reactions, that a creation of energy is linked to a decrease in mass. Supposing that the same is true in a general way, the minus sign just evoked appears as a necessary condition to give dU_{add} a positive value. Correlatively, a positive value of dm would lead to a negative value of dU_{add} . The procedure is the same as the one used in eq. 6 and 7 to give dW a positive value when the system receives work (i.e. when the volume obeys the condition dV < 0) and a negative value when it provides work (i.e. when the volume obeys the condition dV > 0).

From this point of view, eq. 29 can be looked as a preliminary attempt to present in a single formulation, the first law, the second law and the Einstein mass-energy relation. Having noted with eq. 26 that the general relation between dU_{irr} and dU_{rev} is $dU_{irr} > dU_{rev}$, it can be deduced that the general evolution of dm is dm < 0. In this proposal, the adjective "general" is used to remind that the laws of thermodynamics are inspired by experiments made in our near surroundings and on systems made of inert matter.

It is interesting to note that in some recent textbooks (Kondepudi, 2008; Linder, 2011), the need to connect thermodynamics with relativity is evoked. In practice, the use of relativity remains rather absent of thermodynamics courses although this idea was equally suggested by other authors (Tolman, 1928 and 1934; Callen and Horwitz, 1971; Rengui, 1996, Hayward, 1999; Far ás, Moya and Pinto, 2007; Requardt, 2008; Gupta, R. C., Gupta, R. and Gupta, S, 2010).

2.2 The Incidence of this Hypothesis on the State Function Free Energy, Noted G

The state function free energy, noted G, is of commun use in thermodynamics, particularly - but not necessarily - for the study of chemical reactions. Being defined as:

$$G = U + PV - TS \tag{30}$$

its derivation can be written:

$$dG = dU + d(PV - TS) \tag{31}$$

whose significance - as will be seen below - is

$$dG = dU_{rev} - dU_{irr} \tag{32}$$

In the usual understanding of the thermodynamic theory, this last expression would have no sense, because the equality

 $dU_{rev} = dU_{irr}$ being implicitly admitted, the result obtained for dG would appear in all cases under the form dG = 0.

With regards to this topic, the fact that the efficiency of the thermodynamic tool is recognized for a long time seems to

the be the sign that the inequality $dU_{rev} \neq dU_{irr}$ is at least partially taken into account in practice (i.e in thermodynamic calculations) although it remains totally absent from the theory. This is probably the reason of the conceptual difficulties often felt in thermodynamics.

In the new suggested interpretation, which lies on the idea that $dU_{irr} = dU_{rev} - c^2 dm$ (eq. 29), the significance of the term dG becomes:

$$dG = +c^2 dm \tag{33}$$

The justification of this result is the following. Starting with eq. 31, whose expression is:

$$dG = dU + d(PV - TS)$$
^R(32)

we can precise its meaning through the formulation:

$$dG = dU_{rev} + P_e dV + V dP_e - T_e dS - S dT_e$$
(34)

Then, observing from eq. 29 that dU_{rev} can be written $dU_{rev} = dU_{irr} + c^2 dm$, and taking into account that dU_{irr} is defined as $dU_{irr} = T_e dS - P_e dV$, we get for dG:

$$dG = T_e dS - P_e dV + c^2 dm + P_e dV + V dP_e - T_e dS - S dT_e$$
(35)

that is, after simplication:

$$dG = +c^2 dm + V dP_e - S dT_e$$
(36)

In the study of chemical reactions, it is often admitted that dP_e and dT_e are nil, because the external pressure and the

external temperature are supposed constant.

As will be observed with the numerical example examined in section 2.3, if the external pressure P_e and the external

temperature T_e are not constant, their average values, which can be designated P_e^* and T_e^* , are constant (referring to the process which is considered). In such conditions their derivatives dP_e^* and dT_e^* are nil. For this reason, a more general expression of dG consists in writing eq. 34 as:

$$dG = dU_{rev} + P_e^* dV + V dP_e^* - T_e^* dS - S dT_e^*$$
(37)

In such condition (and remembering from eq. 29 that $dU_{rev} = dU_{irr} + c^2 dm$) we get directly for dG the conclusion:

$$dG = c^2 dm \left(= -dU_{add}\right) \tag{38}$$

which shows that a negative value of dG (condition of evolution of a thermodynamic system) corresponds to a negative value of dm.

Knowing that the initial definition of dU_{rev} is $dU_{rev} = T_i dS - P_i dV$ and entering this value in eq. 37, we get for dG (after simplifications and factorisations) the expression:

$$dG = dS(T_i^* - T_e^*) - dV(P_i^* - P_e^*)$$
(39)

Then, combining eq. 38 and 39, we see that:

$$dG = dS(T_i^* - T_e^*) - dV(P_i^* - P_e^*) = c^2 dm$$
(40)

2.3 Numerical Example Showing the Role of dU_{add} in Thermodynamic Calculations

We consider an isolated system (Fig. 2), divided in two parts designated 1 and 2, separated by a diathermic wall. In the initial state, part 1 contains 1 kg of water at $T_{i1} = 10$ °C (= 283 K) and part 2 contains 1 kg of water at $T_{i2} = 70$ °C (= 343 K). Knowing that an exchange of heat will occur between both parts until they reach the same final temperature ($T_{f1} = T_{f2} = T_f$), the difference between the usual interpretation and the new suggested one can be summarized as follows:

Water 1	Water 2
T = 283 K	T = 343 K

Fig. 2

2.3.1 Usual Interpretation

No distinction being made between dU_{irr} and dUr_{ev} , the change in internal energy is simply noted dU and the starting equation is $dU_{syst} = 0$, since the system has been defined as isolated.

The wall separating part 1 and part 2 being fixed, there is no exchange of work between them and, consequently, it can be deduced from eq. 3 that $dU_{syst} = dq_{syst}$.

Assuming that the heat capacity of water ($c = 4186 J K^{-1} kg^{-1}$) can be considered roughly constant over the temperature interval, the final temperature T_f is given by the formula:

$$T = (C_1 T_1 + C_2 T_2) / (C_1 + C_2) = 313 K$$
(41)

where $C_1 = C_2 = 4186 J K^{-1}$ (since C = mc and $m_1 = m_2 = 1 kg$)

The changes in heat of part 1 and part 2 are respectively:

$$\Delta q_1 = C_1 (T_{f1} - T_{i1}) = 4186 (313 - 283) = 125580 J$$
(42)

$$\Delta q_2 = C_2(T_{f^2} - T_{i^2}) = 4186 \ (313 - 343) = -125580 \ J \tag{43}$$

Their changes in entropy are:

$$\Delta S_{1} = \int_{T_{11}}^{T_{11}} C_{1} \frac{dT}{T} = 4185 \ Ln \frac{313}{283} = 422 \ JK^{-1}$$
(44)

$$\Delta S_2 = \int_{T_{12}}^{T_{f2}} C_2 \frac{dT}{T} = 4185 \ Ln \frac{313}{343} = -383 \ JK^{-1}$$
(45)

For the global system, the results are therefore:

$$\Delta U_{syst} = \Delta q_{syst} = \Delta q_1 + \Delta q_2 = 0 \tag{46}$$

$$\Delta S_{syst} = \Delta S_1 + \Delta S_2 = 39 J K^{-1}$$
(47)

showing an increase in entropy, while the internal energy remains constant.

When it is connected to the Einstein relation - an approach which is not frequent - this interpretation leads to the idea that the mass of the system does not vary. The reason is that the change in mass evoked for part 1 (generally noted dm_1 > 0) is exactly compensated by the change in mass concerning part 2 ($dm_2 < 0$)

2.3.2 New Suggested Interpretation

Admitting that the term dw_{syst} can be neglected, as done in the classical interpretation, the attention is exclusively focused on the term dq_{syst} and the produce is the following.

Instead of using the entropy relation $dS = dq_{rev}/T_e + ds_i$ (eq. 14) as a starting basis for discussion, we use the energy relation $T_e dS = dq_{rev} + T_e ds_i$ (eq. 15), keeping in mind that its significance is $dq_{irr} = dq_{rev} + dq_{add}$ (eq. 18).

The integrated form of the term dq_{irr} can be written:

$$\Delta q_{irr} = \int T_e \, dS = T_e^* \int dS = T_e^* \Delta S$$

where T_e^* is the average value of T_e during the process. It constitutes a space-time parameter which can be calculated observing that:

For part 1,
$$T_{e_1}^* = T_2^* = \Delta q_2 / \Delta S_2 = (-125580)/(-383) = 328 K$$
 (48)

For part 2,
$$T_{e2}^* = T_1^* = \Delta q_1 / \Delta S_1 = (125580) / (422) = 298 K$$
 (49)

Therefore, the continuation of the calculation can be done as follows:

From $\Delta q_{irr} = \Delta q_{rev} + \Delta q_{add}$ we have $\Delta q_{add} = \Delta q_{irr} - \Delta q_{rev}$ which gives successively:

$$\Delta q_{add1} = T_2^* \Delta S_1 - \Delta q_{rev1} = 328 \times 422 - 125580 = 12836 \text{ J}$$
(50)

$$\Delta q_{add2} = T_1^* \Delta S_2 - \Delta q_{rev2} = 298 \times -383 - (-125580) = 11446 \text{ J}$$
(51)

The fact that Δq_{add} is positive in both cases is the sign that there is an increase in energy in both part 1 and part 2, although this increase is slightly lower in part 2 (i.e in the part which loses heat, because its initial temperature is the higher)

For the global system, the value of the term $\Delta q_{addSyst}$ is therefore:

$$\Delta q_{addSyst} = \Delta q_{add1} + \Delta q_{add2} = 24282 \text{ J}$$
(52)

If the Einstein mass-energy relation is interpreted under the light of eq. 29 or 39, the corresponding decrease in mass is:

$$\Delta m = -(24282) / \left[(3 \times 10)^8 \right]^2 = 2.69 \times 10^{-13} \text{ kg}$$
(53)

The same result can be obtained through the use of eq. 40. The term dw_{syst} being neglected, this equation is reduced to the expression:

 $\Delta G = \Delta S(T_i^* - T_a^*)$

$$dG = dS(T_i^* - T_e^*) \tag{54}$$

Its integration leads to:

$$\Delta G_1 = 422 \ (298 - 328) = -12660 \text{ J} \tag{55}$$

$$\Delta G_2 = -383 (328 - 298) = -11490 \text{ J}$$
(56)

$$\Delta G_{\text{Syst}} = \Delta G_1 + \Delta G_2 = -24150 J \tag{57}$$

Remembering that $\Delta G = -\Delta q_{add} = +c^2 \Delta m$, it can be noted that the results obtained for eq. 55, 56 and 57, are almost similar to those obtained for eq. 50, 51 and 52. The slight differences come from the fact that the values $T_1^* = 298 K$ and $T_2^* = 328 K$ are rounded.

According to eq. 38, the result obtained for Δm

$$\Delta m = -24150 / \left[(3 \cdot 10^{-8}) \right]^2 = 2.68 \cdot 10^{-13} \text{ kg}$$
(58)

showing a good convergence with the result given by eq. 53

Although this change in mass is too small to be experimentally detectable, it is important from the theoretical point of view because, occurring within a system defined as isolated, it may have an incidence on its potential gravitational energy. As suggested in a very preliminary reflexion (Tane, 2008), its transposition in the context of large geological systems, concerned by internal exchanges of energy, may result in a tendency to increase the Earth-Moon distance, a process which is compensated, at least partially, by meteorites falling. This aspect of the problem cannot be taken into account in the conventional understanding of thermodynamics, since the idea is implicitly admitted that neither the energy of an isolated system nor its mass can vary.

A correlative interesting subject is the possibility that, contrary to inert matter, living matter is characterized by a positive value of *dm* in eq. 30 (Sorli, 2002; Tane 2003).

3. Conclusion

Despite the conceptual difficulties often felt by those who have to learn - or to teach - thermodynamics, its practical efficiency is indisputable. Referring to this situation, the scientific fair play of some authors of thermodynamics textbooks (Reiss, 1965; Nordstrom and Munoz, 1986; Anderson and Crerar, 1993) is a serious help for their readers, because in the same time as they drive them in the art of using the thermodynamic tool, they draw their attention to the possibility that something remains unclear in the theory.

Based on this feeling, the hypothesis advanced in the present paper is not a rejection of the conventional theory but an extension. The concept of increase in entropy, introduced for a long time under the symbol dS_i of the second law of thermodynamics is interpreted here as the symptom of an increase in energy, designated $T_e dS_i$ or dU_{add} , identified with the term - $c^2 dm$ of the Einstein mass-energy relation. Correlatively, the first law is extended, in the sense that the classical postulate $dU_{irr} = dU_{rev}$ is substituted by the postulate $dU_{irr} = dU_{rev} + dU_{add}$, with the consequence that the expression linking both laws takes the form $dU_{irr} = dU_{rev} - c^2 dm$. If this paper is accepted for publication, perhaps it would be interesting that some tests are tempted to introduce the suggested hypothesis in thermodynamics courses.

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