Ann. Acad. Rom. Sci.
Ser. Math. Appl.
ISSN 2066-6594 Vol. 17, No. 3/2025

SOME CONCEPTUAL REFLECTIONS ON TIME IN SYSTEMS WITH HIERARCHIES OF INTERNAL VARIABLES*

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Dedicated to Prof. Liliana Restuccia on the occasion of her 70th anniversary

DOI 10.56082/annalsarscimath.2025.3.339

Abstract

We present some conceptual reflections on time in the context of thermodynamics with internal variables or with internal fluxes with relaxation times of several different orders of magnitude. The combination between reversible and irreversible contributions to the dynamics depends on the observation timescale, and opens new aspects to the usual discussion on the contrast between reversibility and irreversibility. As an illustration of such situations, two different kinds of hierarchies of internal variables are presented. In one of them, all the variables are vectors following linear relaxational evolution equations, with their respective relaxation times following a potential law. In the other one, all the variables have a different tensorial order, in such a way that the variable of order i is the flux of the precedent variable of order $i-1$, but all of them have the same relaxation time. Some mathematical and physical features of both hierarchies are examined.

Keywords: time, non-equilibrium thermodynamics, internal variables, extended irreversible thermodynamics.

MSC: 03D55, 70K70, 80A05, 80A20, 82C35, 82C40.

*Accepted for publication on November 18, 2025

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1 Introduction

The thermodynamics of systems with internal variables [2, 18, 19] has been one of the main fields of work by Professor Liliana Restuccia, especially in anisotropic systems with non-linear couplings amongst the variables, in such different settings as semiconductors, porous media, elastic or anelastic bodies, and considering such phenomena as magnetic relaxation, dielectric relaxation, motion of defects, heat transport or fluid flow, and illustrating general principles such as extensions of the second law and frame indifference [3,4,6–8,12–17,20,22–26,28,30]. On the other side, Professor Restuccia has been interested not only on the formal aspects and applications of thermodynamics, but also in some of its deep conceptual aspects. The aim of this paper is to express some reflections on time from the perspective of systems with internal variables with different relaxation times and explore it in two different kinds of hierarchies of variables.

In one of them, there is a big number of microscopic internal variables, all of them of the same tensorial character (vectors, for instance) with their respective relaxation times following a mathematical hierarchy. In the other case, each variable is the flux of the precedent one, in such a way that they have increasing tensorial orders, and their relaxation times are equal to each other. Thus, the constituents of one of the hierarchies have the same tensorial character but hierarchical values for their relaxation times, whereas the other one is hierarchical in the tensorial order of the constituents but with the same relaxation time. Much more general possibilities may be considered, but we focus our attention in these two simple ones. We show that in some particular situations, the full dynamical complexity of the system may be reduced to a relatively simplified global description, containing only a small number of variables.

2 Some reflections on time in systems with internal variables

The most well-known aspect of discussions about time from a thermodynamic perspective concerns the contrast between the irreversibility of time in thermodynamic systems and the reversibility of time in mechanical systems without friction. The fact that systems with a big number of particles may be described, in principle, from a mechanical perspective and from a thermodynamic perspective, leads to a contradiction between the reversible character of the first description, and the irreversible character of the second

one. A way to sort out from such a contradiction is to take into account the complex mechanical dynamics of the system, in such a way that the high sensitivity of the evolution on small variations of the initial conditions makes that after a relatively short time –the so-called Lyapunov time– the mechanical evolution of the system is no longer predictable, and the reversal of motion –within a narrow margin of errors– does not lead back to the initial conditions, due to the sensibility of motion to small perturbations.

Here, we will refer to another kind of reflection on time when the system has, besides the set of classical conserved thermodynamic variables, a set of additional variables –internal variables, or internal fluxes– whose characteristic relaxation times are considerably shorter than the characteristic evolution times of the classical thermodynamic variables. In those cases, a relevant parameter is the relation between the temporal scale of observation, defined by some characteristic value t_0 or by a characteristic frequency proportional to $1/t_0$, and the characteristic internal times of the system. In a simple relaxation-time approach to kinetic theory, such internal time would be the time between successive collisions, and in a mechanical system with chaotic dynamics, such internal time would be the Lyapunov time characterizing the divergence between different orbits.

When the observation frequency is high (observation time short, smaller than the collision time or the Lyapunov time), the system behaves in a reversible way, in such a way that no relevant information is lost during the observation timescale. This is in contrast to what happens at longer observation timescales or shorter frequencies, where information is irreversibly lost. This combination of different features of the dynamical behavior has two conceptual implications: 1) transport equations should be reversible at short time scales and irreversible at long time scales, and 2) instead of a radical opposition between reversible and irreversible behavior, it would be more illustrative studying a transition from one behavior to the other, in terms of the observation timescale. For instance, a well-known transport equation exhibiting such kind of transition between reversible and irreversible behavior is the Maxwell-Cattaneo-Vernotte equation for heat transport

$$\tau \frac{d\mathbf{q}}{dt} + \mathbf{q} = \lambda \nabla T, \tag{1}$$

with $\mathbf{q}$ the heat flux, T temperature, λ thermal conductivity, and τ relaxation time. When τ is negligibly small, ((1)) reduces to the irreversible Fourier equation, while for τ long or for fast variations of $\mathbf{q}$, the first term on the right-hand side is dominant with respect to the second, and one has a reversible equation. Indeed, when the term in τ is negligible and one has

$\mathbf{q} = -\lambda\nabla T$, reversing the sense of time $\mathbf{q}$ changes the sign, whereas the right-hand side does not change the sign, thus indicating an irreversible behavior. In contrast, when the term in τ is dominant, the subsequent equation is $\tau d\mathbf{q}/dt = -\lambda\nabla T$; in this case, a reversal of time implies that both $\mathbf{q}$ and dt change sign, so that both terms of this equation remain invariant, thus indicating that the equation is reversible, i.e., the same equation is valid in both directions of time, in contrast to Fourier's equation.

Thus, for observation times $t_0 << \tau$ one has reversible behavior whereas for t_0 of the order of τ there is a transition from reversible to irreversible behavior. Indeed, one may express the time τ as $a\tau_0$, with a a dimensionless parameter, and $\tau d\mathbf{q}/dt$ becomes $(\tau/\tau_0)d\mathbf{q}/da$; for τ_0 much smaller than τ, the ratio τ/τ_0 is high and this term is dominant, whereas for τ_0 much longer than τ, this ratio is negligible. This qualitative feature provides a physical motivation for ((1)) which is complementary to the usual motivation to have finite speed of propagation for heat pulses, in contrast to the infinite speed following from Fourier's equation. For observation timescales much longer than τ, $\mathbf{q}$ does no longer behave as an independent variable and T (or the internal energy density u) is sufficient to describe the evolution of the system, whereas for timescales comparable or shorter than τ, $\mathbf{q}$ must be taken as an additional independent variable.

The situation becomes more complex and interesting when instead of a single short-time variable, as for instance $\mathbf{q}$ with relaxation time τ, one has several or many internal variables with different relaxation times. We may consider, as an illustration, two particular situations that we will explore in further detail below: a) the relaxation times τ_i of the respective variables (let us name them $\mathbf{J}_i$) are different, in such a way that $\tau_{i+1} < \tau_i < \tau_{i-1}$;

b) there are many internal variables such that their relaxation times τ_i are equal or closely similar to each other.

In case a), if $\tau_{i+1} < \tau_0 < \tau_{i-1}$ for a particular value I of i, the variables with $I > i$ will behave as independent variables whereas those with $I < i$ will be not. Thus, for shorter and shorter values of t_0, an increasing number of independent variables will arise, and more information will be needed for the description of the system. To make an analogy with human sciences, the transition from a high number to a small number of variables as a function of the observation timescales is similar to the description of a society from the point of view of newspapers, weekly magazines, monthly magazines, annuaries, and books of history. The respective observation timescales t_0 are one day, one week, one month, one year, one or more decades, one or more centuries ... The shorter is the observation timescale, more independent variables are needed, and more news appear. When going from the newspa-

pers to the history books, indeed, much details of information are lost and only long-term features and trends are kept in the description.

Another situation arises when one has many internal variables with the same relaxation time, but different tensorial orders. Since describing each of them would require an enormous and unnecessary effort, a possibility to grasp in a simplified way the problem would be introducing only one or two of such variables, describing the average behavior of them. In this way, the description would be richer than that based on only the slow classical variables, but it would not have the complexity of a description including all the fast variables. A physically relevant question would be how to average the behavior of the fast collectivity.

In the next two sections we will deal in more concrete terms with two hierarchies of internal variables: many variables with a hierarchy of relaxation times, and many variables with the same relaxation time. This kind of problems involving many different temporal and spatial scales are of special interest for the so-called multiscale thermodynamics [21], a powerful mathematical formalism which allows to grasp the essential physical ideas behind such multiscale situation.

3 Hierarchy of variables of the same tensorial order and different relaxation times

In some cases, a physical variable is not a single quantity, but a sum of several different contributions. This happens for instance in polarizable electrical systems or in magnetic systems in which molecules of many different sizes contribute to the electric or magnetic polarization. The diversity of these several contributions is manifested in dynamical situations, in which the contributions of different molecules, or different atoms, or different electronic orbitals, have different relaxation times [9, 14, 16].

Another situation is found when considering heat or electric transport in gases with collision times depending on the velocity of the particles. In such a case, the contributions of particles with different velocities to the heat or the electric flux have different relaxation times and an accurate description of fast phenomena would require to take into account the diverse dynamics of such several contributions. Other physical situations with dynamical hierarchies of variables are found in the rheology of macromolecular systems, in the flow of suspensions of particles of many different sizes, in the flow of fluids in porous media with channels of many different radii, and in the motion of defects of many different sizes.

In all such systems, the steady state situation is characterized by the full flow or by the full magnetic or electric polarizations, and the complexity of the system is not evident, but when the systems are submitted to high-frequency perturbations, characterized by a given period t', the contributions having relaxation times longer than t' exhibit their relaxation differences, whereas the contributions with relaxation times much shorter than t' do not have time enough to follow the perturbation and keep their steady-state value.

Les us assume, for instance, that the internal variable $\mathbf{J}$ (which could be a magnetic polarization, an electric polarization, a heat flux, an electric flux, a fluid flow in porous media, etc) is given by

$$\mathbf{J} = \sum_i \mathbf{J}_i. \tag{2}$$

The subscript i does not refer to the geometric component of the variable along the three axes, but to the different physical contributions to the variable J. As told in the previous paragraph, the i may stand for the contribution of particles of different sizes or different forms to magnetic polarization, or to fluid flow in channels of radius r_i of a porous medium, or to the contribution of particle with characteristic velocity v_i to the heat flow of the electric current, and so on.

Assume that the several contributions have linear relaxation dynamics described by

$$\frac{d\mathbf{J}_i}{dt} = \sum_j \alpha_{ij}\mathbf{J}_j - \sum_j \beta ij\mathbf{J}_{j0}. \tag{3}$$

with α_{ij} and β_{ij} matrices (α_{ij} being the reverse matrix of the relaxation times) and $\mathbf{J}_0$ the steady-state value of $\mathbf{J}_j$. In the case that the matrices α_{ij} and β_{ij} are diagonal, one may rewrite ((3)) as

$$\tau_i \frac{d\mathbf{J}_i}{dt} = -\mathbf{J}_i + \mathbf{J}_{i0}. \tag{4}$$

One may assume for instance that $\mathbf{J}_{i0} = \sigma_i \mathbf{E}_0$, with E_0 an external thermodynamic force and σ_i a transport coefficient. If $\mathbf{J}_i$ is taken as an electric flux, E would be the applied electric field and σ_i the electric conductivity; if $\mathbf{J}_i$ is a heat flux, $\mathbf{J}_{i0}$ would be -$\lambda_i \nabla T_0$, with λ_i the contribution of particles of kind i to the thermal conductivity.

The idea of dynamical hierarchy in the $\mathbf{J}_i$ contributions to $\mathbf{J}$ consists in assuming that the relaxation times τ_i and the transport coefficients σ_i depend not only on temperature T, but also on the numerical label i of

the i-th contribution. We may assume, for instance that $\tau_i = \tau_1 i^p$, and $\sigma_i = \sigma_1 i^m$, with p and m numerical exponents, which may be bigger or lower than 1. In the particular case that i is not a collection of integers but a continuum label x, in such a way that $\mathbf{J} = \int f(x)\mathbf{J}(x)dx$, with $f(x)$ a distribution function, and $\mathbf{J}(x)$ a continuous distribution of contributions to $\mathbf{J}$, each of them satisfying a relaxation equation like ((4)), i.e.

$$\tau(x)\frac{d\mathbf{J}(x)}{dt} = -\mathbf{J}(x) + \sigma(x)\mathbf{E}_0, \tag{5}$$

and, if $\tau(x) = \tau_1 x^p$, $\sigma(x) = \sigma_1 x^m$ and $f(x) = Be^{-cx^n}$, the decay of $\mathbf{J}$ after the electric field or the corresponding thermodynamic force is switched of is [9]:

$$\mathbf{J}(t) = \mathbf{J}_0 e^{-(t/\tau_1)^\beta} \tag{6}$$

with $\mathbf{J}_0$ the initial (steady-state) value of $\mathbf{J}$ and $\beta = n/(n+p)$ =(note that β does not depend on the exponent m nor on the constants c nor B). This kind of decay law is known as stretched exponential decay or Kolhrausch law or William-Watts law and it appears in many different physical systems. If, for instance, n and p are 2, the exponent β is 1/2; if $n = 1$ and $p = 2$, $\beta = 1/3$.

Then, in the mentioned conditions, the whole hierarchy of $\mathbf{J}_i$ (in the discrete-label case i) or of $\mathbf{J}(x)$ (for the continuous label x), each term of the hierarchy decaying in an exponential way and in ((4)) and ((5)), may be replaced by the sum $\mathbf{J}$ of the contributions, which decays as a stretched exponential ((6)). This has two interesting consequences. On one hand, systems whose global internal variables decays as a stretched-exponential dynamics may, in some circumstances, be described by a sum of independent additive contributions which of them decays in an exponential way. This behavior is only a particular case in a much wider set of possibilities. For instance, it would be of interest to study global dynamical behaviors arising from a set of partial evolution equation given by

$$\tau_i\frac{d\mathbf{J}_i}{dt} = -\mathbf{J}_i + \mathbf{J}_{i0} + \gamma_{ij-1}\mathbf{J}_{i-1}, \tag{7}$$

with γ_{ij} a matrix of coupling coefficients. This is a generalization of the set of equations ((4)), with couplings between the constituents of different orders. When there is only a small number of internal variables and the coefficients depend on temperature but do not exhibit any hierarchical dependence, this is a relatively simple problem. When there are many variables and the coefficients exhibit a hierarchical dependence, the mathematical situation is more difficult.

4 Hierarchy of variables of different tensorial order and the same relaxation time

Another kind of hierarchy of variables is found when the variable $\mathbf{Q}^{(i)}$ of tensorial order i, is the flux of the precedent variable $\mathbf{Q}^{(i-1)}$ [5,10,11]. This is found for instance in heat transport, diffusion transport, electric transport or turbulent flows. In this case, one may consider the following set of evolution equations

$$\tau_i \frac{d\mathbf{Q}^{(i)}}{dt} = -\mathbf{Q}^{(i)} + \mathbf{Q}_0^{(i)} + \gamma_{ij+1}\nabla \cdot \mathbf{Q}^{(i+1)} + \gamma_{ij-1}\nabla \mathbf{Q}^{(i-1)}, \tag{8}$$

In the case of heat transport, $\mathbf{Q}^{(1)} = \mathbf{q}$, with $\mathbf{q}$ the heat flux, $\mathbf{Q}_0^{(i)} = -\lambda \nabla T$, and $\mathbf{Q}^{(2)}$ the flux of $\mathbf{q}$. If one stops at this order of approximation, and uses

$$\tau_2 \frac{d\mathbf{Q}^{(2)}}{dt} = -\mathbf{Q}^{(2)} + \gamma_{21}\nabla \mathbf{q}, \tag{9}$$

and one considers that τ_2 is much smaller than τ_1, one has the well-known Guyer-Krumhansl equation [1, 10–12, 29]

$$\tau_1 \frac{d\mathbf{q}}{dt} = -\mathbf{q} - \lambda \nabla T + l^2 \Delta \mathbf{q}, \tag{10}$$

with l the mean-free path of the heat carriers, given by $l^2 = \gamma_{12}\gamma_{21}$ and Δ the Laplacian operator. For very small systems, when $R < l$, the last term becomes dominant over the term in $\mathbf{q}$ and equation (9) is analogous to the Navier-Stokes equation for viscous fluids, with $\mathbf{q}$ playing the role of barycentric velocity $\mathbf{v}$, ∇T th role of ∇p, and l^2/τ_1 the role of kinematic viscosity.

But here we are interested on the full hierarchy (8). The tensors $\mathbf{Q}^{(i)}$ may be interpreted in microscopic terms as higher-order moments of the velocity distribution function. In the case of heat flux $\mathbf{Q}^{(1)}$ would be related to the moment $1/2mC^2\mathbf{C}$, with $\mathbf{C}$ the peculiar molecular velocity, $\mathbf{Q}^{(2)}$ would be proportional to the moment $1/2mC^2\mathbf{CC}$, and $\mathbf{Q}^{(i)}$ to the moment $1/2mC^2\mathbf{C}....^{i-2}...\mathbf{C}$.

A conceptual problem of using the fluxes as independent thermodynamic variables is that, in kinetic theory, the relaxation times of the higher-order fluxes are very similar to each other. In fact, in the relaxation-time approximation, they are all equal to the collision time τ. Therefore, if one takes $\mathbf{q}$ as independent variable, one should take all the higher-order fluxes as independent variables too, because of all them have the same, or similar, values

of the relaxation time. Then, our question is whether the full hierarchy of higher-order variables could be replaced by a relatively simple description with q as the only independent variable, but with renormalized coefficients of the relaxation time and other parameters.

To do so, we go to the time and space Fourier transform of the hierarchy (8), and we express from it the Fourier transform of $\mathbf{q}$ as

$$\mathbf{q}'(\omega, k) = -i\kappa\lambda(\omega, k)T'(\omega, k), \tag{11}$$

with ω and k the frequency and wavevector, respectively, $\mathbf{q}'(\omega, k)$ and $T'(\omega, k)$ the Fourier components of $\mathbf{q}$ and T, and $\lambda(\omega, k)$ an $\omega - k$-dependent generalization for the thermal conductivity. It turns out from the Fourier transform of (8) that $\lambda(\omega, k)$, has the form of a continued-fraction as

$$\lambda(\omega, k) = \lambda_0 / \left[1 + i\omega\tau_1 + l^2k^2/[1 + i\omega\tau_2 + l^2k^2/[1 + i\omega\tau_3 ...]]\right], \tag{12}$$

with λ_0 the usual bulk thermal conductivity. When all τ_i are equal (namely $\tau_1 = \tau_2 = \tau_3 = ... = \tau$, and all l_i are equal (say $l_1 = l_2 = l_3 = ... = l$), expression (11) has a simple asymptotic form, whose consequences we show for steady states and for fast changes.

For steady states ($\omega = 0$) and in systems with a characteristic length L as for instance the radius of nanowires of the thickness of thin layers, and taking $k = 1/L$, this equation yields

$$\lambda(1/L) = 2\lambda_0(L/l)^2 \left[\left(1 + (l/L)^2\right)^{1/2} - 1\right]. \tag{13}$$

This expression describes how the effective thermal conductivity changes as a function of the Knudsen number l/L from the diffusive regime for $l/L << 1$, where collisions amongst particles are dominant and $\lambda(l/L) = \lambda_0$, to the ballistic regime, where collisions with the walls are dominant, for $l/L > 1$, where $\lambda(l/L)$ tends to zero as $\lambda(l/L) = \lambda_0 L/l$.

Had one used expression (9) of the second-order Guyer-Krumhansl equation, one would have found, instead of (12),

$$\lambda(l/L) = \lambda_0/[1 + (l/L)^2]. \tag{14}$$

This also describes a transition of the effective thermal conductivity from $\lambda(l/L) = \lambda_0$, the bulk value corresponding to the collision-dominated regime, to a value $\lambda(l/L)$ which tends to zero for high l/L as $\lambda(l/L) = \lambda_0(L/l)^2$. The linear dependence of λ on l/L for high Knudsen number stemming from (12) fits experimental behavior, whereas the quadratic dependence obtained from (13) is not.

Thus, whereas in a gross qualitative form the Guyer-Krumhansl equation is satisfying, deeper details require the introduction of many higher-order moments, or, alternatively, a slip flow along the wall [1, 10, 11, 29].

Concerning the application of (11) to fast phenomena we calculate the propagation speed V of heat pulses and, from it, we obtain the effective relaxation time for $\mathbf{q}$ including the influence of all the other higher-order fluxes. When the propagation of heat pulses is described by using the Maxwell-Cattaneo-Vernotte equation [(9) with $l = 0$], one obtains $V = (\lambda/\rho c\tau)^{1/2}$, with c the specific heat. When τ tends to 0, i.e. when the Maxwell-Cattaneo-Vernotte equation tends to the Fourier equation, this propagation speed diverges. The finite value of the propagation speed of heat pulses is the main conceptual difference between the classical Fourier theory and the Maxwell-Cattaneo-Vernotte theory. Therefore, the analysis of such a velocity may be useful to identify an effective value for τ in the case than one is using a hierarchy of fluxes.

At the n-th order of approximation of the continued fraction (11), which we denote as $\lambda_n(\omega, k)$, the dispersion equation for heat waves, obtained from $\rho c dT/dt = -\nabla \cdot \mathbf{q}$, is

$$-i\omega = \lambda_n(\omega, k)k^2/\rho c. \tag{15}$$

When all the relaxation times τ_i and all the mean-free paths l_i are equal, the asymptotic expression for $\lambda_n(\omega, k)$ (i.e. for n tending to infinite), has a simple algebraic form and one has

$$i\omega = (\lambda_0/2\rho c l^2)[i\omega\tau + (4l^2k^2 - \omega^2\tau^2)^{1/2}], \tag{16}$$

and the propagation speed turns out to be

$$V^2 = (\lambda_0/\rho c)/[\tau - \rho c l^2/\lambda_0]. \tag{17}$$

The denominator of (16) may be interpreted as the effective relaxation time τ_{eff} including the contribution of all the higher-order fluxes. According to the kinetic energy of monatomic gases in the relaxation-time approximation one has $\lambda_0/\rho c = 5/3(k_B T/m)\tau$ and $l^2 = 3/4(k_B T/m)\tau^2$, with k_B the Boltzmann constant and m the mass of the heat carriers. Thus, $\tau_{eff} = 11/20\tau$, with τ the collision time. When this value is included in the expression $V^2 = (\lambda_0/\rho c\tau_{eff})$ for the propagation speed of heat pulses, it yields a better value than if τ is used [11].

Then, this hierarchy of higher-order tensorial variables with the same relaxation time, leads to an effective relaxation time for the heat flux. Such effective relaxation time renormalizes the contribution of all the higher-order

fluxes and allows an effective Maxwell-Cattaneo-Vernotte equation yielding a better value than the simplest interpretation. Furthermore, in the steady state, it gives a better behavior for the effective thermal conductivity $\lambda(l/L)$ than the Guyer-Krumnhansl equation. These are two examples where a hierarchy of fluxes yields a more accurate result than keeping only the heat flux and its second-order flux.

5 Conclusions

First, we have examined some contributions of thermodynamics of internal variables with different relaxation times to the appreciation of some subtleties of the transition from reversible to irreversible behavior. For a given characteristic observation time, the variables with relaxation times longer than it behave in a reversible way whereas those much shorter than it, behave irreversibly. So, the usual view of a microscopic reversible (mechanical) behavior and a macroscopic irreversible (thermodynamic) behavior becomes richer, and there is a series of successive transitions from reversible to irreversible aspects.

We have pointed out two different kinds of hierarchies of internal variables. In the first one, all the variables are vectorial, and each of them follows a relaxational equation. When the respective relaxation times follow a potential dependence with the order of the internal variable, and under some conditions for the relative number of variables having a same relaxation time, one may replace the full hierarchy by a single internal variable, given by the sum of all the independent contributions but decaying not as a usual exponent, but in a stretched exponential way ((5)).

The second kind of hierarchy is constituted by a set of higher-order fluxes, each of them following an evolution equation of the form ((7)) and having all of them the same relaxation time and the same correlation length. Such a formalism leads to a continued-fraction expansion in the Fourier space, whose asymptotic expression leads, in the steady state, to an effective thermal conductivity depending on the Knudsen number and, for heat pulses, to an effective relaxation time. Such effective expressions are more satisfactory than those obtained by truncating the hierarchy at first or second order.

The vectorial hierarchy could be applied to some cases of magnetic relaxation or dielectric relaxation, whereas the tensorial hierarchy has been applied to heat transport, diffusion and electrical conduction, with special interest on nanosystems, where some characteristic size of the system is comparable or smaller than the carriers's mean-free path [1, 10, 27, 29].

Acknowledgement. I acknowledge the rich influence that have had on my work many years of fruitful collaborations with Sicilian scientists, mainly the following ones: in Messina, Liliana Restuccia and Patrizia Rogolino; in Palermo, Maria Stella Mongiovì, Michele Sciacca and Lidia Saluto; in Catania, Marcello Anile and Vittorio Romano. It has been a pleasure combining science, art, poetry and friendship with them.

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