Exergy as the driver of the inception and of the dynamics of real equilibration processes

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Abstract

In 2018, Richard Gaggioli published a paper titled "*Proposed 2nd Law of Thermodynamics: An assertive statement*", suggesting we look at the Second Law not as a "negative" constraint ("real processes will inevitably display dissipative properties, and the Law can quantify them by means of the Gouy-Stodola lost work") but as the definition of a general "driver" for equilibration processes. He used Available Energy in his analysis, but for generality's sake it is more convenient to adopt Exergy as the relevant thermodynamic variable.

Gaggioli's argument can be summarised as follows:

a) In every real process the exergy of an isolated system decreases;
b) Whenever an open system undergoes a steady process, exergy delivered from other systems will be dissipated at a process-depending rate;
c) Exergy measures "non-equilibrium", be it internal (T, p, c gradients) or external (distance from other systems in the state space), and whenever a system possesses non-zero exergy as a consequence of latent disequilibrium, an equilibration process will ensue;
d) To impede such an onset it is necessary to supply exergy from another system to block the equilibration process.

To proceed further, Gaggioli made an important assumption, an intuitive leap not derivable from the above statements: "*The rate at which a spontaneous process occurs is proportional to the amount of exergy accessible to 'drive' the process and is measurable by the rate of exergy consumption*" (we replaced Available Energy with Exergy in this otherwise *verbatim* quote).

Scope of this paper is to extend Gaggioli's assumption by adapting a model formulated in the '50es by Ginzburg and Landau: this rigorous approach allows us to demonstrate that in any equilibration process a proper measure of the decrease of the system exergy is linked directly and explicitly to the time derivatives of the relevant process variables via a case-dependent functional of the exergy itself. Two applications are developed for a conduction/convection cooling of a solid bar and for the decay of a thermal Oseen-Lamb vortex.

Keywords: exergy; non-equilibrium; Ginzburg-Landau model

1. Introduction

This paper is a continuation of previous studies [15,16] and addresses the problem of the evolution of thermodynamic systems that are in a state of non-equilibrium. Our method is based on a proper adaptation of the Ginzburg Landau equation [8] and relies on a few general hypotheses incorporating Gaggioli's 2018 assumptions [3]. For better reference, let us repeat here some previously published results [16].

The evolutive version of the Ginzburg Landau equation is usually stated as (see [8,12])

$$\frac{\partial \varphi}{\partial t} = -k \frac{\delta F}{\delta \varphi} \qquad (1)$$

where $\frac{\delta F}{\delta \varphi}$ is the variational derivative of *F(j)* w.r.t. *j*.

In the Ginzburg Landau theory the functional F is a function of one or more "order parameters" φ. In [16] we have shown how equation (1) describes the evolution of non-equilibrium systems towards their thermodynamic equilibrium. In that study we considered homogeneous systems and -in a first approximation- neglected local inhomogeneities described by the gradients of the physical variables. In that approach the order parameters are a properly selected set of thermodynamic variables: their evolution is related to the variation of the exergy content E of the system. In non-homogeneous systems, E may be a function of both the thermodynamic variables and of their gradients and, for more complex systems, there could be auxiliary equations relating some of these variables. We demonstrated that, starting from few fundamental assumptions, it is possible to characterize the dynamics of both conservative and dissipative systems by deriving a proper solution to equation (1). Our assumptions are the following [see 15,16]:

1. Any spontaneous process is described by differential equations of first order in time. To describe the process completely it is sufficient to know its initial state, to identify the relevant order parameters φ_k and the material properties: if the initial state is well-posed, the initial velocities are obtained directly from the differential equations, which then give the "velocity" (in the real time domain) at which the spontaneous evolution proceeds.
2. In any equilibration process, there is some amount of mechanical work (possibly equal to zero) delivered to the environment. This is the portion of work that has neither been used by the system to evolve nor dissipated in the equilibration. If we look at the evolution of the system alone, the difference between the maximum theoretical work that may be extracted from the system in its initial state (its exergy a $t=t_0$)) and the part of it delivered to the environment is the "exergetic driver" responsible for the evolution of the system. We indicate this function by *E*[1] .
3. The variation in time of the thermodynamic variables φ_i, $i = 1 \dots n$, of the system is a function of the variation (i.e., of the gradient) of *E*: in any volume *V* of the system, this variation is $\frac{\partial}{\partial t}\int \varphi_i dV$ and must be proportional to $\delta \int E dV$. In the simplest case (homogeneous system), E is a function of the thermodynamic variables φ_i, $i = 1 \dots n$ only, and the gradients $\nabla\varphi_i$ do not appear in the description of the evolution. If inhomogeneities in the thermodynamic variables occur inside the system, their gradients will necessarily enter in the evolution equations since in general they are related to internal energy degradation. The evolution equations become (hereafter repeated indices are implicitly summed over)
$$\frac{\partial\varphi_i}{\partial t} = A_{i,j}\frac{\partial E}{\partial\varphi_j} \tag{2}$$
4. It is convenient to rescale the thermodynamic variables φ_i in such a way that they assume the value zero at equilibrium. In the most general case, the elements of the matrix $A_{i,j}$ in (2) may also depend on the φ_i.
5. We assume that the matrix $A_{i,j}$ is negative semi-definite, and more specifically that it is negative-definite for real dissipative-systems and skew-symmetric for conservative systems[2]. This implies that the function E is a Lyapunov function for the system, since one has
$$\frac{dE}{dt} = A_{i,j}\frac{\partial\varphi_i}{\partial t}\frac{\partial\varphi_j}{\partial t} \le 0 \tag{3}$$
and further the function E, being the exergy of the system, is always positive and it is equal to zero only for $\varphi_i = \varphi_{i,0}$, where $\varphi_{i,0}$ are the equilibrium values of the order parameters. From the Lyapunov Lemma it follows that the thermodynamic equilibrium is stable. Additionally, we shall assume that the function E has just one minimum.
6. There is one equation (2) for every thermodynamic variable φ_i: constitutive equations linking φ_i, φ_j …φ_k can be possibly used to decrease the rank of system (2).
The phase space is spanned by the thermodynamic variables φ_i: it can be a finite-dimensional space of functions depending on time or, for example, the Schwartz space of rapidly decreasing functions on $\mathbb{R}$ or the L^2 space. In this last case, the matrix $A_{i,j}$ can be seen as a differential operator (possibly non-linear) or a vector field. In general, the boundary conditions will determine the properties of the phase space. In this case equation 3) becomes
$$\frac{dE}{dt} = \int \frac{\delta E}{\delta\varphi_i}\frac{\partial\varphi_i}{\partial t}dV = \int \frac{\delta E}{\delta\varphi_i}A_{i,j}\frac{\delta E}{\delta\varphi_j}dV$$
and, in general, one should examine the boundary conditions in order to determine if $\frac{dE}{dt} \le 0$. An example will be given in Section 5.

2. Dissipative systems of a more general type

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[1] The function *E(t)* is sometimes called "the non-equilibrium exergy function", but this notation is somewhat non-rigorous, because the entire exergy content is per definition a non-equilibrium quantity.

[2] Notice that only the symmetric part of $A_{i,j}$ enters in (3), so it is only this part of $A_{i,j}$ that must be negative semi-definite.

From a mathematical point of view, it is natural to require f that the Exergy function of dissipative systems possesses a global minimum corresponding to the equilibrium state[3]. Let usexamine first an exergy functional depending on one thermodynamic variable φ. From a mathematical point of view the physical meaning of this variable is not relevant and we can for the moment keep it unspecified: in real applications, φ can be related to the temperature, the pressure, or the concentration of a given substance. The simplest choice for the dependence of the exergy on φ and its gradient is

$$E = \int_V \left(f(\varphi) + \frac{1}{2} |\nabla\varphi|^2 \right) dV \qquad (4)$$

The previous functional is well known in the Ginzburg-Landau theory [8]: in fact they considered the case in which $f(\varphi)$ possesses two minima and represents the functional describing the phase transitions between two different phases. As stated above, we shall assume that $f(\varphi)$ has only one minimum. The corresponding evolution equation is given by

$$\frac{\partial\varphi}{\partial t} = k' \nabla^2 \varphi - k \frac{df}{d\varphi} \qquad (5)$$

If the system is close to its equilibrium state and a Taylor series is used to approximate the function $f(\varphi)$, at fourth order we obtain:

$$E = \int_V \left(b\varphi^2 (1 + \frac{c}{2} \varphi^2) + \frac{1}{2} a |\nabla\varphi|^2 \right) dV \qquad (6)$$

where a, b and c are process constants. The corresponding evolution equation is:

$$\frac{\partial\varphi}{\partial t} = k' \nabla^2 \varphi - b' \varphi (1 + c' \varphi^2) \qquad (7)$$

Notice that equation (7) arises in several physical applications, like microwave heating, chemical reactions theory, and diffusion processes in biology.

3. A new perspective: exergy as the driver of itself

Scope of this paper is to address the problem of the evolution of the exergy in non-equilibrium thermodynamic systems. The problem of the proper quantification of the exergy in regions far from quasi-equilibrium states is of paramount relevance: in such systems, where some of the intensive properties may become ill-defined, exergy still represents the potential for a system to do work as it relaxes toward an equilibrium state with its environment, and can -albeit ideally- be measured. Furthermore, systems sufficiently removed from equilibrium are characterized by large gradients, continuous energy flows, and the possible emergence of complex "dissipative structures" like those found in living organisms or weather patterns. Thus, while the concept of Exergy Destruction E_d maintains its importance, its calculation requires a different paradigm. It is though generally accepted that even in complex non-equilibrium systems (most importantly, ecological and biological ones), exergy can be used as a "goal function" to describe how a system develops and organizes itself to maximize material and immaterial through-flows under the given constraints and maintain “order”. Since far-from-equilibrium systems are governed by nonlinear interactions, they cannot be described by simple linear equations, and specific theories have been proposed for their treatment, such as Extended Irreversible Thermodynamics (EIT), Stochastic Thermodynamics and Maximum Entropy Production [1,4,6,7,10,11,13,14]. Of particular importance in the present context is the proposed use of Lyapunov Functions [2], where exergy acts as a mathematical "anchor" that shows how a system naturally evolves or relaxes over time.

The novelty of the approach proposed in this paper is to address the problem of the evolution of exergy on the base of the methodology described in the previous section, namely to assume that the order parameter is the exergy itself[4]: φ=e. Now the functional $F(\varphi)$ in (1) cannot be the exergy, as we assumed in (6), but it must be a case dependent functional of it, to be identified on the basis of physical considerations[5]. Eqtn. (6) becomes:

$$F = \int_V \left(f(e) + \frac{1}{2} |\nabla e|^2 \right) dV \qquad (8)$$

and the corresponding evolution equation is[6]:

$$\frac{\partial e}{\partial t} = k \nabla^2 e - k \frac{df}{de} \qquad (9)$$

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[3] This is the simplest possible choice, but the proposed mathematical approach remains valid in phase transitions or in complex phenomena like shape memory alloys, known to display more than one minimum.

[4] In the following, e is the specific exergy, in J/kg, J/m^3 or J/m, depending on the application.

[5] This is analogous to Öttinger’s GENERIC paradigm, in which the matrices L and M must be heuristically specified [11]

[6] Gaggioli’s proposal [3] was to assume $de/dt=-Ke$, which obviously leads to an exponential decrease of exergy in time. Eq. (9) maintains the dependence of de/dt on $e(t)$, but the presence of the ∇^2 operator and the addition of the dissipative function f substantially enrich the solution domain.

which is a diffusion equation for exergy with a term of exergy destruction given by $-k\frac{df}{de}$. Let us examine the form this equation takes in the simple but very general case of the evolution of heat inside a solid by conduction. Assume, for simplicity, that the temperature inside the solid evolves according to the Fourier law and there are no internal sources (Figure 1). Imposing convective boundary conditions on the external surface *B*, the corresponding equations read

$$\begin{cases}\frac{\partial T}{\partial t} = k\nabla^2 T \\ \hat{n}\cdot\nabla T + \alpha(T - T_0) = 0 \qquad on\ B \\ T(\vec{x},0) = T_i(\vec{x})\end{cases} \tag{10}$$

Where T_0 is the temperature of the environment, B is the boundary of the solid, $\hat{n}$ is the outward local normal to the bounday and α is a measure of the heat transfer by convection on *B*. The contribution to the total exergy from each particle of solid at location $\vec{x}$ and time t is:

$$de = \rho c_p dT - T_0\frac{dT}{T} \tag{11}$$

By integrating the previous expression from the actual temperature of the solid at $\vec{x}$ and *t*, $T(\vec{x},t)$ and the reference temperature T_0, the local contribution to the exergy is given by

$$e(\vec{x},t) = \rho c\left(T(\vec{x},t) - T_0 - T_0\, ln\left(\frac{T(\vec{x},t)}{T_0}\right)\right) \tag{12}$$

The derivative of the exergy with respect to t, at any point in the solid, is

$$\frac{\partial e}{\partial t} = c\rho\frac{\partial T}{\partial t}\left(1 - \frac{T_0}{T}\right) = \lambda\nabla^2 T\left(1 - \frac{T_0}{T}\right) \tag{13}$$

where we used $T_t = k^2\nabla^2 T$ and $k^2 = \frac{\lambda}{c\rho}$. The previous expression can be also rewritten as

$$\frac{\partial e}{\partial t} = \nabla\cdot\left(\lambda\nabla T\left(1 - \frac{T_0}{T}\right)\right) - \lambda T_0\left(\frac{\nabla T}{T}\right)^2 \tag{14}$$

If we identify the exergy flux by $j = -\lambda\nabla T\left(1 - \frac{T_0}{T}\right)$ ($-\lambda\nabla T$ being the heat flux) the balance equation becomes:

$$\frac{\partial e}{\partial t} + \nabla\cdot j = -e_d \tag{15}$$

where $e_d = \lambda T_0\left(\frac{\nabla T}{T}\right)^2$ is the rate of exergy destruction per unit volume inside the solid. Also, since $\nabla^2 e = \rho c\nabla^2 T\left(1 - \frac{T_0}{T}\right) - \rho c T_0\left(\frac{\nabla T}{T}\right)^2$, equation (15) can be rewritten as

$$\frac{\partial e}{\partial t} = k^2\nabla^2 e - e_d \tag{16}$$

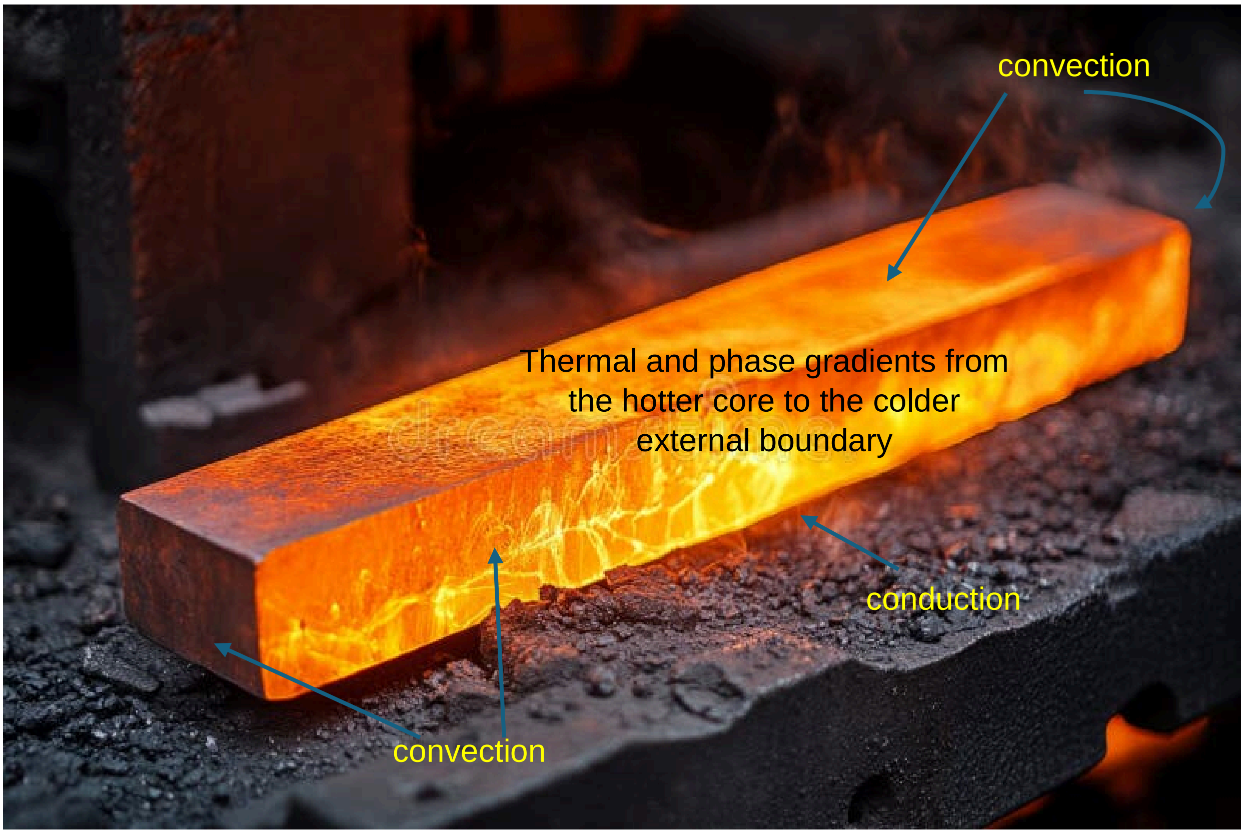

Figure 1: A solid body in thermal non-equilibrium

Equation (16) is indeed formally identical to equation (9) for $e_d = \frac{df}{de}$. This suggests a physical interpretation of the function $f(e)$ in (8): it acts as an exergy "potential" for the exergy destruction. Furthermore, the equation $e_d = \frac{df}{de}$ shows that e_d must be understood as a function of e. In general, the exergy content of the solid is defined by the initial condition at $t = 0$: if the initial condition is given by $T(\vec{x}, 0)$, the initial exergy content is

$$e(t = 0) = \int \rho c \left(T(\vec{x}, 0) - T_0 - T_0\, ln\left(\frac{T(\vec{x},0)}{T_0}\right)\right) dV \qquad (17)$$

where the integral is performed over the volume of the solid. Then, if the temperature evolves according to equation (10), the exergy at a time t is given by

$$e(t) = \int \rho c \left(T(\vec{x}, t) - T_0 - T_0\, ln\left(\frac{T(\vec{x},t)}{T_0}\right)\right) dV \qquad (18)$$

and is in general a monotonic function of time that tends to zero at $t \rightarrow \infty$

The exergy destruction e_d is also specified initially by the initial condition, i.e.

$$e_d(0) = \lambda T_0 \int \left(\frac{\nabla T(\vec{x},0)}{T(\vec{x},0)}\right)^2 dV \qquad (19)$$

and at a time t is given by

$$e_d(t) = \lambda T_0 \int \left(\frac{\nabla T(\vec{x},t)}{T(\vec{x},t)}\right)^2 dV \qquad (20)$$

The function $e_d(t)$ is, in general, a monotonic function of time[7]. If the environment around the solid is at a uniform temperature T_0 or if the boundaries of the solid are adiabatic, it is possible to show that $e_d(t)$ reaches the value zero for $t \rightarrow \infty$. Since both $e(t)$ and $e_d(t)$ are decreasing function of time and the environment around the solid is at a constant T_0, each one of the functions $e(t)$ and $e_d(t)$ traces a trajectory in the plane (e, e_d) that starts at a point $\langle e(0), e_d(0)\rangle$ defined by the initial non-equilibrium conditions and ends in $\langle e = 0, e_d = 0\rangle$ when equilibrium is reached. Some illustrative trajectories are shown in Figure 2. The function $f(e)$ in 9), defined up to a constant, is the area under the corresponding trajectory from $e = 0$ to a generic e, that is

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[7] This is a physically correct assumption for the case under consideration. But it can be shown that for a non-null set of choices of the initial and boundary conditions $e_d(t)$ can be a locally increasing function of time (i.e., it decreases to 0 but not monotonously) [17]

$$f(e) = \int_0^e e_d de \tag{21}$$

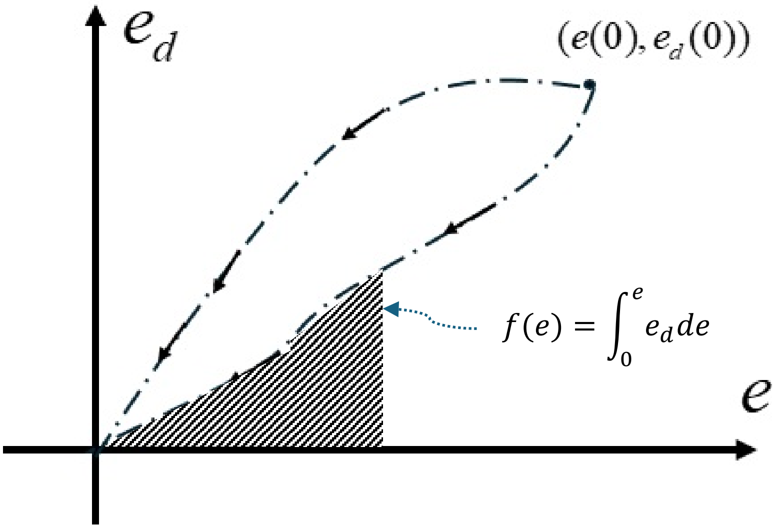

Figure 2: Two possible trajectories with both $e(t)$ and $e_d(t)$ decreasing towards the point (0,0).

4. Application to the evolution of the exergy in a conductive-convective bar.

In the case of a quasi-one-dimensional bar, the equations (10) become

$$\begin{cases} \frac{\partial T}{\partial t} = k^2 \frac{\partial^2 T}{\partial x^2} \\ \left.\frac{\partial T}{\partial x}\right|_{x=0} - \alpha(T|_{x=0} - T_0) = 0 \\ \left.\frac{\partial T}{\partial x}\right|_{x=L} \quad \alpha(T|_{x=L} - T_0) = 0 \\ T(x,0) = f(x) \end{cases} \tag{22}$$

The bar exchanges thermal energy with the environment at temperature T_0 at both ends. We recall that α is a measure of the heat transfer by convection to the surrounding and that the dimensionless parameter $Bi = \alpha L$, where L is the length of the rod, is the Biot number of the system. The system (22) can be solved by the Fourier method. The temperature $T(x,t)$ is given by the following infinite sum:

$$T(x,t) = T_0 + \sum_{n=1} c_n e^{-k^2\lambda_n^2 t}(\alpha\, sin(\lambda_n x) + \lambda_n\, cos(\lambda_n x)) \tag{23}$$

where the Fourier coefficients c_n are given by the integrals

$$c_n = \frac{1}{\left(\alpha + \frac{L}{2}(\alpha^2 + \lambda_n^2)\right)} \int_0^L (\alpha\, sin(\lambda_n x) + \lambda_n\, cos(\lambda_n x))(f(x) - T_0)dx \tag{24}$$

and the eigenvalues λ_n are the positive roots of the transcendental equation (with just one root in each positive interval $(\pi n, \pi(n+1))$.):

$$2\alpha\lambda\, cot(\lambda L) = \lambda^2 - \alpha^2 \tag{25}$$

The eigenfunctions

$$\psi_n(x) = \alpha\, sin(\lambda_n x) + \lambda_n\, cos(\lambda_n x) \tag{26}$$

are orthogonal. Indeed one has $\int_0^L \psi_n(x)\psi_m(x)dx = \left(\alpha + \frac{L}{2}(\alpha^2 + \lambda_n^2)\right)\delta_{n,m}$, where $\delta_{n,m}$ is the Kronecker delta. As an example, let us take the following initial condition

$$T(x,0) = T_0(1 + w\psi_1(x)) \tag{27}$$

where w is a parameter. The corresponding temperature profile at time *t* is given by

$$T(x,t) = T_0\left(1 + w\psi_1(x)e^{-k^2\lambda_1^2 t}\right) \tag{28}$$

The value of the exergy at time t is given by eq. (18), i.e.

$$e(t) = \rho c \int_0^L \left(T(x,t) - T_0 - T_0\, ln\left(\frac{T(x,t)}{T_0}\right)\right) dx \tag{29}$$

The exergy destroyed at time t is given by (see eq.(20)):

$$e_d(t) = \lambda T_0 \int_0^L \left(\frac{T_x(x,t)}{T(x,t)}\right)^2 dx \tag{30}$$

A plot of the temperature $T(x,t)$ at different times is given in Figure 3. The parameters have been chosen as: $w = \alpha = L = 1$. The value of λ_1, the first root of eq. (25), is $\lambda_1 = 1.30654$. Figure 4 displays the plots of $\frac{e_d(t)L}{\lambda T_0}$ and of $\frac{e(t)}{\rho c T_0 L}$ as functions of time. The initial values are respectively 0.101417 and 0.603058. Finally, Figure 5) shows the curve defined by $e(t)$ and $e_d(t)$ in the plane (e, e_d).

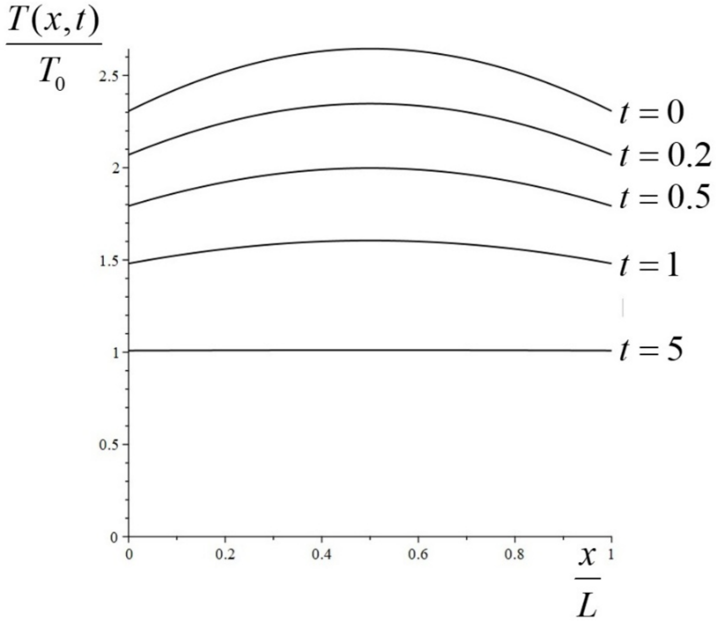

Figure 3: Distribution of the temperature profile (eq. 28) for different values of time.

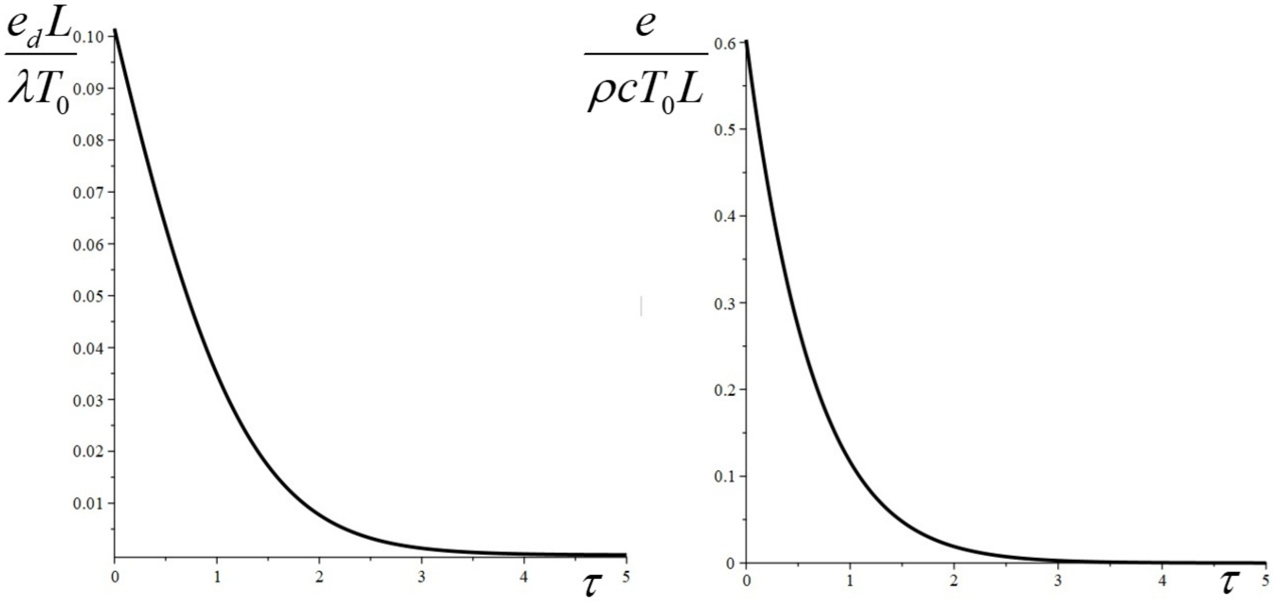

Figure 4: Plots of $\frac{e_d(\tau)L}{\lambda T_0}$and of $\frac{e(\tau)}{\rho c T_0 L}$ as a function of the dimensionless time $\tau = k^2\lambda_1^2 t$.

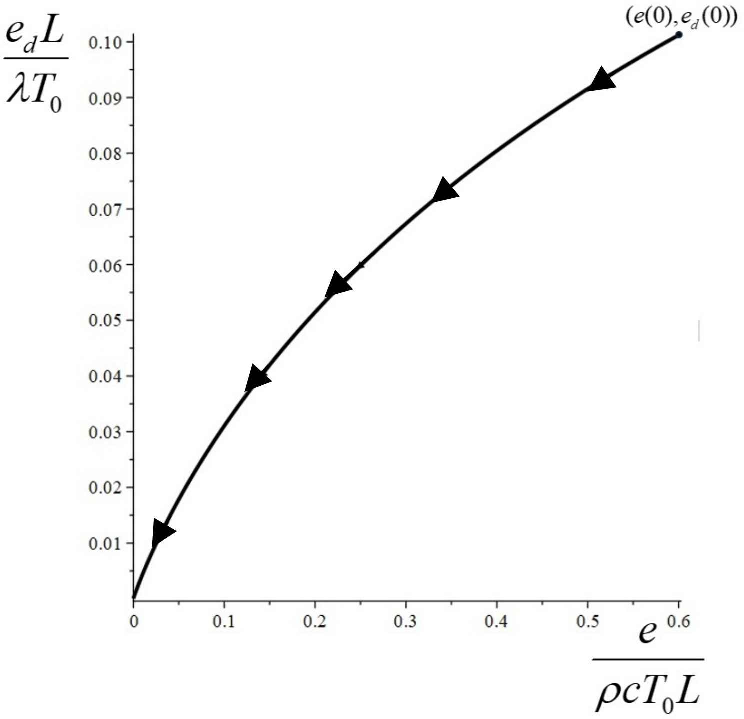

Figure 5: Plot of $\frac{e_d(t)L}{\lambda T_0}$as a function of $\frac{e(t)}{\rho c T_0 L}$: the arrows show the direction of the trajectory.

5. Dissipation in an Oseen-Lamb vortex with thermal coupling

Consider the unsteady flow of an isolated line vortex in a fluid. We assume axial symmetry. In cylindrical coordinates (r, θ, z), the velocity components are $\vec{\mathrm{v}} = (\mathrm{v}_\mathrm{r}, \mathrm{v}_\theta, \mathrm{v}_\mathrm{z})$. By assuming $\mathrm{v}_r = \mathrm{v}_z = 0$, and $\mathrm{v}_\theta = \mathrm{v}_\theta(r, t)$ the Navier Stokes equations for v_θ reduce to:

$$\frac{\partial \mathrm{v}_\theta}{\partial \mathrm{t}} = \nu\left(\frac{1}{\mathrm{r}}\frac{\partial \mathrm{v}_\theta}{\partial \mathrm{r}} + \frac{\partial^2 \mathrm{v}_\theta}{\partial \mathrm{r}^2} - \frac{\mathrm{v}_\theta}{\mathrm{r}^2}\right) \tag{30}$$

where ν is the kinematic viscosity. The evolution of temperature is obtained from energy conservation. By including the effects of viscosity and noticing that $\vec{\mathrm{v}} \cdot \nabla T = 0$, one has

$$\rho \mathrm{c}\frac{\partial \mathrm{T}}{\partial \mathrm{t}} = \mathrm{k}\left(\frac{\partial^2 \mathrm{T}}{\partial \mathrm{r}^2} + \frac{1}{\mathrm{r}}\frac{\partial \mathrm{T}}{\partial \mathrm{r}}\right) + \rho\nu\left(\frac{\partial \mathrm{v}_\theta}{\partial \mathrm{r}} - \frac{\mathrm{v}_\theta}{\mathrm{r}}\right)^2 \tag{31}$$

Let us introduce the thermal diffusivity $\alpha = \frac{k}{\rho c}$, the Prandtl number $Pr = \frac{\nu}{\alpha}$ and the quantity $\tau = \alpha t$ having the dimensions of a square length.It is convenient to make the problem dimensionless by defining a dimensionless velocity $u = \frac{\mathrm{v}_\vartheta}{\sqrt{cT_0}}$ and temperature $\vartheta = \frac{T}{T_0}$. Equations (30-31) then become

$$\begin{cases} \frac{\partial u}{\partial \tau} = Pr\left(\frac{1}{r}\frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial r^2} - \frac{u}{r^2}\right) \\ \frac{\partial \vartheta}{\partial \tau} = \left(\frac{\partial^2 \vartheta}{\partial r^2} + \frac{1}{r}\frac{\partial \vartheta}{\partial r}\right) + Pr\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right)^2 \end{cases} \tag{32}$$

The local exergy is the sum of the kinetic energy and of the exergy due to heat exchange, given by

$$\frac{e}{\rho c T_0} = \frac{1}{2}u^2 + \vartheta - 1 - ln(\vartheta) \tag{33}$$

So that the corresponding total exergy per unit length is ($dB = r dr d\theta$is the area element)

$$E = \int \frac{e}{\rho c T_0} dB = \int \left(\frac{1}{2}u^2 + \vartheta - 1 - ln(\vartheta)\right) dB \tag{34}$$

ϑ and u are our order parameters or thermodynamic variables. According to eq. (2), now we look at an operator $A_{i,j}$ to obtain equations in the Ginzburg-Landau form:

$$\begin{pmatrix} \frac{\partial u}{\partial \tau} \\ \frac{\partial \vartheta}{\partial \tau} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \frac{\delta E}{\delta u} \\ \frac{\delta E}{\delta \vartheta} \end{pmatrix} \tag{35}$$

From eq. (32) it immediately follows that $a_{12} = 0$. Also, from eq. (34) we have $\frac{\delta E}{\delta u} = u, \frac{\delta E}{\delta \vartheta} = 1 - \frac{1}{\vartheta}$. It is clear that in this case the matrix elements $a_{i,j}$ are differential operators. Their explicit expressions are:

$$a_{1,1}(\cdot) = Pr\left(\frac{1}{r}\frac{\partial(\cdot)}{\partial r} + \frac{\partial^2(\cdot)}{\partial r^2} - \frac{(\cdot)}{r^2}\right), \quad a_{2,1}(\cdot) = Pr\left(\frac{\partial(\cdot)}{\partial r} - \frac{(\cdot)}{r}\right)^2 \quad a_{2,2}(\cdot) = \frac{1}{r}\frac{\partial}{\partial r}\left(r\vartheta^2\frac{\partial(\cdot)}{\partial r}\right) \tag{36}$$

or

$$A(\cdot) = \begin{pmatrix} Pr\left(\frac{1}{r}\frac{\partial(\cdot)}{\partial r} + \frac{\partial^2(\cdot)}{\partial r^2} - \frac{(\cdot)}{r^2}\right) & 0 \\ Pr\left(\frac{\partial(\cdot)}{\partial r} - \frac{(\cdot)}{r}\right)^2 & \frac{1}{r}\frac{\partial}{\partial r}\left(r\vartheta^2\frac{\partial(\cdot)}{\partial r}\right) \end{pmatrix}$$

To show that the matrix $A = a_{i,j}$ is negative definite, let us look at the diagonal elements: we have

$$\int \frac{\delta E}{\delta u} a_{1,1} \frac{\delta E}{\delta u} dB = Pr \int u \left(\frac{1}{r}\frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial r^2} - \frac{u}{r^2}\right) r dr d\theta = Pr \int u \frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial(ur)}{\partial r}\right) r dr d\theta \tag{37}$$

Assuming the following boundary conditions $\lim_{r\to\infty}\left(u\frac{\partial(ur)}{\partial r}\right) = \lim_{r\to 0}\left(u\frac{\partial(ur)}{\partial r}\right) = 0$ and integrating by parts we obtain

$$\int \frac{\delta E}{\delta u} a_{1,1} \frac{\delta E}{\delta u} dB = -\,Pr \int \left(\frac{1}{r}\frac{\partial(ur)}{\partial r}\right)^2 dB \tag{38}$$

For the element $a_{2,2}$:

$$\int \frac{\delta E}{\delta \vartheta} a_{2,2} \frac{\delta E}{\delta \vartheta} dB = \int \left(1 - \frac{1}{\vartheta}\right)\left(\frac{\partial^2 \vartheta}{\partial r^2} + \frac{1}{r}\frac{\partial \vartheta}{\partial r}\right) r dr d\theta \tag{39}$$

Assuming the following boundary conditions $\lim_{r\to\infty}\left(r\frac{\partial\vartheta}{\partial r}\right) = \lim_{r\to 0}\left(r\frac{\partial\vartheta}{\partial r}\right) = 0$ and integrating by parts we obtain

$$\int \frac{\delta E}{\delta \vartheta} a_{2,2} \frac{\delta E}{\delta \vartheta} dB = -\int \frac{1}{\vartheta^2}\left(\frac{\partial\vartheta}{\partial r}\right)^2 dB \tag{40}$$

For the non diagonal term $a_{2,1}$:

$$\int \frac{\delta E}{\delta \vartheta} a_{2,1} \frac{\delta E}{\delta u} dB = Pr \int \left(1 - \frac{1}{\vartheta}\right)\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right)^2 r dr d\theta \tag{41}$$

which is not negative definite for $\vartheta > 1$, i.e. if $T > T_0$. However, the variation of the exergy, eq. (34) is

$$\frac{dE}{dt} = \int \left(\frac{\delta E}{\delta u} a_{1,1} \frac{\delta E}{\delta u} + \frac{\delta E}{\delta \vartheta} a_{2,1} \frac{\delta E}{\delta u} + \frac{\delta E}{\delta \vartheta} a_{2,2} \frac{\delta E}{\delta \vartheta}\right) dS \tag{42}$$

and from eqs. (37) through (42) we get

$$\frac{dE}{dt} = -\int \frac{1}{\vartheta^2}\left(\frac{\partial\vartheta}{\partial r}\right)^2 dB - Pr \int \left(\frac{1}{r}\frac{\partial(ur)}{\partial r}\right)^2 dS + Pr \int \left(1 - \frac{1}{\vartheta}\right)\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right)^2 dB \tag{43}$$

The sum of the last two terms on the right-hand side of eq. (43) can be written as

$$-\,Pr \int \left(\frac{1}{r}\frac{\partial(ur)}{\partial r}\right)^2 dB + Pr \int \left(1 - \frac{1}{\vartheta}\right)\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right)^2 dB = -\,Pr \int \left(\frac{1}{\vartheta}\right)\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right)^2 dB - 4\,Pr \int \frac{u}{r}\frac{\partial u}{\partial r} dB \tag{44}$$

Finally, the last term on the right-hand side of eq. (44) vanishes:

$$-4\,Pr \int \frac{u}{r}\frac{\partial u}{\partial r} dB = 4\pi u^2\big|_0^\infty = 0 \tag{45}$$

where we have used the boundary conditions $\lim_{r\to\infty}(u) = \lim_{r\to 0}(u) = 0$. So the matrix $a_{i,j}$ is not formally negative definite, but the boundary conditions indicate that its action on the phase space is equivalent to a negative definite matrix. Indeed, eqs. (43) and (44) give

$$\frac{dE}{dt} = -\int \frac{1}{\vartheta^2}\left(\frac{\partial\vartheta}{\partial r}\right)^2 dB - Pr \int \frac{1}{\vartheta}\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right)^2 dB \tag{46}$$

showing that exergy decreases in time. The self similar solution of the velocity filed in (32) is usually written as

$$u(r,t) = \frac{\Gamma}{2\pi r}\left(1 - e^{-\frac{r^2}{4\,\mathrm{Pr}\,t}}\right) \tag{47}$$

This solution can be extended to a one parameter family of solutions by

$$u(r,t) = \frac{\Gamma}{2\pi r}\left(1 - e^{-\frac{r^2}{R^2 + 4\,\mathrm{Pr}\,t}}\right) \tag{48}$$

where R is a given reference radius. Notice that the above assumptions on the boundary conditions are satisfied for this type of solutions. The equation for the temperature is not trivial. If we assume the same type of symmetry like in equation (48), by setting

$$T(r,t) = \frac{4\Gamma^2 Pr}{\pi^2(R^2 + 4\,\mathrm{Pr}\,t)} F\left(\frac{r^2}{R^2 + 4\,\mathrm{Pr}\,t}\right) \tag{49}$$

one has that the function $F(x)$, where x is defined by $x = \frac{r^2}{R^2+4\,\mathrm{Pr}\,t}$, solves the following differential equation

$$x\frac{d^2F}{dx^2} + (x\,\mathrm{Pr}+1)\frac{dF}{dx} + \mathrm{Pr}\,F = \frac{\left((x+1)e^{-x}-1\right)^2}{16x^2} \tag{50}$$

Notice that the function on the right-hand side of (50) is non-negative for $x > 0$ and its limits for $x \to 0$ and $x \to \infty$ vanishes. The solution of (50) can be written in terms of the exponential integral function.

6. Conclusions

Scope of this study is to expand on an idea formulated by Richard Gaggioli in 2018, namely that the exergy of a system is the genuine driver of its evolution towards equilibrium. Physically this is also somewhat intuitive: the farther a system is from its equilibrium state, the higher its exergy and correspondingly higher its “tendency to equilibrium” (towards its zero-exergy level, or “dead state”), activated by diffusion and dispersion of internal and external (=with its environment) gradients. Quantifying this tendency is a different story: Gaggioli proposed a linear dependence of the time derivative of the exergy (always negative as stipulated by the Second Law) from the instantaneous value of the exergy itself, but such an assumption leads to an exponential decay of the total exergy of the system irrespective of the boundary conditions, a fact not confirmed by our experience. In line with other non-equilibrium paradigms (especially Grmela & Öttinger’s GENERIC model) we revived a model formulated by Ginzburg & Landau in 1954, that prescribes that the time evolution of any relevant thermodynamic property (in the G-L language, “order parameter”) is related to the derivative of the exergy w.r.t. this property. The novelty of our approach is that we treat exergy itself as “an order parameter” and link its time derivative to an exergy functional, possibly case dependent and subjected to the physical constraints that act as control functions. In this new approach, the decay is no longer necessarily exponential but depends on the relevant exergy components (mechanical, thermal, chemical, etc.) and on the gradients of the physical variables, if present. The mathematical treatment is more complicated, but the results are encouraging: in a previous paper we showed that the model properly represents the exergy destruction due to dissipative effects in a gas turbine expansion, and in this paper we extend the treatment to the case of a solid rod subject to realistic boundary conditions and to the decay of an Oseen-Lamb vortex coupled with thermal diffusion. The introduction of an exergy functional as the “process driver” leads to a generality loss w.r.t. Gaggioli’s model, because the functional must include the boundary conditions and is thus case-dependent, but also allows for a more rigorous and congruent application to different physical situations.

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7. References

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