Hysteresis in nonequilibrium steady states: the role of dissipative couplings

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In this work we analyzed one of the simplest mathematical models dealing with hysteretic behaviour, the Preisach model and re-interpreted it from the stand point of the extended theory of irreversible thermodynamics in order to develop a more physically sound explanation of the phenomena resting on the essential role of non-equilibrium couplings in hysteretic systems and relating the experimental observation of hysteresis with the ratio of relaxation times of the various irreversible processes in the system.

Keywords: Non-equilibrium coupling; hysteresis; dissipative phenomena; relaxation times

En este trabajo analizamos uno de los modelos matemáticos más simples para describir el comportamiento conocido como histéresis: el modelo de Preisach. Este modelo es reinterpretado desde el punto de vista de la teoría extendida de la termodinámica de procesos irreversibles, con el fin de desarrollar una descripción físicamente mejor fundada de tales fenómenos. Este análisis está basado en el papel esencial de los acoplamientos fuera de equilibrio en sistemas con histeresis y relaciona la observación experimental de la histéresis con la razón entre los tiempos de relajación para los diferentes procesos irreversibles en el sistema.

Descritores: Acoplamientos fuera de equilibrio; histéresis; fenómenos disipativos; tiempos de relajación

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To Professor Leopoldo García-Colín Scherer with deepest appreciation because after him, our paths will never be the same.

1. Introduction

The presence of hysteresis and thermal relaxation together is a common situation in physical systems characterized by metastable energy landscapes (magnetic hysteresis, plastic deformation, superconducting hysteresis, incongruent phase growth in solids), and their interpretation still represents a challenge to nonequilibrium thermodynamics. It must be realized that a hysteretic system is governed by intrinsically out of equilibrium, history dependent constitutive laws, so that the local equilibrium hypothesis of linear irreversible thermodynamics has to be abandoned. Hysteresis is an ubiquitous phenomenon exhibited by systems of very different nature [1]. Macroscopically, hysteresis shows up as a lag in the response to an external driving, accompanied by a dependence on previous history and by energy dissipation. From a microscopic point of view, hysteresis reflects the presence of multiple metastable configurations accessible to the system. Thermodynamic approaches to hysteresis have been attempted by several authors [2], but no conclusive results have been reached yet. The main difficulty is that a hysteretic transformation, no matter how slow is the variation of the external driving force, is characterized by a certain proportion between the energy reversibly stored or released by the system and the energy irreversibly dissipated as heat because of hysteresis losses, and we have no general principles helping us to separate these two energy contributions. Of course, nonequilibrium thermodynamics has been applied with success to a number of situations, such as chemical reactions or transport phenomena, where suitable relationships between irreversible flows and thermodynamic forces can be assumed. It is not so for hysteresis phenomena, where irreversibility arises from the nonlinear and branching character of the system constitutive laws and hence it is necessary an extended thermodynamical theory to take these features into account [3–5].

On general grounds, hysteresis is the consequence of the existence of many metastable free energy minima. These metastable states are the result of the coupling of characteristic structural features (such as magnetic domain walls in ferromagnets, dislocations in mechanical systems, Abrikosov vortices in type-II superconductors, internal stresses in incongruent phase growth phenomena in solid matrices, etc.) among themselves or with environmental disorder, so that when the system is not able to reach thermodynamic equilibrium during the observational (experimental) time, the system will remain in temporary local minima of its free energy, and its response to external noise will become history dependent (e.g. represented by a non-markovian partition function). On the other hand, the fact that the system is not in equilibrium makes it spontaneously approach equilibrium, and this will give rise to relaxation effects even if no external perturbation is applied to the system and these in turn could interact via dissipative couplings according to their specific ratio of relaxation times. Hence fluctuation-dissipation phenomena are responsible for the observed hysteretic behaviour.

In the last few years, much of the attention on hysteresis has focused on dynamic effects, arising from a competition between the time scale for relaxation from a nonequilibrium state and the time scale of the driving force [6]. Interestingly, however, many systems display hysteresis even when they are driven exceedingly slowly. Examples can be found in all branches of physics. It is only recently that this so-called quasistatic hysteresis in these systems has been associated with the presence of disorder. Disordered systems present a
complex free energy landscape in configuration space, with multiple local minima separated by large energy barriers. The barriers are so large compared to thermal fluctuations that these systems, on practical time scales, remain trapped in a metastable configuration. They move from one local minimum to another only when the motion is driven by an external field. This motion takes place very far from equilibrium and gives rise to avalanches of the system response, which are found to distribute in a very wide range of sizes. The actual state of the system depends on its overall previous history which often gives rise to striking memory properties. In spite of its fundamental interest and technological relevance, a general analysis of the energy balance in these quasistatic hysteretic processes is not yet available. The main difficulties lie in:

1. The multiplicity of metastable configurations available.
2. The dependence of the current state of the system on its previous history.
3. The intrinsically dissipative character of the evolution.

In condensed matter, hysteresis often accompanies a phase transition, which by nature results from the cooperative effect of a large number of degrees of freedom. This has recently led some authors to analyze it by means of Langevin type [7] or master equations [8] with infinitely many degrees of freedom, and to propose various scaling laws for the area of the hysteresis loop. A mean field treatment of this problem [9] reduces it to an ordinary differential equation for the order parameter, with some slowly time dependent external parameter such as the magnetic field. Noise can be incorporated into the problem. Similar equations appear naturally to describe mechanical or electrical systems, as well as lasers [10]. Hysteresis effects may appear if the equilibria of the dynamical system with a static parameter undergo a bifurcation, and scaling laws have also been found in this case [11, 12]. Hence an extended thermodynamical theory whose potentials are generalized homogeneous functions of its natural variables [13] results the best scenario for a consistent phenomenological description.

2. Dynamic models of hysteresis

The theory of hysteresis operators developed in the past years has proved to be a powerful tool for solving mathematical problems in various branches of physics and chemistry with applications such as solid mechanics, material fatigue, ferromagnetism, phase transitions, and many others. On the other hand, the nonconvex free energy functionals (typically, double-well potentials) usually considered in phase-field models may induce hysteresis effects by themselves; however, they are by far too simplistic to give a correct account of the complicated loopings due to the storage and deletion of internal memory that are observed in thermoplastic materials or ferro-magnets. Therefore, there is certainly a deficiency in present phase-field theories [14, 15] and a need for a theory involving irreversible hysteresis operators (incidentally, as quoted by Krejci [15], the ancient Greek word “hysteresis” just means “deficiency” or “need”!). An additional motivation comes from the fact that hysteresis operators also arise quite naturally already in simple classical phase-field models [14, 15].

One of the very firsts mathematical models developed in order to explain, at least qualitatively, hysteresis was proposed by Preisach [16] in the context of magnetic hysteresis. More recently a modern mathematical reinterpretation of Preisach’s model is due to Mayrergoyz [17]. Mayrergoyz’s treatment if very simple and general lacks of some fundamental issues of the physical phenomena of hysteresis. Mayrergoyz’s model introduced the concept of static hysteresis in a general mathematical framework where “...the past exerts its influence upon the future through instantaneous values of output...” [17]. This assertion is physically hard to sustain as instantaneous here means that the propagation velocity of a perturbation is infinite, which violates the soft principle of causality [18] and thus gives rise to unphysical parabolic transport equations. Then the hysteresis operators defined arise in a physically untenable way since the general problem prescribed by its statistics map to a generalized one-dimensional random walk (with step size [1], up or down) with gaussian measure that characterize an equilibrium system. This fact goes straight to the physical limitations of such simple models. Nevertheless such model points out the very important issue of hysteresis as an energy-driven process in a transparent way so one is tempted to preserve its structure and put it in an irreversible thermodynamics framework. The main equation of Mayrergoyz’s (cf Eq. (1) of [17]) model is

\[ f(t) = \hat{\Gamma} u(t) = \int_{\alpha \geq \beta} \mu(\alpha, \beta) \tilde{\gamma}_{\alpha,\beta} u(t)\, d\alpha d\beta. \] (1)

With \( u(t) \), a time dependent field (or input), \( f(t) \), the response (or output) and \( \mu(\alpha, \beta) \) an hysteresis operator depending on discrete time-steps \( \alpha, \beta \). We propose a physical interpretation of this equation from the point of view of the physical theory of stochastic processes [19, 13].

The effect of an ensemble of time dependent fields (labeled \( j = 1, 2, \ldots \)) in a non markovian approximation is given (in the case of several scalar outputs) by

\[ \mathcal{F}(t) = \sum_j \int_{-\infty}^{t} \hat{L}_{i,j}(t - t') \odot \tilde{U}_j(t')\, dt'. \] (2)

Here \( \mathcal{F}(t) \) is a nonequilibrium output, \( \hat{L}_{i,j} \) are time propagation operators (memory kernels), for several processes \( i, j = 1, 2, \ldots \); \( \tilde{U}_j \) are time-dependent applied fields, and \( \odot \) is the most general scalar product in field’s space [20]. As we see, the propagators \( \hat{L} \) play roles very similar to Mayrergoyz’s weighted hysteresis operator \( \mu(\alpha, \beta) \tilde{\gamma}_{\alpha,\beta} \) but instead of discreticize the process in equilibrium time steps take the whole time dependent irreversible dynamics of the system. Their physical meaning will be made clear in the next paragraph.
In the linear approximation we could write down Green function kernels, that up to first order gives [21, 23]

\[
\mathcal{F}_{\xi}(t) = \sum_{j} \int_{-\infty}^{t} \lambda_{\xi,j} \theta^{t-t'} \tilde{x}_{j} \odot \tilde{U}_{j}(t') \, dt'.
\] (3)

In this equation \(\lambda_{\xi,j}\) are amplitudes of perturbation, that is quantities related to how much energy was involved in the processes. \(\tau_{\xi,j}\) are macroscopic relaxation times of the system to such processes, a measure of how fast the processes occurred, and \(\tilde{x}_{j}\) are unit-vectors in the direction of the associated thermodynamic flow. The physical meaning of the product of the amplitudes with the exponential term, that is, the linear perturbation expression of \(\mathcal{F}\) is then that of a potential energy that could be easily related to chemical potentials, indirectly measurable by experiments.

\[ N = - \oint \frac{dQ}{T} \geq 0 \iff \oint \frac{dQ}{T} + \oint dN = 0 = \oint d\Psi, \] (4)

where \(N\) is the uncompensated heat. The last equation in terms defines the existence of a function \(\Psi\), whose 1-form is an exact differential. If the process is reversible we note that in the reversible limit of the compensation function \(\Psi\) is just Clausius’ entropy. This clarifies the physical meaning of the function \(\Psi\), because in equilibrium (i.e. all segments of the cycle are reversible) this function reduce to Clausius’ entropy [3].

A local field expression will be more useful [5], hence

\[
\frac{d\Psi}{dt} = \int_{V} \left[ \frac{\partial \Psi}{\partial t} + \nabla \cdot (\tilde{u}_\rho \Psi) \right] dV,
\]
\[
\frac{dN}{dt} = \int_{V} \rho \sigma_{ne} dV, \] (5)
\[
\rho \frac{d\Psi}{dt} = -\nabla \cdot \left( \frac{Q^C}{T} \right) + \rho \sigma_{ne}^{\dagger}. \] (6)

The physical meaning of \(\sigma_{ne}^{\dagger}\) is that of the local rate of uncompensated heat production, and is not to be confused with the so-called entropy production except in cases where local equilibrium conditions hold. Entropy is well-defined just in reversible segments of the cycle. We then define the densities or local quantities as usual, noting that the local form of the second law of thermodynamics, namely \(\rho \sigma_{ne}^{\dagger}\) imposes conditions on the evolution of the local densities. In order to make explicit these conditions one defines the heat flux \(J^C\) and the uncompensated heat production \(\sigma_{ne}\) as follows

\[
J^C = \frac{Q^C}{T} = \sum_{a} \frac{\tilde{Q}_{a}}{T} = \sum_{a} \tilde{Q}_{a} - \mu_{a} \tilde{T}_{a} + \ldots, \] (7)
\[
\sigma_{ne} = -T^{-1} \sum_{a} (\mathcal{P}_a - \mu_{a} \delta) : \nabla \tilde{u} + \tilde{Q}_{a} \cdot \nabla \ln T
\]
\[
- T^{-1} \sum_{a} \tilde{J}_{a} \cdot (\nabla \mu_{a} - \mathcal{F}_{ext,a}) + \ldots \geq 0. \] (8)

According to this stochastic thermodynamical theory the output is related with the actual input via dynamic propagation operators of irreversible nature. These operators are then associated with dissipation and thus are characterized by relaxation times. We will see later that the experimental observation of hysteresis depends on the ratio of this relaxation time with the relaxation time associated with the kinetic mechanism of the associated irreversible processes.

### 3. Thermodynamic formalism

The aforementioned problem could be traced off to its roots by means of a thermodynamical analysis, as follows [3, 5, 24–30]. According to Clausius [31] the total amount of heat dissipated in a cycle process is given by

\[
d_{\Psi} = \frac{d_{\mathcal{E}} + p d_{v} - \sum_{a} \mu_{a} d_{C_{a}} - \sum_{a} \mathcal{X}_{a} \cdot d_{\mathcal{P}_{a}} + \ldots}{T}, \] (9)

where \(T^{-1}\) is an integrant factor for the 1-differential form related to \(\Psi\) [32].

We see that Eq. (9) is nothing but the formal extension of the celebrated Gibbs equation of equilibrium thermodynamics for the case of a multicomponent nonequilibrium system in the presence of irreversible processes. This extended Gibbs relation is brought about by in the theory by imposition of some consistency conditions on the nonequilibrium part of the distribution function. These conditions are based on the principle of material independence and tensorial homogeneity plus the integrability conditions [33] that turned out to be generalized forms of the Maxwell relations of equilibrium thermodynamics [5]. According to this measure a steady state
of lower entropy production is more favorable. This is nothing but the Prigogine theorem of minimal entropy production that will be in the core of the following discussion.

Given these facts the Prigogine theorem states imposes stability conditions on Eq. (9), namely that a nonequilibrium steady state is characterized by a constant value of $d \Psi^l \tau$ (or equivalently a constant value of $\sigma_{\text{occ}}$), the equilibrium state being the steady state with zero uncompensated heat production. So if one of the terms in Eq. (9) say the stress contribution changes it must be a change in another term, say the concentration gradient in order to ensure that continuity of $\Psi^l \tau$ will lead the system to an steady state or will maintain the stability of the system in this steady state. There is a strong experimental evidence supporting this claim [2].

In order to make an explicit analysis of relaxation times and their relation with the experimental observation of hysteresis. Let us consider again the linear non-markovian expression for the output $F_i(t)$. We define its stochastic time derivative (in the case of processes having long term memory due to an intrinsic stochastic evolution, and thus involving some kind of feedback it is known to be formally incorrect to take the limit $\Delta t \to 0$ in order to perform a time derivative, since the dynamic evolution takes place in finite time steps. An interesting discussion could be found in [22]. So we have to calculate time derivatives taking this into account. In the present case the best option is the use of stochastic Itô-type differentiation) [34, 35] with a proper time $T$ as:

$$\frac{d F_i(t)}{dT} = \sum_j \lambda_{i,j} e^{\frac{T}{\tau_{i,j}}} \overline{U_j(t')}.$$  \hspace{1cm} (10)

Then we recognize that in the thermodynamic limit $d F_i(t)/dT \approx F_i$ which is also given by some constitutive equations and this in turns gives a relation for the relaxation time $\tau_{i,j}$ in terms of the proper time $T$

$$\tau_{i,j} = \frac{T}{\ln \left( \frac{\overline{F_i(t')} - \sum_{j \neq k} \lambda_{i,j} e^{\frac{T}{\tau_{i,j}}} \overline{U_j(t')} \left| \overline{U_k(t')} \right|}{\lambda_{i,k} \overline{U_k(t')}} \right)}.$$  \hspace{1cm} (11)

If we identify this stochastic proper time $T$ with the observation time, we note that the ratio of relaxation times to observation time $\tau_{i,j}/T$ depends on system specific properties. It is just this fact what makes that for some systems it is possible to experimentally observe hysteresis while for other processes it is not. If the ratio of relaxation to observation times is closer to unity then hysteresis shows up as a manifestation of this dynamical coupling. This range is the one in which hysteresis shows up experimentally, for if we look at very short relaxation times (of the order of few collision times) the process is of a microscopic character (hence the low value of the uncompensated heat production) thus we cannot observe hysteresis and also if we look up for processes with a very high value of $\Gamma$ the relaxation time approaches zero and we are in a non-stationary situation in which all relaxation modes mix so we again cannot experimentally see

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**4. Working example: solid-gas absorption hysteresis loops in metal hydrides**

Hysteresis in solid-gas systems is commonly associated with the existence of two empiric quasistatic states for the external constraints (v.g. temperature and/or composition). During the gas absorption process, the measured chemical potential (which in macroscopic isothermal conditions depends on the gas partial pressure) is higher than that observed in the desorption process. In Fig. 1 we show a schematic representation of this hysteresis process.

It is frequent to find hysteresis in solid-gas systems for which a phase transformation occurs. We briefly describe how the phenomena of hysteresis as showed in the case of the absorption-desorption loops of a gas in a solid could be well understood in the context of an extended irreversible thermodynamic formalism and that such phenomena are consequence of the existence of dissipative internal processes (mainly stress release) within the solid matrix.

Let us consider, a metal-hydrogen system as some of these systems show huge hysteresis loops at room temperature and moderated hydrogen pressures (around 1–10 bar). We then consider a physical system containing some amount of a prototype hydride as LaNi$_5$H$_6$ whose kinetic behavior is characterized by the Johnson-Mehl-Avrami kinetic law [36, 37].

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**Figure 1.** Schematic absorption (——) and desorption (- - -) for an idealized solid-gas system showing a phase transformation. $P_0$ values indicate the initial gas pressures for both absorption and desorption processes. The arrows schematically indicate the gas pressure evolution during the reaction. The experimentally observed quasistationary paths connecting both branches of the hysteresis loop are shown.
We could write down an expression representative of the dissipative phenomena inducing hysteresis in the case of gas absorption and desorption in a solid media, in the following form, up to first order

$$\Delta\alpha(t) = \int_{-\infty}^{t} \lambda_{\alpha,p} e^{-(t-t')} \mathcal{X} : \overline{\mathcal{P}}(t') \, dt'$$

$$= \int_{-\infty}^{t} \lambda_{\alpha,p} e^{-(t-t')} \|\overline{\mathcal{P}}(t')\| \, dt',$$

where $\Delta\alpha(t)$ is the change in normalized composition, $\lambda_{\alpha,p}$ a cross-effect (Onsager-like) amplitude coefficient, $\mathcal{P}$ the stress tensor and $\tau_{\alpha,p}$ a relaxation time for the effect of stress on concentration. $\mathcal{X}$ is a 2-tensor whose components are proportional to those of the propagation of stress and $\| \cdot \|$ the trace.

Recalling Eq. (9) we note that in a steady state ($\dot{\mathcal{V}} = \Gamma$ with $\Gamma$ the uncompensated heat production, a constant) the net effect of a change in one or more components of the stress tensor will be:

1. It will create a heat flux in the direction of maximal propagation of stress.
2. It will create a density gradient in that direction.
3. It will affect the diffusive mass transfer in that direction.
4. The diffusive and thermal effect will change the local value of the chemical potential so the rate of reaction will change.
5. Obviously there will be changes in other components of the stress tensor because of mass conservation.

Thus given a kinetic model for the chemical reaction and experimental data (a phenomenological law) on the rate of change of the stress we will be able to write down a closed expression for the system representing the observed phenomena of hysteresis.

If we consider our physical system to obey the empirical Johnson-Mehl-Avrami kinetics [36, 37]

$$\dot{\alpha} = k(T) f(\Delta p) N (1 - \alpha)^{N-1},$$

being $\alpha$ the normalized concentration, $\dot{\alpha}$ its temporal rate of change, $k(T) = K_0 e^{-E_{ac}/RT}$ and $f(\Delta p) = p - p_{\infty}$ are appropriate phenomenological laws and $N = 2$ for the present case. The normalized concentration kinetics [38] is then, given by Eq. (15) and is thus a closure condition for the phenomenological description.

Also if we consider as an approximation that our system is macroscopically thermally insulated and density preserving, then Eq. (11) in a steady state of constant uncompensated heat production $\Gamma$ reads

$$\Gamma T = \mu_{\alpha} \frac{dC_{\alpha}}{dt} + \mathcal{X}_{\alpha} : \mathcal{P} \delta + \mu \|\mathcal{X}_{\alpha}\| p_{\alpha}.$$  \hspace{1cm} (15)

Then we need to propose a constitutive equation for the stress, we will use the Young-Jacobi linear aproximation for the force, namely $X_{\alpha} = \mathcal{P}/2p$ with the following result

$$\Gamma T = 2\mu_{\alpha} K_0 e^{-E_{ac}/RT} (p - p_{\infty})(1 - \alpha)t + \frac{P_a}{2}.$$  \hspace{1cm} (16)

Here $K_0 = 10^4 \text{ min}^{-1} \text{ Pa}^{-1}$ is a pre-exponential factor and the empiric activation energy will be ranging from 40 to 45 $\text{kJmol}^{-1}$. These values are consistent with several experimental observations [39, 40].

If we graph these irreversible equations in the form of partial pressure versus time we obtain the experimentally verifiable hysteretic behavior. It has been stated on stability grounds that two segments on different paths (absorption-desorption) are doubly-connected by a finite time cycle that it is indeed of an irreversible nature in at least one of the branches. This fact is also in strong accordance with experimental evidence. For the experimentalist it is also obvious that as the cycle gets closer to one equilibrium path its tendency towards that particular state increases, a common feature of irreversible cycles [5]. One thing however should be pointed out: the branches of the irreversible cycle connecting the absorption-desorption curves had been called quasistatic paths when they are really formed of quasistationary states for as the experimentalist would note the two curves are not symmetric.

In Fig. 2 we plotted the absolute value of the change in the gas phase partial pressure during both absorption and desorption processes from an initial $P_0$ step of $\pm 1$ bar. The solid line indicates that the observed kinetic evolution of pressure is the same for both processes; gas absorption and desorption. This is reasonable since the activation energies are the same for both processes ($E_a = 40 \text{ kJmol}^{-1}$). If we consider now that the desorption process is characterized by the same $k_0$ but with a larger value for $E_a (= 45 \text{ kJmol}^{-1})$, we obtain the dotted curve in Fig. 2. This reflects a slower desorption process compared with the absorption one.

**Figure 2.** Simulation of the gas pressure drop (increase) during the absorption (desorption) reaction. Where (—) represents the $\Delta P$ change for equal activation energies for absorption and desorption, and (- - -) represent the $\Delta P$ change for different activation energies for absorption and desorption.
However, when we look at the pressure in the solid extracted from the solute chemical potential, the behavior is quite different. We display in Fig. 3 the computed values for the pressure in the solid for the three above-mentioned cases. It stands up immediately that even for similar activation energies for absorption and desorption, the pressure excursion at the maximum differs by 1.8 bar. This is more than 1 bar which is the difference between the equilibrium pressures (labeled as $P_\infty$) in both processes, as it can be appreciated in Fig. 1. This fact reflects the hysteresis behavior experimentally observed. The relaxation times for both intrinsic processes are different. We note that the mass flux as given by the kinetic law and the stress field change, are responsible for a change in the chemical potential of the solid phase which in turns account for the 0.8 bar excess pressure. Moreover, if the activation energy is now higher for the desorption process (45 kJ mol$^{-1}$), the curves for absorption and desorption differ at the maximum by 6.7 bar. This difference means that, if both absorption and desorption processes are characterized by two different mechanisms (which it seems to be the case), the observed hysteresis must be higher than in the situation of symmetrical kinetic paths. An immediate conclusion would be that the dynamic evolution of the gas phase pressure does not necessarily reflect the behavior of the solid. This is a very important statement since most of the experimental setups used to determine the time evolution of such a systems are conceived in the hypothesis that the gas pressure changes correlates with the behavior of the solid.

To continue as in our general case analysis the stochastic time derivative of the normalized concentration

$$\frac{d\alpha(t)}{dt} = \lambda_{\alpha,P} e^{-\frac{\tau}{\lambda_{\alpha,P}}} ||P(t')||,$$

also

$$\tau_{\alpha,P} = \frac{T}{\ln \left( \frac{\Gamma T}{\lambda_{\alpha,P} ||P(t')||} \right)} - \frac{P_\alpha}{2\rho\mu_\alpha \lambda_{\alpha,P}}. \quad (18)$$

Again, the ratio of relaxation time to observation time $\tau/T$ depends on system specific properties such as magnitude of the stress, chemical potential and uncompensated heat production, all of these weighted by the amplitude $\lambda_{\alpha,P}$. For the case presented in Fig. 4 of absorption/desorption with an activation energy of 40 kJ mol$^{-1}$ and proper time $T \approx 7.5$ s). In Fig. 4 we plot the ratio $\tau/T$ versus uncompensated heat production $\Gamma$. The region plotted is the one in which hysteresis shows up experimentally.

In the formalism used in this work, it is also possible to introduce supplementary internal processes in the description of the solid-gas interaction. It has been pointed out [40] that heat transfer limitations play an important role. This effect can be easily incorporated to the model in the following way. One consider the third-kind boundary conditions for the heat transfer Fourier equation which states that

$$\frac{Q}{C} \frac{dT}{dt} = C \frac{dT}{dt} + k_{th}(T - T_0), \quad (19)$$

where $Q, C$ and $k_{th}$ are the total heat released (consumed) during the absorption (desorption), the total heat capacity and the apparent thermal conductivity, respectively. It is easy to understand that while $Q$ is intrinsic to the reactive system, $C$ and $k_{th}$ are overall quantities depending on the experimental setup. The Fourier equation can be rearranged in the following form

$$T(t) - T_0 = \int_0^t \left[ \frac{Q}{C} \frac{dT}{dt} - k_{th} \frac{dT(t)}{dt} - T_0 \right] dt'.$$
This integro-differential equation for $T(t)$ must be solved self-consistently with Eqs. (9), (16) and (18). However, one does not expect fundamental differences in the conclusions already evoked in an earlier work [40]. The main point in this procedure is to show how one can introduce new supplementary phenomena, characterized by its own relaxation time, in the context of the general formalism of extended thermodynamics.

5. Conclusions

Summarizing, we have pointed out that the Mayergoyz-Preisach hysteresis operators can be mapped into Green function propagators in the context of stochastic physical processes. In this picture, an extended irreversible thermodynamics formalism it is useful to write down equations relating the uncompensated heat production (which plays the same role as the entropy production in local equilibrium phenomena) with the internal coupled modes. As a working example we choose the case of a metal hydride system known to show huge hysteresis loops. We were able to estimate the difference in the chemical potential of hydrogen between the gas and the solid phases during the absorption (or desorption) in process. We have indicate how other modes, as heat flux, could be introduced. Finally, we analize the crossed relaxation times obtained from the simulations for such a system. Along this work, we tried to be more emphatic in the physical interpretation, than in the formalism in order to obtain more insight in this kind of chemical phenomena and to expose hysteresis as a direct consequence of dissipation and macroscopic irreversibility characterized by well known rates of change.

18. The soft principle of causality states that no effect could take place simultaneously with its cause because of non-locality. The hard principle of causality implies that no effect could precede its cause. In nonequilibrium processes possibly the best formal framework for this assertion is given by Kramers-Kröning relations (see, for instance, S.R. de Groot & P. Mazur. Nonequilibrium thermodynamics, Chap. 8). For a detailed description in terms of linear response theory, see for example, J.P. Boon and S. Yip, Molecular Hydrodynamics, (Dover Publications, New York, 1980). (Sec. 2.6, 2.7 and 2.9 of Chap. 2).
20. In the case of vector and tensor outputs this scalar product is to be replaced by the appropriate tensor product consistent with the Curie principle of tensor homogeneity of irreversible thermodynamics.
21. The derivation of equations of this form [Eqs. (2) and (3)] for linear non-markovian stochastic processes is well known long ago. For an introduction in the context of the theory of stochastic processes see, for instance, van Kampen, op. cit., Wax, N., Selected Papers on Noise and Stochastic Processes, (Dover, New York, 1954); N. Kubo et al., Statistical Physics II: Nonequilibrium phenomena, (Springer-Verlag, Berlin, 1991).
23. Linear non-markovian equations have been derived from hyperbolic transport equations in the past [L.S. García-Colín and M.A. Olivares-Robles, Physica A 220 (1995)] 165, an outstanding example can be found in a seminal paper by Green on the Statistical (Stochastic) foundations of nonequilibrium physics [M.S. Green, J. Chem. Phys. 20 (1952) 1281]. Hyperbolic transport nevertheless, has been observed since the theory of viscoelastic phenomena of Maxwell, and the heat conducting problems of Cattaneo and Vernotte [J.C. Maxwell, The collected papers of James Clerk Maxwell, (Dover, 1967); C. Cattaneo, Sulla Conduzione del Calore, Atti del Seminario Matematico e Fisico dell’Università di Modena 3 (1948-49) 83–101; P. Vernotte, Les Paradoxes de la Théorie continue de l’équation de la chaleur, Comptes Rendus 246 (1958) 3154] and it stands as one of the cornerstones of the extended theory of irreversible processes, since for far from equilibrium systems nonequilibrium implies non-locality. Also an hyperbolic transport equation is obtained as a continuous limit of a one dimensional persistent random walk [S. Goldstein, Quat. J. Mech. Appl. Math.


27. B.C. Eu, *Semiclassical Theories of Molecular Scattering*, (Springer Verlag, 1984)


38. $\dot{\alpha} = dC_a/dt$, so concentration changes are normalized to unit.
