Evolution rate of thermodynamic systems

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Abstract
Time is absent in the common idea of classical thermodynamics; instead it is always ideally present considering work and heat *exchanged* or state functions *change*. In irreversible thermodynamic time seems to be considered and rate of change is introduced. Actually time is often not at the attention focus when searching for law to understand the system's evolution. A proposal to introduce the time in thermodynamics trough the classical Hamilton's principle, shows a possible interpretation of some process in an unified principle considering MaxEP and minimum evolution time for systems. At the same time it is evidenced that the irreversibility contribute to the slowing down of natural phenomena

Nomenclature

A	section [m^2]	v	velocity [m s^{-1}]
D	diameter [m]	V	volume [m^3]
E	total energy [J]	z	height [m]
f	friction factor	$\dot{W}$	power [W]
g	gravity factor [m s^{-2}]	greek	
h	specific enthalpy [J kg^{-1}]	β	concentrated loss factor
I	defined by eq.7)	τ	time [s]
L	length [m]	θ	defined by eq. 9)
$\mathscr{L}$	Lagrangian eq. 6)		
$\dot{m}$	mass flow rate [kg s^{-1}]	subscript	
p	pressure [Pa]	0	ambient
$\dot{Q}$	heat exchange [W]	$1,2$	sections
R	pressure losses eq. 9)	e	external
s	specific entropy [J K^{-1}kg^{-1}]	g	generated
S	entropy [J K^{-1}]	i,j,n	index
$\dot{S}$	entropy change [W K^{-1}]	rev	reversible
T	temperature [K]	t	total

1. Introduction

Time is absent in the common idea of classical thermodynamics; instead it is always ideally present considering work and heat *exchanged* or state functions *change*. In irreversible thermodynamic time seems to be considered and rate of change is introduced. Actually time is often not at the attention focus when searching for law to understand and model the system's evolution

In 1922 Lotka [1] proposed maximum power as the condition to develop life starting from Ostwald's principle of "maximum transformation in a given time" and Schrodinger, in 1943, the entropy as a parameter to analyse the life [2]. In 1996 Bejan [3] formulated the "constructal law" introducing then more explicitly the time [4].

The problem of evolution and of its rate is common in irreversible thermodynamics literature but at present there is not a generally accepted solution.

The variational method is very important in mathematical and theoretical physics because it allows us to describe natural systems by physical quantities independently from the frame of reference used [5,6]. Moreover, the Lagrangian formulation can be used in a variety of physical phenomena, and a structural analogy between different physical phenomena has been pointed out; indeed, the most important result of the variational principle consists of obtaining both local and global theories [7,8]: global theory allows us to obtain information directly about the mean values of the physical quantities, while the local one yields information about their distribution [8-13]. Numerous and interesting papers in the field are collected in the book edited by S. Sieniutycz and H. Farkas [14].

2. Entropy Production and related Principles

The entropy concept and its production in non-equilibrium processes form the basis of modern thermodynamics and statistical physics [14-18]. Entropy has been proved to be a quantity that is related to non-equilibrium dissipative process. A great contribution was made by Clausius who, in 1854–1862, introduced the notion and give the name entropy, and the Brussels Irreversible Thermodynamic school give the bases to Prigogine, in 1947, to enounce the minimum entropy production principle MinEP [8, 18, 19]. This principle it is not widely applicable and is questioned [18, 19, 20]. Furthermore, the maximum entropy production principle (MaxEP) has been introduced and used by several scientists throughout the twentieth century in their studies of the general theoretical issues of thermodynamics and statistical physics. By this principle, a non-equilibrium system develops following the thermodynamic path that maximizes internal entropy production under present constraints [8-13, 18]. The second law of thermodynamics states that for an arbitrary adiabatic process the entropy of the final state is equal to (reversible process) or larger than that of the initial state, what means that the entropy tends to grow because of irreversibility. Considering the statistical interpretation of the entropy, it not only tends to increase, but will also increase to a maximum value. Consequently, the MaxEP may be viewed as the natural generalization of the Clausius–Boltzmann–Gibbs formulation of the second law [18]. 'The relationship between the minimum entropy production principle and MaxEP is not simple; indeed, these variation principles are absolutely different: although the extremum of one and the same function, the entropy production, is sought, these principles include different constraints and different variable parameters. As a consequence, these principles should not be mutually opposed since they are applicable to different boundary conditions of a non-equilibrium system' [18]. The same opinion is expressed in by Hillert and Agren [19]. It has been proposed [8-13, 18] that the MaxEP, rather than the Prigogine principle, is an universal principle governing the evolution of non-equilibrium dissipative systems.

Theoretical and mathematical physics study idealized systems and one of the open problems is the understanding of how real systems are related to their idealization. In phenomena out of equilibrium, irreversibility manifests itself because the fluctuations of the physical quantities, which bring the system apparently out of stationarity, occur symmetrically about their average values [21]. The 3-steady-state definition allows us to obtain that for certain fluctuations the probability of occurrence follows an universal law and the frequency of occurrence is controlled by a quantity that has been related to the entropy generation. Moreover, this last quantity has a purely mechanical interpretation that is related to the ergodic hypothesis [12], which proposed that an isolated system evolves in time visiting all possible microscopic states. Moreover, considering that the open system is the one with perfect accessibility represented as a probability space in which is defined a PA-measure and a Borel function process, the ergodic hypothesis itself is a consequence of the 3-steady-state definition owing to the hypothesis. The principle of maximum entropy generation represents the macroscopic effect of these theories that, conversely, are its statistical interpretation.

Applications of the maximum irreversible principle have been done by one of the authors in biophysics [22], in molecular physics [23, 24], in fluid flow analysis [25] and in energy engineering [26].

Bruers [15] made a comparison between different Entropy Principle showing the existence of at least five different extremum EP covering different fields of experience and in general not conflicting because boundary conditions and constraints are very different. Mainly he pointed out the confusion and misinterpretation due to vague statements and concepts.

3. Some criticism

The introduction of entropy in classical thermodynamics is related to equilibrium state and reversible transformation. In that context entropy is a state function depending only on the equilibrium state of the system considered and only entropy differences can be evaluated. The introduction of "entropy production" (or generation) comes from the necessity to avoid inequalities and use only equation from mathematical point of view. Nothing is really "produced".
The second law states:

$$\oint \frac{\delta Q_i}{T_i} \le 0 \qquad 1)$$

Defining dS and writing:

$$dS = \left(\frac{\delta Q}{T}\right)_{rev} = dS_e + dS_g \qquad 2)$$

dS_g is considered the produced or generated entropy and is always $\geqq 0$. The quantity dS_e should be better defined as the entropy variation that will be obtained exchanging reversibly the same fluxes throughout the system boundaries.
Then entropy is not more then a parameter characterising the thermodynamic state and the term due to internal irreversibility, dS_g, measures how far the system is from the state that will be attained in a reversible way.
Anyway the definition and identification of the thermodynamic system is fundamental.
Literature do not consider time also when entropy production is discussed in MaxEP or MinEP. Very often, as in the case the system considered is in stationary state, all transformations refer to the same time interval and time derivative could be avoided as in classical thermodynamics.

4. Reversibility and time

Here is introduced a possible method to consider time in thermodynamic.
Let's consider an open system exchanging heat with different thermodynamic sources at temperatures T_i ,ambient temperature T_0 included. Mass fluxes at different inlet and outlet sections have specific values of enthalpy, kinetic and potential energies.
Then the First and Second Laws state [27]:

$$\begin{aligned} \frac{dE}{d\tau} &= \sum_{i=0}^{n} \dot{Q}_i - \dot{W} + \sum_{in} \dot{m}h_t - \sum_{out} \dot{m}h_t \\ \dot{S}_g &= \frac{dS}{d\tau} - \sum_{i=0}^{n} \frac{\dot{Q}_i}{T_i} - \sum_{in} \dot{m}s + \sum_{out} \dot{m}s \ge 0 \end{aligned} \qquad 3)$$

where E and S are total energy (internal, kinetic and potential) and entropy of the system; h_t are the total enthalpies (including kinetic and potential energy) related to mass fluxes.
Combining the equations 3), we can write:

$$\dot{W} = -\frac{d}{d\tau}(E - T_0 S) + \sum_{i=1}^{n}\left(1 - \frac{T_0}{T_i}\right)\dot{Q}_i + \sum_{in} \dot{m}(h_t - T_0 s) - \sum_{out} \dot{m}(h_t - T_0 s) - T_0 \dot{S}_g \qquad 4)$$

which for reversible conditions becomes:

$$\dot{W}_{rev} = -\frac{d}{d\tau}(E - T_0 S) + \sum_{i=1}^{n}\left(1 - \frac{T_0}{T_i}\right)\dot{Q}_i + \sum_{in}\dot{m}(h_t - T_0 s) - \sum_{out}\dot{m}(h_t - T_0 s) \qquad 5)$$

The system is reversible and conservative, the work can be expressed as $W_{rev} = \int pdV$, the temperature T_0 is usually considered the ambient temperature and assumed constant.
Defining the thermodynamic Lagrangian for the reversible condition in analogy with Lavenda [28]

$$\mathscr{L} = \dot{W}_{rev} + \frac{d}{d\tau}(E - T_0 S) \qquad 6)$$

with all the member functions of time, the Hamilton principle says that, the integral

$$I = \int_{t_1}^{t_2} \mathscr{L}\, dt \qquad 7)$$

will assume an extremal value, which means that with a defined energy exchange the required time will be minimum [6].
Introducing a dissipative function we obtain equation (4) and using the same procedure as before we can say the time will be minimum [6]. The power exchange will be lower than the reversible one; because the same work will be obtained in more time. In others words the irreversibility increases the time necessary to obtain a change.
As an example let's consider a tank as in figure 1.

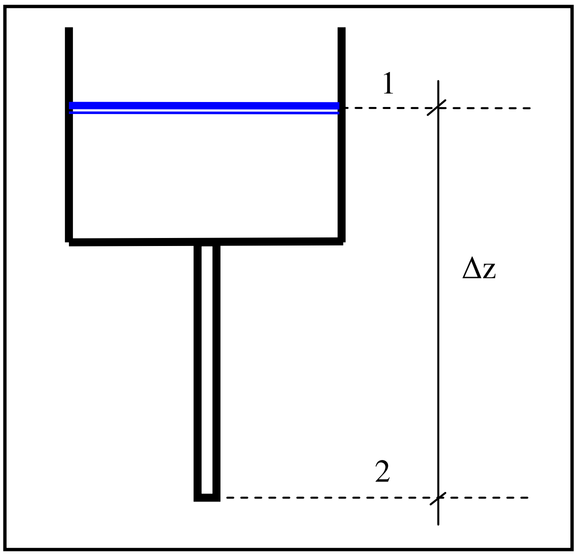

Figure 1 – Tank filled with water having section 1 and 2 in contact with atmosphere.

Assuming equations 3) in stationary state and substituting the heat exchange $\dot{Q}$ from the first in the second one, then considering the definition of enthalpy and entropy, it is easy to obtain the generalized Bernoulli's equation for a system having one input and one output section.
With the hypothesis the velocity $v_1 << v_2$, the equation gives;

$$\frac{v_2^2}{2} + g(z_2 - z_1) + R = 0 \qquad 8)$$

being:

$$R = \sum_i \left(f_i \frac{L_i}{D_i} + \sum_n \beta_{ni} \right) \frac{v_i^2}{2} = \theta \frac{v_i^2}{2} \qquad 9)$$

the parameter related to friction irreversibility (see [29] also), then we obtain:

$$v_2 = \sqrt{\frac{2g(z_1 - z_2)}{1+\theta}} \qquad 10)$$

If the surface level is variable, the time needed to lose a certain mass can be evaluated using the continuity equation, $v_2 A_2 \rho\, d\tau = -A_1 \rho\, dz$. Then for a given value of z in first approximation:

$$d\tau = -\frac{A_1}{A_2}\sqrt{\frac{1+\theta}{2g}} \cdot \frac{dz}{\sqrt{z}} \qquad 11)$$

clearly showing the growth of time required by the irreversibility being $\theta > 0$.

5. MaxEP and time

Paulus and Gaggioli [29] discussed some case of flowing fluid in pipes. They found different minimum and maximum EP, but without time evaluation.
They considered first the case of flow in pipe with defined dimensions and mass flow showing that the stable state corresponds to MaxEP, due to internal friction. When the boundary condition considered is that with specified pressure drop, stable all the others, the authors affirm the EP is minimum. In our opinion the stable condition is always that of MaxEP, because only one flux is physically possible [9, 18, 19, 30]
The forth case considered, Fanno flow, and fifth one, Rayleigh flow, give MaxEP.
When considering the normal shock case, they wrote it works with MinEP. We believe that as they chose an isentropic transform, that means a reversible one, the solution obtained agrees with the conclusion of preceding paragraph, being the mass flow the fastest possible.
More interesting is the third case, corresponding to the our example of fig. 1, but with two pipes of different diameter. They shows in this case that the mass flow rate is distributed in the pipes to obtain MinEP and the pressure drop is the same. But this is the MinEP for the entire system. Looking at each pipe the dissipation due to the friction is the same as when the system has a single pipe, maintaining the pressure drop and dimension. So at each pipe we have MaxEP and for system MinEP. The situation can be explained considering that; when a pipe is added the frictional constraints do not change, mass flow will be augmented to achieve minimum time for the "evolution" of the system, all the system, toward the equilibrium state. One pipe more adds a degree of freedom and the system move to the stationary point of a saddle where we can find a contemporary minimum and maximum condition [31]
Those conclusions well agree with the evolution of a stream composed of two liquids with very different viscosity, presented by Bejan [3] and with the adaptive changes of systems that reduce the resistance to the flows [3]. The "constructal law" is consistent with MaxEP when considering how fast the nature runs.

6. Conclusions

The proposal to introduce the time in thermodynamics trough the classical Hamilton's principle, shows a possible interpretation of some process in an unified principle considering MaxEP and minimum evolution time for systems.
At the same time it is evidenced that the irreversibility contribute to the slowing down of natural phenomena.
The irreversibility give a chance to modify the time and path of system's evolution in multiple way.

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