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HIGHER-ORDER RELAXATION MAGNETIC PHENOMENA AND A HIERARCHY OF FIRST-ORDER RELAXATION VARIABLES

DAVID JOU [a b] AND LILIANA RESTUCCIA [c *]

ABSTRACT. In previous papers one of us (LR) has studied thermodynamic theories for magnetic relaxation phenomena due to several internal variables. In particular, she has obtained equations involving time derivatives of the magnetic field **B** up to the n-th order, and time derivatives of the magnetization **M** up to (n + 1)-th order. Such kind of equations generalize other kinds of physical phenomena, such as stresses τ as a function of small strains ε, and electrical polarizations **P** as a function of the electric field **E**. The aim of the present work is to provide a particular illustration of the theory, relating the mentioned n-th order relaxation equation to a hierarchy of first-order relaxation equations. Though this is only a simple situation, it may be helpful to relate the general equation to the microscopic structure of the system. Furthermore, we study in detail the form of the entropy and its consequences on the hierarchy of relaxation equations.

1. Introduction

The selection of the state space of independent variables is a relevant step in the formulation of nonequilibrium thermodynamics (Meixner and Reik 1959; Prigogine 1961; De Groot and Mazur 1962; Dormann *et al.* 1967; Kluitenberg 1984; Muschik 1989, 1993; Maugin and Muschik 1994; Luzzi *et al.* 1998; Maugin 1999; Luzzi *et al.* 2001; Öttinger 2005; Lebon *et al.* 2008; Jou *et al.* 2010; Min *et al.* 2012; Vignesh *et al.* 2018) and it depends not only on the system but also on the time scales and lenght scales accessible to observation. Here, we illustrate some aspects of this general problem in the concrete case of magnetic relaxation. A theory for magnetic relaxation phenomena was developed by Restuccia and Kluitenberg (1989) (see also Restuccia 2010, 2014) in the framework of thermodynamics of irreversible processes with internal variables (Kluitenberg 1984; Muschik 1989, 1993; Maugin and Muschik 1994; Maugin 1999; Öttinger 2005). It was shown that if n different types of microscopic irreversible phenomena give rise to magnetic relaxation, it is possible to describe these microscopic phenomena introducing n macroscopic axial vectorial internal variables in the expression of the entropy. The total specific magnetization **m** is split in n+1 parts $\mathbf{m}^{(k)}$ $(k = 1, ..., n)$, i.e.

$$\mathbf{m} = \mathbf{m}^{(0)} + \sum_{k=1}^{n} \mathbf{m}^{(k)}. \tag{1}$$

The following set C of independent variables was assumed

$$C = C\left(u, \varepsilon_{\alpha\beta}, \mathbf{m}, \mathbf{m}^{(1)}, ..., \mathbf{m}^{(n)}\right), \tag{2}$$

where u is the specific internal energy and $\varepsilon_{\alpha\beta}$ is the strain tensor. Using the same procedure applied in Meixner and Reik (1959), by eliminating the internal variables the following relaxation equation generalizing Snoek equation was obtained

$$\chi_{BM}^{(0)}\mathbf{B} + \chi_{BM}^{(1)}\frac{d\mathbf{B}}{dt} + ... + \chi_{BM}^{(n-1)}\frac{d^{n-1}\mathbf{B}}{dt^{n-1}} + \frac{d^n\mathbf{B}}{dt^n} =$$

$$\chi_{MB}^{(0)}\mathbf{M} + \chi_{MB}^{(1)}\frac{d\mathbf{M}}{dt} + ... + \chi_{MB}^{(n)}\frac{d^n\mathbf{M}}{dt^n} + \chi_{MB}^{(n+1)}\frac{d^{n+1}\mathbf{M}}{dt^{n+1}}, \tag{3}$$

where $\mathbf{M}$ is the magnetization vector, defined by $\mathbf{M} = \rho\ \mathbf{m}$, with ρ the density mass of the considered body, and $\chi_{BM}^{(m)} \quad (m = 0, 1, ..., n-1)$ and $\chi_{MB}^{(m)} \quad (m = 0, 1, ..., n+1)$ are characteristic phenomenological constants of the particular material, describing the dynamical features of the relation between the time-varying magnetic field $\mathbf{B}$. This magnetic relaxation relation has the same mathematical structure of the following stress-strain relation for mechanical distortional phenomena in isotropic media, derived by Kluitenberg (1968), assuming that n microscopic phenomena give rise to inelastic strains (slip, dislocations, etc.) and the total strain tensor $\varepsilon_{\alpha\beta}$ is split in n+1 parts, $\varepsilon_{\alpha\beta}^{(0)}$ and $\varepsilon_{\alpha\beta}^{(k)}\ (k = 1, ..., n)$,

$$R_{(d)0}^{(\tau)}\tilde{\tau}_{\alpha\beta} + R_{(d)1}^{(\tau)}\frac{d\tilde{\tau}_{\alpha\beta}}{dt} + ... + R_{(d)n-1}^{(\tau)}\frac{d^{n-1}\tilde{\tau}_{\alpha\beta}}{dt^{n-1}} + \frac{d^n\tilde{\tau}_{\alpha\beta}}{dt^n} =$$

$$R_{(d)0}^{(\varepsilon)}\tilde{\varepsilon}_{\alpha\beta} + R_{(d)1}^{(\varepsilon)}\frac{d\tilde{\varepsilon}_{\alpha\beta}}{dt} + ... + R_{(d)n}^{(\varepsilon)}\frac{d^n\tilde{\varepsilon}_{\alpha\beta}}{dt^n} + R_{(d)n+1}^{(\varepsilon)}\frac{d^{n+1}\tilde{\varepsilon}_{\alpha\beta}}{dt^{n+1}}. \tag{4}$$

$R_{(d)m}^{(\tau)}\ (m = 0, 1, ..., n-1)$, $R_{(d)m}^{(\varepsilon)}\ (m = 0, 1, ..., n+1)$ are material constants and $\tilde{\tau}_{\alpha\beta}$ and $\tilde{\varepsilon}_{\alpha\beta}$ are the deviators of the stress tensor and of the strain tensor, respectively.

If n arbitrary microscopic phenomena give rise to the total polarization vector, by introducing n partial polarization vectors as n macroscopic vectorial internal variables in the expression of the entropy, the following dielectric relaxation equation was obtained by Restuccia and Kluitenberg (1988) in the isotropic case (see also Kluitenberg 1973, 1977, 1981; Restuccia and Kluitenberg 1990)

$$\chi_{EP}^{(0)}\mathbf{E} + \chi_{EP}^{(1)}\frac{d\mathbf{E}}{dt} + ... + \chi_{EP}^{(n-1)}\frac{d^{n-1}\mathbf{E}}{dt^{n-1}} + \frac{d^n\mathbf{E}}{dt^n} =$$

$$\chi_{PE}^{(0)}\mathbf{P} + \chi_{PE}^{(1)}\frac{d\mathbf{P}}{dt} + ... + \chi_{PE}^{(n)}\frac{d^n\mathbf{P}}{dt^n} + \chi_{PE}^{(n+1)}\frac{d^{n+1}\mathbf{P}}{dt^{n+1}}, \tag{5}$$

where $\mathbf{E}$ and $\mathbf{P}$ are the electric strength field and the polarization vector, respectively, and $\chi_{EP}^{(k)}\ (k = 0, 1, ..., n-1)$ and $\chi_{PE}^{(k)}(k = 0, 1, ..., n+1)$ are constant quantities.

The aim of the present work is to relate the n-th order relaxation equation (1) (involving time derivatives of the magnetic field $\mathbf{B}$ up to the n-th order, and time derivatives of the magnetization $\mathbf{M}$ up to (n + 1)-th order) to a hierarchy of first-order relaxation equations. In this way we relate the general equation to the microscopic structure of the system.

From the practical point of view, such general equations are necessary in view of the wide diversity of materials involving clusters of atoms in a macromolecule, as clusters of molecules, as aggregating magneto-particles, in a material.

The new techniques in nanotechnology and the possibilities of faster measurements have made possible the detailed experimental analysis of both the dynamical and the structural aspects of these physical phenomena.

Finally, we obtain the form of the entropy and its consequences on the hierarchy of relaxation equations. We try the paper to be as simple and pedagogical as possible, with a minimum of physical complexity related to the mathematical structure of the equations.

2. Description of the model: a dynamical hierarchy

In the model to be considered we focus our attention on a magnetic system composed of n sets of spins $(i = 1, 2, ..., n)$, such that there are $N^{(i)}$ magnetic particles of the kind i, each of them having mass m_i, radius r_i, spin S_i, and so on. These spins may refer to nuclear spins, molecular spins, nanoparticle spins as molecular aggregate spins, with different masses, which imply different relaxation times. Thus, their inertia, relaxation time, magnetization and susceptibility will be different for each set of particles. These differences will show up especially in dynamical phenomena.

Here, we will discuss a simple situation in which the time scales, τ_i $(i = 1, 2, ..., n)$, of the several variables $\mathbf{M}^{(i)}$, the magnetizations of the i-th set, are sufficiently separated to be considered as a hierarchy of equations with minimal couplings amongst them. We propose the following hierarchy of dynamical equations

$$\frac{d\mathbf{M}^{(1)}}{dt} + \frac{1}{\tau_1}\,\mathbf{M}^{(1)} = \frac{\chi_1}{\tau_1}\,\mathbf{B} + \beta_1\,\mathbf{M}^{(2)},$$

$$\frac{d\mathbf{M}^{(2)}}{dt} + \frac{1}{\tau_2}\,\mathbf{M}^{(2)} = \frac{\chi_2}{\tau_2}\,\mathbf{B} + \gamma_1\,\mathbf{M}^{(1)} + \beta_2\,\mathbf{M}^{(3)},$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\frac{d\mathbf{M}^{(i)}}{dt} + \frac{1}{\tau_i}\,\mathbf{M}^{(i)} = \frac{\chi_i}{\tau_i}\,\mathbf{B} + \gamma_{(i-1)}\,\mathbf{M}^{(i-1)} + \beta_i\,\mathbf{M}^{(i+1)},$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\frac{d\mathbf{M}^{(n)}}{dt} + \frac{1}{\tau_n}\,\mathbf{M}^{(n)} = \frac{\chi_n}{\tau_n}\,\mathbf{B} + \gamma_{(n-1)}\,\mathbf{M}^{(n-1)}. \tag{6}$$

We have assumed that $\tau_1 > \tau_2 > \tau_3 > ... > \tau_n$. We will denote $\frac{\chi_i}{2\,\chi_{(i-1)}\,\tau_i} \equiv \gamma_i$. In these equations χ_i is the magnetic susceptibility of particles i, τ_i the magnetic relaxation time, β_i a coefficient that couples variables i and i + 1, and γ_i a coefficient coupling variables i to $i-1$. This coupling may be physically realized, for instance, through the magnetization of the slower of the couple of the variables i and $i-1$, namely $i-1$, which adds to the external applied magnetic field $\mathbf{B}$ acting on $\mathbf{M}^{(i)}$. Since $\mathbf{M}^{(i-1)}$ is much slower than $\mathbf{M}^{(i)}$, the value of $\mathbf{M}^{(i-1)}$ will not appreciably change during the relaxation of $\mathbf{M}^{(i)}$. On the other side, since $\mathbf{M}^{(i+1)}$ is much faster than $\mathbf{M}^{(i)}$, $\mathbf{M}^{(i+1)}$ will relax in a very short time and will also keep practically constant in its final relaxed value during the relaxation on $\mathbf{M}^{(i)}$.

Differentiating equation $(6)_1$, using $(6)_2$ for the time derivative of $\mathbf{M}^{(2)}$, and using $(6)_1$ to express $\mathbf{M}^{(2)}$ in terms of $\mathbf{M}^{(1)}$, $\frac{d\mathbf{M}^{(1)}}{dt}$ and $\mathbf{B}$, one gets

$$\frac{d^2\mathbf{M}^{(1)}}{dt^2} + \xi_M^{(11)}\,\frac{d\mathbf{M}^{(1)}}{dt} + \xi_M^{(01)}\,\mathbf{M}^{(1)} = \xi_B^{(11)}\,\frac{d\mathbf{B}}{dt} + \xi_B^{(01)}\,\mathbf{B} + \beta_1\,\beta_2\,\mathbf{M}^{(3)},$$

with the coefficients

$$\xi_M^{(11)} \equiv \frac{1}{\tau_1} + \frac{1}{\tau_2},$$

$$\xi_M^{(01)} \equiv \frac{1}{\tau_1\tau_2} - \beta_1\gamma_1,$$

$$\xi_M^{(11)} \equiv \frac{\chi_1}{\tau_1},$$

$$\xi_B^{(01)} \equiv \frac{\chi_1}{\tau_1\tau_2} + \beta_1\frac{\chi_2}{\tau_2}. \tag{7}$$

We now differentiate equation $(7)_1$, use the corresponding evolution equation of hierarchy (6) for $\frac{d\mathbf{M}^{(3)}}{dt}$, and use $(6)_1$ and $(6)_2$ to express $\mathbf{M}^{(2)}$ and $\mathbf{M}^{(3)}$ in terms of $\mathbf{M}^{(1)}$, $\frac{d\mathbf{M}^{(1)}}{dt}$ and $\mathbf{B}$, and we get

$$\frac{d^3\mathbf{M}^{(1)}}{dt^3} + \xi_M^{(22)}\,\frac{d^2\mathbf{M}^{(1)}}{dt^2} + \xi_M^{(12)}\,\frac{d\mathbf{M}^{(1)}}{dt} + \xi_M^{(02)}\,\mathbf{M}^{(1)} =$$

$$\xi_B^{(22)}\,\frac{d^2\mathbf{B}}{dt^2} + \xi_B^{(12)}\,\frac{d\mathbf{B}}{dt} + \xi_B^{(02)}\,\mathbf{B} + \beta_1\beta_2\beta_3\,\mathbf{M}^{(4)}. \tag{8}$$

Note that $\xi_M^{(ab)}$ is the coefficient multiplying the a-th derivative of $\mathbf{M}^{(1)}$ in the equation corresponding to the b-th order of approximation, and analogously for $\xi_B^{(ab)}$, but for the a-th derivative of the magnetic field $\mathbf{B}$. The corresponding coefficients are given by

$$\xi_M^{(22)} \equiv \xi_M^{(11)} + \frac{1}{\tau_3},$$

$$\xi_M^{(12)} \equiv \xi_M^{(01)} + \gamma_2\beta_2 + \frac{1}{\tau_1\tau_3} + \frac{1}{\tau_2\tau_3},$$

$$\xi_M^{(02)} \equiv \frac{\gamma_2\beta_2}{\tau_1} + \frac{1}{\tau_1\tau_2\tau_3},$$

$$\xi_B^{(22)} \equiv \xi_B^{(11)},$$

$$\xi_B^{(12)} \equiv \xi_B^{(01)} + \frac{\chi_1}{\tau_1\tau_3},$$

$$\xi_B^{(02)} \equiv \frac{\gamma_2\beta_2\chi_1}{\tau_1} + \frac{\beta_1\beta_2\chi_3}{\tau_3} + \frac{\chi_1}{\tau_1\tau_2\tau_3}. \tag{9}$$

In principle, one may obtain a series of recurrence relations for the coefficients corresponding to higher-order equations. Here, we stop our calculations, which become increasingly lengthy and cumbersome, as they already illustrate the basic concept that hierarchy (6) may be written in the form of higher-order relation equation of the form we are considering. It is also useful to express the hierarchy (6) in the Fourier space, in order to

study the frequency-dependent behaviour of the system, which is more easily observable than its time evolution. This leads to the hierarchy

$$(1+i\omega\tau_i)\tilde{\mathbf{M}}^{(i)} + \gamma_i\,\tilde{\mathbf{M}}^{(i-1)} + \beta_i\,\tilde{\mathbf{M}}^{(i+1)} = \tilde{\mathbf{M}}^{(i)}(\omega) + \chi_i\,\mathbf{B}. \tag{10}$$

From here, for instance, an effective frequency-dependent susceptibility $\chi(\omega)$ may be obtained, having the structure of a continued-fraction expansion, which is a well-known and powerful mathematical technique with an underlying physical basis for the description of many physical quantities, as for instance time-correlation functions, and transport coefficients (Mori 1965; Nagano *et al.* 1980; Madureira *et al.* 1998; Alvarez and Jou 2007).

3. Thermodynamic formalisms

The hierarchy (6) is relatively intuitive. When $\frac{d\mathbf{M}^{(i)}}{dt}=0$ (steady state) and for vanishing couplings of the variables of different orders, the sum of the equations yields $\mathbf{M}=\chi\mathbf{B}$, with $\mathbf{M}$ being the total magnetization (the sum of all $\mathbf{M}^{(i)}$), and χ being the sum of the several magnetic susceptibilities. The terms in the temporal derivatives $\frac{d\mathbf{M}^{(i)}}{dt}$ are classical in relaxation theory; the terms in β_i and γ_i establish a connection between $\mathbf{M}^{(i)}$ and the slow magnetization $\mathbf{M}^{(i+1)}$ and the fast magnetization $\mathbf{M}^{(i-1)}$. Here, we want to reexamine the hierarchy (6) from a thermodynamic perspective, by illustrating the informations obtained from the second law of thermodynamics. We consider that the entropy S of the system is a function of internal energy U, volume V, and all the $\mathbf{M}^{(i)}$, which are independent variables. Thus, we assume

$$S = S\left(U, V, \mathbf{M}^{(1)}, \mathbf{M}^{(2)}, ..., \mathbf{M}^{(n)}\right). \tag{11}$$

Though we have written the volume V, for the sake of formal completeness, we will not consider here effects related to the change of volume, because we are interested on other physical aspects. We will consider that the entropy s per unit mass has the form

$$\rho s = \rho u - \alpha_1\mathbf{M}^{(1)}\cdot\left[\mathbf{M}^{(1)}-\alpha_{1,2}\mathbf{M}^{(2)}\right] - \alpha_2\mathbf{M}^{(2)}\cdot\left[\mathbf{M}^{(2)}-\alpha_{2,3}\mathbf{M}^{(3)}\right] - ...$$

$$- \alpha_i\mathbf{M}^{(i)}\cdot\left[\mathbf{M}^{(i)}-\alpha_{i,i+1}\mathbf{M}^{(i+1)}\right] - ... - \alpha_n\mathbf{M}^{(n)}. \tag{12}$$

The terms in $\mathbf{M}^{(i)}\cdot\mathbf{M}^{(i)}$ are obvious; besides them, we have also included couplings between i and $i+1$, as it has been done in the dynamical hierarchy (6). When one takes into account that $\rho\,du/dt = \mathbf{B}\cdot(d\mathbf{M}/dt)$ one has

$$\rho\frac{ds}{dt} = \frac{d\mathbf{M}^{(1)}}{dt}\cdot\left[\theta^{-1}\mathbf{B} - 2\,\alpha_1\mathbf{M}^{(1)} - \alpha_1\alpha_2\mathbf{M}^{(2)}\right] +$$

$$\frac{d\mathbf{M}^{(2)}}{dt}\cdot\left[\theta^{-1}\mathbf{B} - 2\,\alpha_2\mathbf{M}^{(2)} - \alpha_1\mathbf{M}^{(1)} - \alpha_2\alpha_{2,3}\mathbf{M}^{(3)}\right] + ...$$

$$+\frac{d\mathbf{M}^{(i)}}{dt}\cdot\left[\theta^{-1}\mathbf{B} - 2\alpha_{i+1}\mathbf{M}^{(i+1)} - \alpha_i\mathbf{M}^{(i)} - \alpha_i\alpha_{i,i+1}\mathbf{M}^{(i+1)}\right] + ...$$

$$+\frac{d\mathbf{M}^{(n)}}{dt}\cdot\left[\theta^{-1}\mathbf{B} - \alpha_n\mathbf{M}^{(n)}\right]. \tag{13}$$

From here, in the linear approximation, between fluxes $\frac{d\mathbf{M}^{(i)}}{dt}$ and their corresponding conjugate thermodynamic forces according to (13), follow evolution equations of the form

$$\frac{d\mathbf{M}^{(i)}}{dt} = k_i \left[\theta^{-1}\mathbf{B} - 2\,\alpha_i \mathbf{M}^{(i)} - \alpha_{i-1}\,\mathbf{M}^{(i-1)} - \alpha_i\,\alpha_{i,\,i+1}\mathbf{M}^{(i+1)} \right], \tag{14}$$

with k_i positive material constants. Note that further terms coupling $\frac{d\mathbf{M}^{(i)}}{dt}$ to the forces conjugate to $\frac{d\mathbf{M}^{(i)}}{dt}$ could have also been considered. These laws have the form of the hierarchy (6), provided the following identifications are made

$$k_i \equiv \frac{\chi_i\,\theta}{\tau_i}, \quad \alpha \equiv \frac{1}{2\,\chi_i\,\theta}, \quad \alpha_{i,\,i+1} \equiv -2\,\tau_i\,\beta_i. \tag{15}$$

This leads to

$$\frac{d\mathbf{M}^{(i)}}{dt} + \frac{1}{\tau_i}\,\mathbf{M}^{(i)} = \frac{\chi_i}{\tau_i}\,\mathbf{B} - \frac{\chi_i}{2\,\chi_{i-1}\tau_i}\,\mathbf{M}^{(i-1)} + \beta_i\,\mathbf{M}^{(i+1)}, \tag{16}$$

which is indeed the general form (6) characterizing the hierarchy of equations (6). We see that the thermodynamic requirements lead to equation (16) - namely, $(6)_3$ -. Otherwise, one could have taken as zero the coefficient $\gamma_i \equiv \chi_i/(2\,\chi_{i-1}\tau_{i-1})$. A further information given by non-equilibrium thermodynamics stems from the Onsager-Casimir reciprocity relations. By writing, for instance,

$$\frac{d\mathbf{M}^{(1)}}{dt} = -\frac{1}{\tau_1}\,\mathbf{M}^{(1)} + \beta_1\,\mathbf{M}^{(2)}, \tag{17}$$

$$\frac{d\mathbf{M}^{(2)}}{dt} = \gamma_1\,\mathbf{M}^{(1)} - \frac{1}{\tau_2}\,\mathbf{M}^{(2)}, \tag{18}$$

it follows that $\beta_1 = \gamma_1$.

4. Conclusions

We have presented a hierarchy of n first-order relaxation equations (6) for variables $\mathbf{M}^{(1)}$, $\mathbf{M}^{(2)}, ..., \mathbf{M}^{(i)}, ..., \mathbf{M}^{(n)}$, leading to an n-th order relaxation equation for the evolution of $\mathbf{M}^{(1)}$ as a function of the time derivatives of $\mathbf{B}$ in (8). The different variables have been assumed to describe the contribution of particles of different masses (and therefore different inertia) to the magnetization of the system. Here, we have ordered the $\mathbf{M}^{(i)}$ according to decreasing relaxation times, namely $\tau_1 > \tau_2 > ... > \tau_n$ (for instance, one could consider a power law distribution of the relaxation times as $\tau_i = \tau_n r^{(n-i)}$, with r a number $r > 1$). The observed dynamics of the system will depend on the range of observable times. If, for instance, the observational times are such that $t_{obs} > \tau_3$, the description of the system will be based on $\mathbf{M}^{(1)}$, $\mathbf{M}^{(2)}$ and $\mathbf{M}^{(3)}$. In this case, the relaxation of the remaining variables $\mathbf{M}^{(4)}$, $\mathbf{M}^{(5)}, ..., \mathbf{M}^{(n)}$ will be too fast to be observable and they will act as a Markovian noise in the equations for $\mathbf{M}^{(1)}$, $\mathbf{M}^{(2)}$ and $\mathbf{M}^{(3)}$.

We have outlined that non-equilibrium thermodynamics yields non-trivial information on the coupling terms between variables i and $i-1$ and $i+1$ in the equations of state (12). These information could be wider if we had assumed couplings between a wider range of variables, as for instance $i-2$, $i-1$, i, $i+1$, $i+2$ in (12). The range of couplings amongst

the variables will depend on the separation of their corresponding time scales: if they are sufficiently separated, only the next-neighbouring variables in the hierarchy will be coupled. Note that the generalized relaxation equation (3) comes from the dynamical hierarchy (13), but the reciprocal is not true. The latter may be useful as a particular model from which (13) may be obtained. Let us, eventually, note that one could generalize the hierarchy proposed here by incorporating non-local terms, which would be useful to describe the different ranges of spatial separation of different kinds of particles.

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[a] Universitat Autònoma de Barcelona,
Departament de Física, Grup de Física Estadistica,
08193 Bellaterra, Catalonia, Spain

[b] Institut d'Estudis Catalans
Carme 47, Barcelona 08001,
Catalonia, Spain

[c] Università degli Studi di Messina
Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra
Viale F.S. D'Alcontres, 31, 98166 Messina, Italy

[*] To whom correspondence should be addressed | email: lrestuccia@unime.it

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