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Entropy production in irreversible processes with friction

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Established expressions for entropy production in irreversible processes are generalized to include friction explicitly, as a source of irreversibility in the interaction between a system and its surroundings. The net amount of heat delivered to the system does not come now only from the reservoir, but may have an additional component coming from the work done against friction forces and dissipated as heat. To avoid ambiguities in interpreting the different contributions to entropy increase, the latter is also written in terms of the heat directly exchanged between the system and surroundings and of the fraction of frictional work that is lost in the system.

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I. INTRODUCTION AND MOTIVATION

There has been a renewed interest in deriving expressions for the entropy produced in irreversible processes involving a system and its surroundings, which have been presented within the framework of the so-called rectification of thermodynamic inequalities and may be of relevance for the study of mesoscopic devices or of biological or macromolecular systems [1]. In particular, rectified forms of the second law have been discussed in connection with theorems for irreversible work that have found application in the field of molecular dynamics [1–3]. Thermodynamical analysis based on entropy production and its maximization has also been recently applied in fusion research to discuss turbulent heat transport in tokamak discharges, in an attempt to explain the transition from a low- to a high-confinement plasma state and the triggering of an internal transport barrier [4].

In a very schematic manner, recall that the first law for a given system reads

$$dU = đQ + đW, \tag{1}$$

where dU is the infinitesimal change in its internal energy, $đQ$ the infinitesimal amount of heat it absorbs, $đW$ is the infinitesimal work done on it, and the symbol $đ$ designates an infinitesimal change in a quantity that is not a state variable. In addition, if $đQ_{\mathrm{rev}}$ and $đW_{\mathrm{rev}}$ are, respectively, the heat and work inputs to the system in a reversible transformation between the same initial and final states as in (1), then

$$dU = đQ_{\mathrm{rev}} + đW_{\mathrm{rev}}. \tag{2}$$

Recall still that the contribution of a given process to the entropy increase of the universe is

$$dS_{\mathrm{univ}} = dS + dS_0, \tag{3}$$

with dS and dS_0 the entropy changes of the system and surroundings, respectively. One also has, with the the surroundings behaving as a reservoir at absolute temperature T_0 and giving off the heat $đQ_0$,

$$dS_0 = -\frac{đQ_0}{T_0}, \tag{4}$$

and, with T designating the system's absolute temperature,

$$dS = \frac{đQ_{\mathrm{rev}}}{T}. \tag{5}$$

Thus, combining (1)–(5) and assuming further that the effective heat lost by the surroundings equals the net heat flow to the system, meaning

$$đQ_0 = đQ, \tag{6}$$

the result

$$dS_{\mathrm{univ}} = \frac{đW - đW_{\mathrm{rev}}}{T} + \left(\frac{1}{T} - \frac{1}{T_0}\right)đQ \tag{7}$$

is obtained, equivalent to

$$dS_{\mathrm{univ}} = \frac{đW_{\mathrm{diss}}}{T} + \left(\frac{1}{T} - \frac{1}{T_0}\right)đQ \tag{8}$$

if the dissipative work

$$đW_{\mathrm{diss}} = đW - đW_{\mathrm{rev}} \tag{9}$$

is defined [1].

Consider now the example of a cylinder containing a gas that is slowly and isothermally compressed by a piston for which sliding friction is not negligible, which constitutes a case study for irreversible quasistatic processes [5]. Clearly, in this situation, the work $đW$ done on the gas is the same as the work $đW_{\mathrm{rev}}$ it would receive in a reversible transformation between the same states, since both processes are quasistatic [6]. Going back to (7)–(9), one would then wrongly conclude that dS_{univ} would vanish for this transformation, in marked violation of the second law for a process where there is dissipative work and entropy is certainly produced out of friction. So there seems to be a problem with (7)–(9), at least concerning their applicability when there are friction forces acting on the system's boundary, hence this paper, whose purpose is precisely to address such a problem. The importance of this work stems not only from the relevance that results for entropy increase such as (7)–(9) have for several

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1539-3755/2008/78(2)/021137(5)

interdisciplinary branches of contemporary physics [1,4], but also from the fact that it has to do with fundamental thermodynamics and the very essence of the second law. One has actually to ascertain how to write a rectified form of the second law accounting explicitly for the dissipative work due to friction, which has evident implications for engineering applications, as well as for the analysis of mesoscopic systems in which some effects or interactions may have to be modeled as friction. Indeed, the latter is an integral, almost unavoidable feature of nature and it deserves to make its appearance, *per se*, in the equations of basic thermodynamics. Moreover, the subject addressed here deals with quite simple, essentially college-level physics, which by no means diminishes its interest but adds pedagogical value instead, making it, for instance, a valuable auxiliary tool to be used in the classroom to illustrate how the first and second laws combine together in the machinery of macroscopic thermodynamics.

II. ANALYSIS AND DISCUSSION

So, where lies the problem with (7) and (8)? Precisely in assumption (6). Indeed, keeping in mind that

$$dU_0 = -\text{đ}Q_0 - \text{đ}W_0 \tag{10}$$

for the change in internal energy of the surroundings, where $\text{đ}W_0$ designates the work output from the latter, and that

$$dU + dU_0 = 0 \tag{11}$$

because of energy conservation, since system and reservoir evolve as an isolated set, (1), (6), (10), and (11) put together imply

$$\text{đ}W_0 = \text{đ}W. \tag{12}$$

However, when there is work $\text{đ}W_{\text{fric}}$ performed against friction forces, (12) does not apply but has to be replaced by

$$\text{đ}W_0 = \text{đ}W + \text{đ}W_{\text{fric}}, \tag{13}$$

which, in turn, and accounting once more for (1), (10), and (11), leads to

$$\text{đ}Q_0 = \text{đ}Q - \text{đ}W_{\text{fric}} \tag{14}$$

instead of (6). Equation (14) means that the net amount of heat lost by the surroundings does not correspond entirely to the total heat received by the system, the actual difference between these two heat terms leading to a very clear, intuitive physical interpretation: the work that is lost due to friction, and becomes thus unavailable for useful purposes, ends up dissipated as heat. Combining (1)–(5), and (13), one then gets

$$dS_{\text{univ}} = \frac{\text{đ}W_0 - \text{đ}W_{\text{rev}}}{T} + \left(\frac{1}{T} - \frac{1}{T_0}\right)\text{đ}Q_0, \tag{15}$$

or, using (14),

$$dS_{\text{univ}} = \frac{\text{đ}W - \text{đ}W_{\text{rev}}}{T} + \frac{\text{đ}W_{\text{fric}}}{T_0} + \left(\frac{1}{T} - \frac{1}{T_0}\right)\text{đ}Q, \tag{16}$$

or further

$$dS_{\text{univ}} = \frac{\text{đ}W_{\text{diss}}}{T} + \left(\frac{1}{T} - \frac{1}{T_0}\right)\text{đ}Q_0 \tag{17}$$

if the dissipative work is redefined according to

$$\text{đ}W_{\text{diss}} = \text{đ}W_0 - \text{đ}W_{\text{rev}}. \tag{18}$$

The results in (15)–(18) have a broader domain of validity and generalize (7)–(9), the two ensembles being equivalent only if $\text{đ}W_{\text{fric}}$ vanishes, in which case (13) and (14) degenerate into (6) and (12). Eventually, it would be possible to reconcile the two sets if the system could be, somehow, extended to include friction, yet such a point of view would be of a rather limited interest since, quite generally, it would not be possible to draw clear-cut physical boundaries between such an extended system and its surroundings [7].

Rewriting (18) with the help of (13) yields

$$\text{đ}W_{\text{diss}} = \text{đ}W - \text{đ}W_{\text{rev}} + \text{đ}W_{\text{fric}}, \tag{19}$$

where the two distinct sources of mechanical irreversibility become apparent: friction, via $\text{đ}W_{\text{fric}}$, but also the deviation, as measured by $\text{đ}W - \text{đ}W_{\text{rev}}$, of the transformation from a quasistatic process in which both system and surroundings would evolve through a series of quasiequilibrium states [8]. The last term on the right-hand side (RHS) of (15)–(17) represents entropy production arising from thermal irreversibility due to heat exchange between the system and reservoir when they are at different temperatures, but it is not clear if the heat actually transferred from one to the other is $\text{đ}Q_0$ or $\text{đ}Q$. On the other hand, looking now at (17), it is tempting to interpret the first term on its RHS as the entropy produced from dissipation in the system, yet the second term on the RHS of (16) apparently suggests that the heat produced due to friction is entirely dissipated in the surroundings. The ambiguity pervading the interpretation of (15)–(17) stems from the fact that, because of $\text{đ}W_{\text{fric}}$, neither $\text{đ}Q_0$ nor $\text{đ}Q$ corresponds to the heat exchanged between system and reservoir.

To address the problem from a more complete and detailed perspective, it is convenient to explicitly include in the analysis the heat $\text{đ}Q_{\text{exch}}$ directly transferred from the surroundings to the system, as well as the fraction α of $\text{đ}W_{\text{fric}}$ that is dissipated in the latter, so

$$\text{đ}Q = \text{đ}Q_{\text{exch}} + \alpha\text{đ}W_{\text{fric}} \tag{20}$$

and

$$\text{đ}Q_0 = \text{đ}Q_{\text{exch}} - (1-\alpha)\text{đ}W_{\text{fric}}. \tag{21}$$

From a physics point of view, whereas (13) and (14) comply with the first law and thus suffice to guarantee energy conservation, they do not convey the whole story as far as the second law and entropy production are concerned, as they do not tell where $\text{đ}W_{\text{fric}}$ ends up being lost as heat. Hence the need for the additional step in (20) and (21) which, when incorporated in (15) or (16), gives

$$dS_{\text{univ}} = \frac{\text{đ}W - \text{đ}W_{\text{rev}}}{T} + \left(\frac{\alpha}{T} + \frac{1-\alpha}{T_0}\right)\text{đ}W_{\text{fric}} + \left(\frac{1}{T} - \frac{1}{T_0}\right)\text{đ}Q_{\text{exch}}. \tag{22}$$

Each term on the RHS of (22) now carries a precise and clear physical meaning: the first accounts for entropy increase due to departures from quasistatic conditions, the second represents frictional dissipation which, depending on α, can take place in the system, in the reservoir, or in both, and the third arises from heat transfer between the system and surroundings when they are not in thermal equilibrium. Equations (13)–(22) generalize previous results [1]: together with their analysis and interpretation above, they provide several equivalent rectified forms for the second law in which the role of friction is explicitly accounted for.

Without going into a detailed discussion of the microscopic interpretations of heat and work, the perspective here adopted has been the standard one, which is conveyed by (1) and defines heat as the difference between the total change in internal energy of the system and the macroscopically measurable work done on it [9,10]. Other authors prefer a stricter definition whereby heat is only the term $\text{đ}Q_{\text{exch}}$ in (20), meaning the amount of energy directly transferred to the system from other systems that is not work, whereas a quantity such as $\alpha\text{đ}W_{\text{fric}}$ is not seen as frictional work converted into heat but rather as an increase in the so-called internal thermal energy of the system [11,12]. Note, however, that (22) is independent of which interpretation one follows, as each and every energylike quantity entering it is uniquely defined and, therefore, measurable, even if indirectly as $\text{đ}W_{\text{fric}}$ and $\text{đ}Q_{\text{exch}}$. For instance, following (14), $\text{đ}W_{\text{fric}}$ can be accessed via the difference between the macroscopic works $\text{đ}W_0$ and $\text{đ}W$, whereas, as suggested by (1) and (20), $\alpha\text{đ}W_{\text{fric}}$ and hence also α can be retrieved if the internal-energy change dU and the work $\text{đ}W$ are measured adiabatically, which implies setting $\text{đ}Q_{\text{exch}}$ equal to zero. If α cannot be obtained in this manner, one can always go back to either (15) or (16), in which all work- or heat-assimilated quantities can be retrieved by standard procedures.

Still regarding the definitions of heat and work, it is instructive to check that the expressions derived are consistent with the classical explanation of Joule's famous experiment, according to which the work of a descending weight that causes a paddle wheel immersed in water to rotate is converted into heat due to friction with the water molecules. The subsequent rise in the water's temperature enabled Joule to equivalently express the calorie c, defined as the heat capacity per unit mass of liquid water, in units of mechanical work. In an ideal paddle-wheel experiment, α is equal to unity whereas $\text{đ}Q_{\text{exch}}$ and $\text{đ}Q_0$ vanish, as well as $\text{đ}W$ and $\text{đ}W_{\text{rev}}$, the latter because the reversible transformation would be a purely heating process. Then, (13) and (20) become

$$\text{đ}W_0 = \text{đ}W_{\text{fric}} \tag{23}$$

and

$$\text{đ}Q = \text{đ}W_{\text{fric}}, \tag{24}$$

agreeing with the conventional interpretation that work is converted into heat through friction, and (15)–(18) or (22) yields

$$dS_{\text{univ}} = \frac{\text{đ}W_0}{T}. \tag{25}$$

Combining (25) with the main result of the experiment which, for a mass m of water, can be stated as

$$\text{đ}W_0 = mc\,dT, \tag{26}$$

gives the following well-known formula for the entropy increase associated with water heating:

$$dS_{\text{univ}} = \frac{mc\,dT}{T}. \tag{27}$$

As a simple, illustrative example consider once more the slow, quasistatic isothermal compression, or expansion, of a gas by, or against, a nonfrictionless piston [5]. Using the pressurelike quantity P_{fric}, henceforth assumed constant, to represent the sliding-friction force divided by the piston cross-sectional area, one has

$$\text{đ}W_{\text{fric}} = \mp P_{\text{fric}}dV, \tag{28}$$

with dV the infinitesimal change in the gas volume and the upper and lower signs on the RHS of (28) corresponding to actual compression or expansion of the gas, respectively [13]. Then, with T and T_0 the same, (22) simplifies to [8]

$$dS_{\text{univ}} = \mp \frac{P_{\text{fric}}dV}{T_0} \tag{29}$$

or, after integration,

$$\Delta S_{\text{univ}} = \mp \frac{P_{\text{fric}}(V_f - V_i)}{T_0}, \tag{30}$$

an eminently obvious result which, remember, could not be retrieved from (7)–(9), and where the subscripts f and i designate, respectively, the final and initial states of the gas.

A further interesting case is that of an irreversible quasistatic adiabatic compression, or expansion, of a gas which, for the sake of simplicity, is here considered to be ideal, whence

$$PV = nRT \tag{31}$$

and

$$U = nc_V T, \tag{32}$$

where P is the gas pressure, n its amount in moles, c_V its molar specific heat at constant volume, and R the ideal gas constant. The evident restriction for an adiabatic transformation is that heat transfer from the surroundings to the system and vice versa is not allowed, so $\text{đ}Q_{\text{exch}}$ must vanish and (22) and (28) become

$$dS_{\text{univ}} = \mp\left(\frac{\alpha}{T} + \frac{1-\alpha}{T_0}\right)P_{\text{fric}}dV. \tag{33}$$

To integrate (33), T must first be expressed in terms of V, which can be done by combining (1), (20), (31), and (32) with the quasistatic pressure work

$$\text{đ}W = -PdV \tag{34}$$

to obtain

$$VdP = -[\gamma P \pm (\gamma-1)\alpha P_{\text{fric}}]dV \tag{35}$$

and, upon integration,

$$[P \pm (1-\gamma^{-1})\alpha P_{\text{fric}}]V^{\gamma} = [P_i \pm (1-\gamma^{-1})\alpha P_{\text{fric}}]V_i^{\gamma}, \tag{36}$$

with

$$\gamma = 1 + \frac{R}{c_V} \tag{37}$$

the standard ratio between specific heats. Subsequently, introducing in (33) the expression for T derived from (31) and (36), one can write for the entropy increase

$$\Delta S_{\text{univ}} = nc_V \ln\left\{1 \pm (1-\gamma^{-1})\frac{\alpha P_{\text{fric}}}{P_i}\left[1-\left(\frac{V_f}{V_i}\right)^{\gamma}\right]\right\} \mp \frac{(1-\alpha)P_{\text{fric}}(V_f-V_i)}{T_0}. \tag{38}$$

Notwithstanding the absence of heat exchange between system and reservoir in such an adiabatic process, the same restriction as in Joule's experiment, note that there may indeed be heat fluxes to the system, to the reservoir, or to both coming from the work done against friction forces, as put forward by α in (20) and (21). For instance, when α becomes unity, $\text{đ}W_{\text{fric}}$ is fully dissipated as heat in the system, which means that not only the gas, but also the container and its piston, must be thermally insulated from the surroundings [14].

III. SUMMARY AND CONCLUSIONS

Motivated by the difficulties found in applying the existing results to the simple model of a gas slowly compressed by a piston with sliding friction, the writing of expressions for entropy production in irreversible transformations has been reconsidered in a detailed discussion illustrated with examples and carried out strictly within the framework of classical thermodynamics. More precisely, rectified forms of the second law have been obtained for computing the contribution of a given process to the increase in the entropy of the universe that explicitly include friction as a source of irreversibility and are, therefore, of general validity. To unambiguously interpret every term leading to entropy production, the latter has been written in terms of the heat directly exchanged between system and surroundings and of the fraction of the work produced by friction that is dissipated in the system. In addition to the standard contributions to entropy increase identified with heat transfer between system and reservoir, when their temperatures are different, and with work that is not performed quasistatically, an additional term now arises related to frictional dissipation, which may occur in the system, in the surroundings, or in both.

The results here revealed are of an interdisciplinary nature and of a rather broad interest, the simplicity behind their derivation making them easy to grasp even by an undergraduate who has acquired a basic knowledge of the first and second laws in an introductory physics course. Furthermore, they are expected to be important for several branches of physics and engineering, even at the mesoscopic level, particularly in those applications where dissipation identified with frictional work must be taken into account.

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[7] Note that, in the approach here adopted, namely in (13) and (14), the boundary between system and surroundings can be regarded as a third subsystem receiving work $\text{đ}W_{\text{fric}}$ and giving it off as heat, thus keeping its internal energy constant. Evidently, it has been assumed that the boundary has a vanishing heat capacity, otherwise it would have to be included in the energy balance.

[8] Remember that the work $\text{đ}W$ delivered to the system in a quasistatic process is identical to the work $\text{đ}W_{\text{rev}}$ delivered to it in a reversible transformation between the same initial and final states [6]. The actual difference between the two processes lies in the work performed by the surroundings $\text{đ}W_0$, or more precisely in the fraction of the latter that is lost due to friction and

is thus not transferred to the system in an irreversible quasistatic transformation.

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[10] The heat absorbed by a system can then be viewed as the microscopic work done on its particles because of interactions at the atomic level with the neighboring particles of the surroundings [9], which most easily extends to incorporating as heat the energy dissipated due to frictional work at the system's boundary.

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[12] Without disputing which interpretation of the first law is best suited, remark nonetheless that, by not considering the frictional contributions to energy conservation as heat [11], additional formal effort is needed when it comes to the conventional statement of the second law according to which entropy change is given, at least as far as the reservoir is concerned, by the ratio between heat received and absolute temperature. Indeed, if the term $(1-\alpha)\bar{d}W_{\text{fric}}$, which contributes explicitly to dS_0 as put forward by (4) and (21), is not regarded as heat, the second law has then to be rephrased to accommodate that part of the internal energy to be identified as thermal.

[13] Note that the choice of signs is such as to verify the obvious condition $\bar{d}W_{\text{fric}}>0$.

[14] Needless to say, both (30) and (38) yield nil when P_{fric} is set to zero, as it should be for quasistatic transformations that become reversible in the absence of friction. It can also be verified that, when α or P_{fric} is zero and so the net amount of heat delivered to the system vanishes, the classical quasistatic adiabatic result for an ideal gas $PV^{\gamma}=P_iV_i^{\gamma}$ is recovered from (36).