On the Quantification of Non-equilibrium Exergy for Thermodynamic Systems Evolving According to Cattaneo's Equation

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Abstract

This paper is a follow-up of previous work aimed at the identification and quantification of the exergy of macroscopic non-equilibrium systems. Assuming that both energy and exergy are *a priori* concepts, it is possible to show that a system in an initial non-equilibrium state relaxes to equilibrium releasing (or absorbing) an additional amount of exergy, called <u>non-equilibrium exergy</u>, which is fundamentally different from Gibbs' Available Energy and depends on both the initial state and the imposed boundary conditions. The existence of such a quantity implies that all iso-energetic non-equilibrium states can be ranked in terms of their non-equilibrium exergy content, any point of the Gibbs plane corresponding therefore to a possible initial distribution, each one with its own exergy-decay history. The non-equilibrium exergy is always larger than its equilibrium counterpart and constitutes the "real" total exergy content of the system, i.e., the real maximum work extractable (or absorbable) from the system. The application of the method to heat conduction problems led to the calculation of a "relaxation curve", i.e., to the determination of the time-history of the relaxation towards equilibrium that takes place in finite rather than infinite time interval. In our previous works, use was made of the Fourier heat diffusion equation. In this study, the Cattaneo heat transfer equation is used instead, in an attempt to extend the validation range of the procedure. Cattaneo introduced in 1948 a second time derivative term that renders the diffusion equation hyperbolic and avoids an infinite speed of propagation. A finite propagation velocity of thermal disturbances affects the value of the non-equilibrium exergy: this paper presents the new results and offers a discussion of the implications.

Keywords: Non-equilibrium thermodynamics; Cattaneo equation; exergy; heat diffusion.

1. Introduction

In previous works [1-2] we derived the evolution in time of the exergy for systems outside of equilibrium. The approach posits the local equilibrium hypothesis and makes use of standard constitutive evolution equations. These two elements are both necessary to derive conclusions but, we must stress, they are not dependent on each other. The Fourier heat law, assumed to be the constitutive equation in [1-2], has been -and rightly so- criticized from a phenomenological point of view, because it implies an infinite "transport velocity" for small temperature signals (see e.g. [3-8]). If the initial thermal inhomogeneities are large enough, one expects to observe deviations of the real evolution of the temperature with respect to the profile provided by the Fourier law. If the Cattaneo equation is taken as the constitutive evolution equation for the temperature, it is again possible to derive the evolution of the exergy from an initial non-equilibrium state to the final equilibrium. The Cattaneo equation has been criticized (see e.g. [3,7]) since it is commonly believed that it is incompatible with the Second Law. The problem is physical rather than mathematical, and we will show that, under the hypothesis of a finite velocity of the temperature signal, it is possible to obtain a negative value of the exergy destroyed in the balance equation (i.e. a positive entropy production, see e.g. [2] or [9]).

By changing the constitutive equations, the evolution of the exergy towards the value zero, corresponding to the "dead state", changes as well. The exergetic content of the initial non-equilibrium state however does not depend on the modes of evolution of the temperature. As we shall see, these characteristics are evident in our approach.

The paper is organized as follows: in Section 2 we discuss the correct boundary conditions to be applied in the case of Cattaneo's equation: as usually, we assume that the Newton law of cooling holds and then we take into account the delay in the heat transfer. This is necessary to obtain a well-posed problem. In subsection 2.1 we obtain the solution by using the classical Fourier analysis and assuming, for simplicity, a "zero velocity" in the initial distribution of the temperature. In subsection 2.2 we discuss the solution obtained, showing how the Cattaneo solution displays a faster approach to equilibrium than its Fourier counterpart. Also, to be consistent with the derivation of the model, it is shown that the Cattaneo number must be bounded somehow by the first Fourier eigenvalue. In Section 3 we introduce the exergy of the system, showing how the balance equation complies with the Second Law. In Section 4 we present the

example of a sphere with radial initial conditions: we obtain both analytical and numerical results and we make a comparison with the results obtained assuming the classical Fourier law as constitutive equation for the evolution of the temperature. Finally, in Section 5, we discuss the method and the results and try to provide a systematic view of our work.

2. Cattaneo's Equation and the Proper Convective Boundary Conditions

Consider a given distribution of mass at an initial temperature distribution $T(\vec{x}, 0)$, and assume that the temperature evolves according to Cattaneo's law. We shall refer in general to the mass distribution as "the solid". The physical assumption behind Cattaneo's equation is the introduction of a relaxation time τ, measuring the delay in the appearance of a heat flux after a temperature gradient is imposed on the solid. The introduction of the relaxation time avoids the problem of an infinite speed of heat propagation in the Fourier's law [4-5,8]. Under these assumptions, the local energy balance results in a law of heat conduction different than Fourier's:

$$\tau \frac{\partial \vec{q}}{\partial t} + \vec{q} = -\lambda \nabla T \tag{1}$$

From the conservation of energy

$$\rho c \frac{\partial T}{\partial t} = -\nabla \cdot \vec{q} \tag{2}$$

one obtains the so-called Cattaneo equation

$$\frac{\partial T}{\partial t} + \tau \frac{\partial^2 T}{\partial t^2} = k^2 \nabla^2 T \tag{3}$$

where $k^2 = \lambda / \rho c$ is the thermal diffusivity. The finite speed of propagation of the signal is given by the constant $u = k/\sqrt{\tau}$ and diverges if $\tau = 0$, in which case from equation 3) one recovers the usual Fourier equation.

The mathematical model for the heat conduction with convective boundary conditions reads

$$\begin{cases} \dfrac{\partial T}{\partial t} + \tau \dfrac{\partial^2 T}{\partial t^2} = k^2 \nabla^2 T \\ \hat{n} \cdot (\vec{q} + \tau \dfrac{\partial \vec{q}}{\partial t}) = \lambda \alpha (T - T_0) \\ T(\vec{x}, 0) = T_1(\vec{x}) \\ T_t(\vec{x}, 0) = T_2(\vec{x}) \end{cases} \tag{4}$$

where T_0 is the temperature of the environment, $\hat{n}$ is the normal to the boundaries of the solid (going outward) and α is a measure of the heat transfer by convection between the boundaries of the solid and the surrounding. The functions $T_1(x)$ and $T_2(x)$ identify the two initial conditions of the problem ($T_t(x)$ hereafter denotes the partial derivative with respect to t). Equations (4) for $\tau = 0$ result in the Fourier model of heat conduction. In the Fourier's case the boundary condition reduces to $\hat{n}. \nabla T + \alpha(T - T_0) = 0$. In the Cattaneo's case the boundary condition $\hat{n}.\left(\vec{q} + \tau \frac{\partial \vec{q}}{\partial t}\right) = \lambda \alpha (T - T_0)$ differs from the usual Fourier condition, because it must take into account the delay between the heat flux and the temperature gradient at the boundary between the solid

and the environment. Such a formulation is necessary for the well-presentation of the problem.

It is easy to see that the boundary conditions in Eq. (4) can be written as $\hat{n}. \nabla T + \alpha(T - T_0) = 0$, i.e. they have the same form as in the Fourier's case (that is when the evolution of temperature is described by $\frac{\partial T}{\partial t} = k^2 \nabla^2 T$). One must pay attention though to the <u>different physical meaning</u>: the temperature gradient is proportional to $\vec{q}(\vec{x}, t + \tau) \approx \vec{q}(\vec{x}, t) + \tau \frac{\partial \vec{q}}{\partial t}$ and not simply to $\vec{q}(\vec{x}, t)$. It is apparent that the boundary condition $\hat{n}.\left(\vec{q} + \tau \frac{\partial \vec{q}}{\partial t}\right) = \lambda \alpha (T - T_0)$, which in force of Eq. (1) can be written as well as $\hat{n}. \nabla T + \alpha(T - T_0) = 0$, is Cattaneo's version of Newton's law of cooling.

2.1 Time Evolution of the Temperature in the Solid

In this subsection we consider the general case of heat conduction in solids with a convective heat exchange between the environment and the boundaries. We make the problem dimensionless by introducing a change of coordinates: $\theta = {}^t/_{2\tau}$ and $\vec{\xi} = {}^{\vec{x}}/_L$, where L is a characteristic length of the solid. Also, we define the Cattaneo number $C = {}^{k^2 \tau}/_{L^2}$ and the Biot number $Bi = \alpha L$. We assume for simplicity that $T_t(\vec{x}, 0) = T_2(\vec{x}) = 0$. Then the system of Eq. (4) can be rewritten as

$$\begin{cases} \dfrac{\partial T}{\partial \theta} + \dfrac{1}{2} \dfrac{\partial^2 T}{\partial \theta^2} = 2C \nabla^2 T \\ \hat{n} \cdot \nabla T + Bi(T - T_0) = 0 \\ T(\vec{\xi}, 0) = T_1(\vec{\xi}) \\ T_t(\vec{\xi}, 0) = 0 \end{cases} \tag{5}$$

We look for a solution of equations 5) by the method of separation of variables. Due to the term T_0, the boundary conditions are inhomogeneous. We introduce the temperature $T(\vec{\xi}, \theta) = T_0 + v(\vec{\xi}, \theta)$, where T_0 is the stationary temperature and the function $v(\vec{\xi}, \theta)$ measures the deviation from the stationary solution. In this way it is easy to see that the function $v(\vec{\xi}, \theta)$ solves the same differential Eq. (5) but with homogeneous boundary conditions, i.e. $\hat{n}. \nabla v + Biv = 0$. Now it is possible to apply the separation of variables to the function $v(\vec{\xi}, \theta)$, so we set $v(\vec{\xi}, \theta) = w(\vec{\xi})W(\theta)$. The differential equation gives $\frac{W_\theta + 1/2 W_{\theta\theta}}{W} = 2C \frac{\nabla^2 w}{w}$, implying that $\nabla^2 w$ must be proportional to w. So, we derive the Helmholtz equation for the function $w(\vec{\xi})$

$$\begin{cases} \nabla^2 w + \mu^2 w = 0 \\ \hat{n} \cdot \nabla w + Biw = 0 \end{cases} \tag{6}$$

Under the stipulated boundary conditions, the Helmholtz operator is self-adjoint: it possesses real eigenvalues and the corresponding eigenvectors are orthogonal (see e.g. [10]). If $w_n(\vec{x})$ is the eigenfunction corresponding to the eigenvalue μ_n, we have

$$\int w_n(\vec{\xi}) w_m(\vec{\xi}) dV = f_n \delta_{n,m} \tag{7}$$

We assume also that the set of eigenvectors is complete. Corresponding to each w_n there is a function W_n satisfying $(W_n)_\theta + 1/2 (W_n)_{\theta\theta} + 2C\mu_n^2 W_n = 0$, so we get

$$W_n(\theta) = e^{-\theta}\left(a_n \sin(\Delta_n\theta) + b_n \cos(\Delta_n\theta)\right) \qquad (8)$$

where $\Delta_n^2 = 4\mu_n^2 C - 1$. If the initial condition $T_t(\vec{\xi},\theta) = 0$ is taken into account, then $b_n = \Delta_n a_n$ and the solution of the problem (5) is given by the infinite sum

$$T(\vec{\xi},\theta) = T_0 + e^{-\theta}\sum_{n=1}^\infty c_n w_n(\vec{\xi}) F_n(\theta) \qquad (9)$$

where

$$F_n = \sin(\Delta_n\theta) + \Delta_n\cos(\Delta_n\theta)$$

and, thanks to the orthogonality Eq. (7), the coefficients c_n are given by

$$c_n = \frac{1}{\Delta_n f_n}\int \left(T_1(\vec{\xi}) - T_0\right)w_n(\vec{\xi})dV \qquad (10)$$

2.2 Discussion of the Solution

Let us discuss the solution 9). The dependence of the values Δ_n on the eigenvalues μ_n is given by $\Delta_n^2 = 4\mu_n^2 C - 1$. Also, the eigenvalues μ_n depend on the value of the Biot number Bi. Since the Cattaneo number and the Biot number are two independent quantities, it is possible that some of the values of Δ_n are purely imaginary. In the Fourier's case in fact C=0, and all of them are imaginary. On the contrary, now we may only have a finite number of such values. The remaining values (infinitely many) are real and account for the oscillatory behavior of a Cattaneo typical heat diffusion process. This oscillatory behavior is modulated by the smoothing exponential $e^{-\theta}$.

A comparison between the time evolution of the temperature according to Cattaneo's equation and the evolution of the temperature according to Fourier's equation near the parabolic limit (i.e., for very small values of Cattaneo number C) has been given in [11]: in particular these authors have shown that if the same initial condition $T(r,0)$ is assigned, the solutions of the Fourier and Cattaneo equations remain rather close at all times.

However, which one of the two solutions approaches faster the equilibrium value has not been discussed. If we focus on the time evolution of the solution of Eq. (9), we can identify two different cases according to the value of the first eigenvalue

   i. $4\mu_1^2 C - 1 > 0$

   ii. $4\mu_1^2 C - 1 < 0$

In the first case the solution approaches T_0 with an envelope modulated by the exponential $e^{-\theta}$, while in the second case the modulation is given by the exponential $e^{-\theta(1-\sqrt{1-4\mu_1^2 C})}$. Comparing these time behaviors with those of the parabolic heat equation, we notice that in the Fourier's case the solution approaches T_0 as $e^{-k^2\mu_1^2 t/L^2}$. In order to use the same dimensionless time scale, for any fixed C of the

Cattaneo solution, we can write the Fourier exponential as $e^{-2C\mu_1^2\theta}$.

So, in the case i. above, if $C < \frac{1}{2\mu_1^2}$, Cattaneo's solution pproaches T_0 faster than the Fourier solution. In the second case <u>Cattaneo's solution approaches T_0 faster than the Fourier solution whatever the values of C and μ_1</u>. At first sight these observations seem to be in contrast with the perception that the "Fourier temperature" spreads out faster than the "Cattaneo temperature", due to the fact that the solutions of Cattaneo equation are solutions of a damped-wave equation and have a finite speed of propagation. Actually, although the effect of the heat flux is instantaneously felt in the Fourier's model, a finite effective heat propagation speed, based on the penetration depth, can be defined also in this case [12]. The penetration depth is the depth to which significant temperature effects propagate within the solid [13]. From this point of view the effective speed of propagation for the Fourier's model may be, under certain conditions, smaller than the effective speed of propagation of the Cattaneo model (which is different from the group velocity of the temperature waves).

The above considerations suggest to provide a practical estimate of the range of variation of the Cattaneo number $C = k^2 r/R^2$. Equation 3) is derived under the physical assumption $\vec{q}(\vec{x},t+\tau) = -\lambda\nabla T(\vec{x},t)$ <u>in the limit of a small τ</u>. This means that the Cattaneo number must be small in Eq. (14) or (15). The adoption of Cattaneo equation with arbitrary values of C may lead to unphysical solutions. It is indeed possible to show that for sufficiently large values of C, local negative temperatures are obtained from Eq. (15) at some time t^*, even in the case of very reasonable initial conditions. In this work we shall therefore limit the range of C from 0 to $C \approx \frac{1}{4\mu_1^2}$ (so that Δ_1^2 is small, positive or negative and Δ_n is positive for $n > 1$).

A more serious objection to the Cattaneo equation has been given in [14]: in that work, the authors showed that, if a suitable external source of heat is taken into consideration, then for any choice of the value of the Cattaneo number C, there are points of the solid where negative temperature arises. Indeed, this happens for every equation of hyperbolic type if the external source has a resonant frequency with those of the material. In Eq. (3) there is no external source term, but in future works we plan to investigate also this case in more detail.

3. Cattaneo's Exergy

In this section we calculate the maximum work that can be extracted from a solid in the process of exclusive interaction with the environment, i.e. the exergy content of the solid (see e,g [1-2]). To calculate this quantity, we notice that Cattaneo equation is based on the physical assumption that a gradient of temperature at time t produces a heat flux at a later time $t + \tau$. This means that a gradient of temperature at time t will produce an entropy flux at time $t + \tau$, and that obviously there will be an exergy flux with the same delay. Under the local equilibrium, the analytic expression for this flux at time t and for a portion of solid Δx is given by (see e.g. [1,2])

$$E(\vec{x},t) = \rho c \left(T(\vec{x},t) - T_0 - T_0 \ln\left(\frac{T(\vec{x},t)}{T_0}\right)\right) \tag{11}$$

The contribution from the entire solid is found by integrating over the domain of interest:

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

The total non-equilibrium exergy of the system at time t can be calculated as the difference between the exergy at time 0 and the exergy at time t:

$$E(t) = \rho c \int \left(T(\vec{x},0) - T(\vec{x},t)\right) d\vec{x} - \rho c T_0 \int \ln\left(\frac{T(\vec{x},0)}{T(\vec{x},t)}\right) d\vec{x} \tag{13}$$

and the total non-equilibrium exergy is found by taking the limit as $t \to \infty$:

$$E = \rho c \int \left(T(\vec{x},0) - T_0\right) d\vec{x} - \rho c T_0 \int \ln\left(\frac{T(\vec{x},0)}{T_0}\right) d\vec{x} \tag{14}$$

The exergy current associated with the temperature flow inside the solid is described by the balance equation

$$\frac{\partial E}{\partial t} + \nabla \cdot \vec{j} = e \tag{15}$$

where

$$\vec{j} = -\lambda \nabla T \left(1 - \frac{T_0}{T}\right) \tag{16}$$

is the exergy flux, i.e. the exergy crossing the boundary surface of the solid. The exergy destruction per unit volume e is given by

$$e = -\lambda T_0 \left(\frac{\nabla T}{T}\right)^2 \tag{17}$$

and is definite negative, as it must be, because the time change in E is always larger than the exergy flux. Equation (16) is the same as in the Fourier's case (see [1-2]) but again the physical meaning is different. In fact, the gradient of temperature in Cattaneo's equation is proportional to the heat flux at time $t + \tau$, i.e. to $\vec{q}(\vec{x},t+\tau)$. So, we expect that the exergy flux should be defined by

$$\vec{j}(\vec{x},t) = q(\vec{x},t+\tau)\left(1 - \frac{T_0}{T(\vec{x},t)}\right) \tag{18}$$

Indeed, if we assume that τ is small and expand around $\tau = 0$, we obtain from (18)

$$\vec{j}(\vec{x},t) \approx \left(\vec{q}(\vec{x},t) + \tau \frac{\partial \vec{q}}{\partial t}\right)\left(1 - \frac{T_0}{T(\vec{x},t)}\right) \tag{19}$$

and from Eq. (1) we recover Eq. (16). It is rather clear that Eq. (14) for the total non-equilibrium exergy of the solid is the same for the Cattaneo and for the Fourier cases, as it should be: the difference is in the evolution path of the exergy, i.e. Eqs. (13) or (11), not in the total value, provided in both cases by the integration in time from 0 to ∞.

4. The Case of a Sphere with Radial Initial Conditions

In the case of a sphere the set of Eqs. (4) becomes (in dimensionless spherical coordinates, with $\xi = rR$ and $t = 2\tau\theta$)

$$\begin{cases} \frac{\partial T}{\partial \theta} + \frac{1}{2}\frac{\partial^2 T}{\partial \theta^2} = C\left(\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2\frac{\partial T}{\partial \xi}\right) + \frac{1}{\xi^2 \sin(\psi)}\frac{\partial}{\partial \psi}\left(\sin(\psi)\frac{\partial T}{\partial \psi}\right) + \frac{1}{\xi^2 \sin^2(\psi)}\frac{\partial^2 T}{\partial \phi^2}\right) \\ \hat{n}\cdot\nabla T\big|_{\xi=1} + Bi(T-T_0)\big|_{\xi=1} = 0 \\ T(\xi,0) = T_1(\xi) \\ T_\theta(\xi,0) = 0 \end{cases} \tag{20}$$

We are assuming that the initial distribution is spherically symmetric. At the surface of the sphere there is a heat exchange with the surroundings at temperature T_0. The Biot number is defined as $Bi = \alpha R$, where R is the radius of the sphere.

Setting $T = T_0 + \frac{u(\xi,\theta)}{\xi}$, we get

$$\begin{cases} \frac{\partial u}{\partial \theta} + \frac{1}{2}\frac{\partial^2 u}{\partial \theta^2} = C\frac{\partial^2 u}{\partial \xi^2} \\ R\frac{\partial u}{\partial \xi}\bigg|_{\xi=1} + (Bi-1)u\big|_{\xi=1} = 0 \\ u(\xi,0) = \xi\left(T_1(\xi) - T_0\right) \\ u_\theta(\xi,0) = 0 \end{cases} \tag{21}$$

This is a one-dimensional problem. Notice that in $\xi = 0$ we must have $u(0,t) = 0$, since $T(\xi,\theta) = \frac{u(\xi,\theta)}{\xi} + T_0$ must be bounded. Then, by separation of variables, we have that $u(r,\theta) = W(\theta)\chi(r)$.. The function $\chi(r)$ is given by $\chi(r) = c\sin\left(\mu\frac{r}{R}\right)$ where μ, due to the boundary conditions, is any solution of the transcendental equation $(Bi - 1)\sin(\mu) + \mu\cos(\mu) = 0$. It is possible to show that this equation has an infinite number of real roots μ_n. The function $W(\theta)$ is given by $W(\theta) = b_n e^{-\theta}(\sin(\Delta_n\theta) + \Delta_n\cos(\Delta_n\theta))$

where

$$\Delta_n^2 = 4\mu_n^2 C - 1.$$

We then have that

$$u(\xi,\theta) = e^{-\theta}\sum_n b_n\left(\sin(\Delta_n\theta) + \Delta_n\cos(\Delta_n\theta)\right)\sin(\mu_n\xi) \tag{22}$$

The orthogonality relations

$$\int_0^1 \sin(\mu_n\xi)\sin(\mu_m\xi)d\xi = \delta_{m,n}\frac{1}{2}\left(\frac{\mu_n^2 + Bi(Bi-1)}{\mu_n^2 + (Bi-1)^2}\right) \tag{23}$$

result in

$$b_n = \frac{2}{\Delta_n}\frac{(Bi-1)^2 + \mu_n^2}{Bi(Bi-1) + \mu_n^2}\int_0^1 \xi(T_1(\xi) - T_0)\sin(\mu_n\xi)d\xi \tag{24}$$

and the temperature of the sphere is explicitly described by

$$T(\xi,\theta) = T_0 + \frac{e^{-\theta}}{\xi}\sum_n b_n\left(\sin(\Delta_n\theta) + \Delta_n\cos(\Delta_n\theta)\right)\sin(\mu_n\xi) \tag{25}$$

We take as an example the following initial condition

$$T(r,0) = T_0\left(1 + w\left(1 - \left(\frac{r}{R}\right)^2\right)\right) \tag{26}$$

The evolution of temperature is described by the series

$$\frac{T(\xi,\theta)}{T_0} = 1 + 4w\frac{e^{-\theta}}{\xi}\sum_n \frac{\left((Bi-1)^2 + \mu_n^2\right)\left(3Bi - \mu_n^2\right)\sin(\mu_n)}{\Delta_n\left(Bi(Bi-1) + \mu_n^2\right)\mu_n^4} F_n(\theta)\sin(\mu_n\xi) \tag{27}$$

where

$$F_n(\theta) = \sin(\Delta_n\theta) + \Delta_n\cos(\Delta_n\theta)).$$

A plot of the temperature described by Eq. (27) and of the corresponding Fourier temperature (with the proper rescaling of time, as explained in subsection 2.2 above) is given in Figure 1. Readers will notice that there is a "bump" appearing in the temperature profile in the Cattaneo's case for θ between 2 and 4: this is due to the hyperbolic nature of the equation: it oscillates for small values of the dimensionless time and then approaches equilibrium like the Fourier solution on the left. The bump corresponds to the first (i.e. the larger) oscillation. For comparison, we write also the Fourier series:

$$\frac{T(\xi,\theta)}{T_0} = 1 + \frac{4w}{\xi}\sum_n G(Bi,\mu_n)\sin(\mu_n\xi)e^{-\frac{\mu_n^2 k^2}{R^2}t} \tag{28}$$

where

$$G(Bi,\mu_n) = \frac{\left((Bi-1)^2 + \mu_n^2\right)\left(3Bi - \mu_n^2\right)\sin(\mu_n)}{\left(Bi(Bi-1) + \mu_n^2\right)\mu_n^4}.$$
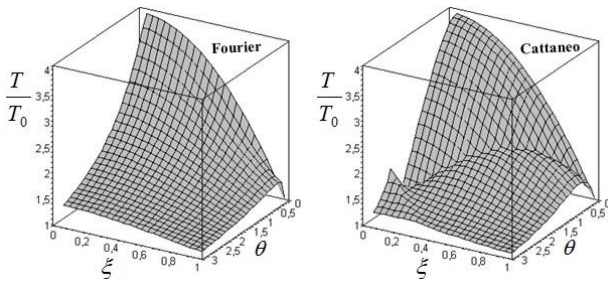

Figure 1: Time evolution of the temperature in the Fourier and in the Cattaneo case. The first 50 terms of the sum (27) have been used. The parameters are: $B = 5$ $C = \tau = 0.05$, $R = k = 1$, $w = 3$.

The total exergy, from formula 14), is given by

$$\frac{E}{\rho cVT_0} = \frac{8}{3} + \frac{2(w^2+5)}{5w} - 2\sqrt{\left(\frac{w+1}{w}\right)^3}\,\mathrm{arctan\,h}\left(\sqrt{\frac{w}{w+1}}\right) \tag{29}$$

whereas the time evolution of the exergy is given by Eq. (12). A plot of the total exergy, Eq. (29), as a function of the parameter w is reported in Fig. 2: notice that the initial temperature profile, given by Eq. (26), increases towards the

center of the sphere for $w > 0$ and decreases for $-1 < w < 0$, whereas for $w=0$ the temperature is stationary. As expected, the total exergy has a global minimum for $w=0$, when the initial profile corresponds to the equilibrium temperature.
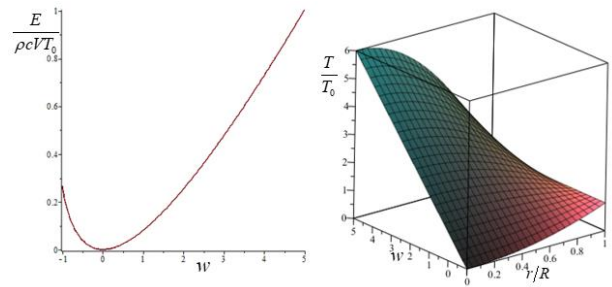

Figure 2: Plot of the total exergy, Eq. (29), as a function of the parameter w (left) and of the corresponding initial profile of temperature, equation 26), as a function of w and r/R. The total exergy has a minimum for $w=0$, corresponding to the initial profile equal to the equilibrium profile.

A plot of the time evolutions of the exergy is given in Figure 3. For comparison, the exergy of the Fourier case is reported as well (again, we rescaled the time for the Fourier case as explained in section 3).
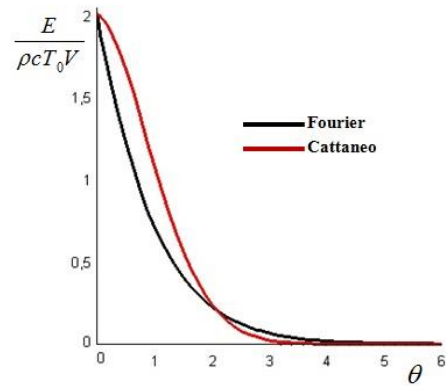

Figure 3: Time evolution of the exergy as given by equation 12). The first 50 terms of the sum in Eq. (27) have been used. The parameters are: $Bi=5$, $C = \tau = 0.05$, $R=k=1$, $w=3$.
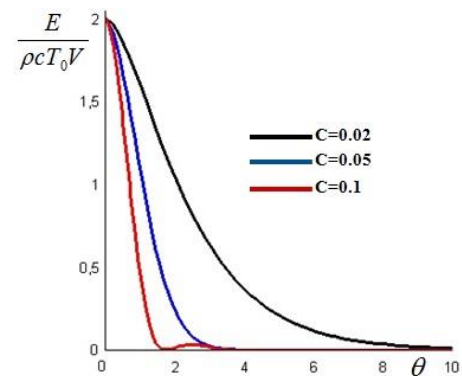

Figure 4: Time evolution of the exergy for different values of C. The first 50 terms of the sum in equation 27) have been used. The other parameters are: $Bi = 5$, $R = k = 1$, $w = 3$.

In figure 4 we report a plot of the evolution of the exergy corresponding to three different values of the Cattaneo number C. The exergy destruction is faster for higher values of C. As can be noticed, the exergy decrease may be not monotonic in time (there is a small "bump" for *C=0.1* around $\theta = 2$): according to us, this effect is again due to the hyperbolic nature of the equation: for small values of θ, when the solution is not yet suppressed by the exponential decay, the oscillations (visible in Figure 1) may provide a temperature gradient sufficient to produce a small and brief increase in the exergy content. The effect is more pronounced for higher values of C, since the oscillations are larger.

5. Conclusions

The time variation of the exergy of a solid body was computed by means of Cattaneo heat diffusion equation. The results show two important points: first, that the evolution in time of the intrinsic energy content (i.e., the exergy) of a system depends not only on the imposed boundary conditions but also on its internal dynamics; second, that though the values of the non-equilibrium exergy derived in this paper are different from those calculated in a previous paper where the classical Fourier equation was used instead, at long times the two curves overlap, and their integrals (i.e., the initial non-equilibrium exergy content of the system) do not differ. This paper provides another contribution: often, Cattaneo equation has been criticized as being "incompatible" with the Second Law. In our derivation above, we demonstrate that if the ratio of the Cattaneo number to the value of the first (larger and thus energy-carrying) eigenvalue of the Cattaneo diffusion equation exceeds a well-defined limit, the temperature in the solid may locally assume negative values, which of course is unphysical: but as long as the limit $C = 4\mu_1^2$ is abided by, all thermodynamic quantities behave correctly and smoothly and satisfy Second Law. Further, the exergy destroyed (17) is always negative definite: physically, this corresponds to the fact that the gradient of temperature in Cattaneo's model is proportional to the heat flux at time $t + \tau$, as shown by equations 18) and 19). If this constraint is not taken into account, an exergy destruction not complying with the Second Law would have been obtained.

Nomenclature

Entity and units	Symbol
Biot number	Bi
Cattaneo number	C
Specific heat, J/(kgK)	c
Exergy, J	E
Heat flux, W/(m2)	$\vec{q}$
Temperature, K	T
Time, s	t
Volume, m3	V
Density, kg/m3	ρ
Dimensionless length	ξ
Relaxation time, s	τ
Dimensionless time	θ

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