

# Study of thermoelastic growth during martensitic transformations

Antoni Planes and Jordi Ortín

*Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Catalonia, Spain*

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The possibility of local elastic instabilities is considered in a first-order structural phase transition, typically a thermoelastic martensitic transformation, with associated interfacial and volumic strain energy. They appear, for instance, as the result of shape change accommodation by simultaneous growth of different crystallographic variants. The treatment is phenomenological and deals with growth in both thermoelastic equilibrium and in nonequilibrium conditions produced by the elastic instability. Scaling of the transformed fraction curves against temperature is predicted only in the case of purely thermoelastic growth. The role of the transformation latent heat on the relaxation kinetics is also considered, and it is shown that it tends to increase the characteristic relaxation times as adiabatic conditions are approached, by keeping the system closer to a constant temperature. The analysis also reveals that the energy dissipated in the relaxation process has a double origin: release of elastic energy  $W$ , and entropy production  $S$ . The latter is shown to depend on both temperature rate and thermal conduction in the system.

## I. INTRODUCTION

A first-order diffusionless structural phase transition is acknowledged to take place in thermoelastic equilibrium when, at each temperature, a local balance condition between chemical and nonchemical forces is satisfied at the interfaces.<sup>1,2</sup> The chemical force is provided by the free-energy difference between the two phases and drives the transition, while the nonchemical forces are mainly associated with the development of strain energy in the material and oppose the transition. In these conditions, domain growth of the new phase represents a decrease in the free energy of the system and a simultaneous increase in elastic strain energy (both interfacial and volumic) that mutually compensate. In ideally thermoelastic conditions the transition extends in a temperature range but does not show an observable thermal hysteresis. In this sense the process is reversible: Once a given two-phase configuration has been achieved at a given temperature, reverting the sense of the external control parameter (temperature in the case considered), the system follows a reverse path that coincides exactly with the forward path.

Several bcc metallic alloy systems (mainly those based in noble metals) undergo structural transitions of the martensitic type which show thermoelastic behavior almost perfectly.<sup>3-5</sup> The conditions for a system to be able to undergo a thermoelastic martensitic transformation have been discussed by several authors.<sup>6,7</sup> Essentially, those conditions can be summarized by the need of elastic accommodation of the transformation shape change, favored by: (i) a small chemical driving force at the transition temperature, (ii) a small transformation shape deformation, and (iii) a matrix with a high elastic limit. When accommodation of the domains of the product phase gives rise to plastic relaxation the transition is no longer thermoelastic, and this is reflected in a large thermal hysteresis as observed in steels.<sup>8</sup>

In practice, however, even when plastic relaxation is

negligible the thermoelastic systems show hysteresis in their martensitic transformation to a different extent depending on the system.<sup>9</sup> Moreover, detailed observations using optical<sup>10</sup> and coupled acoustic and calorimetric<sup>11</sup> methods have revealed that thermoelastic transitions actually take place through a series of discontinuities, accompanied by generation of elastic waves usually detected in the ultrasonic frequency range (the so-called acoustic emission). The same kind of behavior has been revealed by Monte Carlo numeric simulations of the martensitic transformation based on a thermoelastic potential.<sup>12</sup>

The purpose of the present paper is the thermodynamic and kinetic study of the energy relaxation process associated with each of the discontinuities just described, adopting a phenomenological point of view. In Sec. II we define the problem of energy dissipation in the context of thermoelastic equilibrium; the evolution of the system in thermoelastic and out-of-equilibrium conditions is addressed in Sec. III. Then, in Sec. IV we generalize the theory to take into account the roles of (i) the evolution of the external temperature and (ii) the latent heat of transition. Finally, in Sec. V, we comment on the validity of our treatment to study hysteretic transition paths in thermoelastic systems and give the conclusions.

## II. LOCAL THERMOELASTIC EQUILIBRIUM

Let us consider a crystalline solid undergoing a diffusionless first-order phase transition so that the low-temperature phase (the  $L$  phase) has a different crystallographic structure than the high-temperature phase (the  $H$  phase). In the transition considered, the  $L$  phase is obtained from the  $H$  phase essentially by a homogeneous shear deformation accompanied by a small volume change. Growth of a crystal of the new phase inside the other phase in the conditions described results, in principle, on the building up of elastic strain energy inside the solid.

Here we are interested in situations where the amount of plastic deformation in the crystal is practically negligible. The thermodynamic driving force for transformation from  $H$  to  $L$  is opposed by the stresses elastically built up inside the crystal, to achieve a local thermoelastic equilibrium: Experimentally one observes that growth is arrested while the temperature is kept constant, but a temperature change displaces the equilibrium point and the  $L$  phase grows on cooling or shrinks on heating.

In addition to the concept of growth in thermoelastic equilibrium, one must consider that the symmetry properties of the high-temperature phase usually result in an important degeneracy  $g$  of the low-temperature phase. This means that the structural transformation can give rise to  $g$  structures of the  $L$  phase differing in their crystallographic orientation with respect to the  $H$  phase but energetically equivalent in the absence of externally applied forces. Considering the transforming crystal as being free of external stresses, it follows that the  $g$  structures of the  $L$  phase (called variants) have equal probability of growing. Actually, the variants tend to form in self-accommodating groups which minimize the internal strain fields in the crystal and hence the stored elastic energy.<sup>13-15</sup> From this picture it comes out that the elastic strain energy in the system, which increases during thermoelastic growth of isolated single variants, can partially be released every time that two or more variants form a self-accommodating group. This is one of the relaxation mechanisms that the system operates to prevent an indefinite increase in elastic strain energy, which would finally lead to plastic accommodation.<sup>16</sup> The energy relaxed in this way may appear as entropy production in the crystal or may give rise to elastic waves propagating inside the crystal and eventually detectable as acoustic emission.

### A. Model

Let us consider a coarse reticulation of the crystal under study such that one cell of the grid typically contains a fully transformed single variant of a self-accommodating group. It must be mentioned that the need of optimum strain accommodation gives rise, in practice, to self-accommodating groups of sizes varying within one order of magnitude. Hence the size of individual cells in our grid may vary from group to group in the crystal. The dimension chosen for a cell is much larger than the linear dimension of the crystal unit cell and slightly smaller but in the same order of magnitude than the linear dimension of the self-accommodating group considered.

Let us define the transformation state in cell  $i$  by means of a local variable  $x_i$  which gives the molar fraction in cell  $i$  transformed to the  $L$  phase. The transformation state of the overall system is then defined by a vector  $\mathbf{x} = \{x_i\}$ , and the transformed fraction of the complete crystal is:

$$X = \sum_{i=1}^N x_i M_i \left( \sum_{i=1}^N M_i \right)^{-1}, \quad (1)$$

where  $N$  is the number of cells in the grid and  $M_i$  is the mole number in the  $i$ th cell.

We study now the thermoelastic growth of a single variant in cell  $i$ , keeping unchanged the transformation state of the remaining cells  $j \neq i$ .

Assuming for cell  $i$  a condition of local thermoelastic equilibrium, the free energy of this cell is given by:

$$g_i = x_i g_i^L + (1 - x_i) g_i^H + g_i^{\text{el}}, \quad (2)$$

where  $g_i^L$  and  $g_i^H$  are the free energies of phases  $L$  and  $H$  respectively, dependent on the local temperature  $\tau_i$  of cell  $i$ , and  $g_i^{\text{el}}$  is the elastic energy stored in the cell, dependent on all the  $x_j$ , i.e., on the transformation state of the overall system.

Given that in the following we will be referring solely to cell  $i$ , we eliminate now the subindex  $i$  to simplify the notation. In local thermoelastic equilibrium, each configuration of the cell will minimize its free energy. For  $x_{j \neq i}$  constant and at a given temperature the condition of thermoelastic equilibrium is then given by

$$\left( \frac{\partial g}{\partial x} \right)_{\tau} = 0, \quad (3)$$

which leads to

$$(g^L - g^H) + \frac{\partial g^{\text{el}}}{\partial x} = 0. \quad (4)$$

The difference in free energy between phases  $L$  and  $H$  is a function of the local temperature  $\tau$  of cell  $i$  such that

$$\frac{\partial (g^L - g^H)}{\partial \tau} > 0. \quad (5)$$

Next we impose a local stability condition:  $x$  increases when  $\tau$  decreases. Taking the derivative of Eq. (4) with respect to  $x$  and imposing this condition leads to

$$\frac{\partial^2 g^{\text{el}}}{\partial x^2} > 0. \quad (6)$$

### B. Energy dissipation

However, in some interval of  $x$  the elastic energy of the system might not verify Eq. (6) if, for instance, the martensitic variant considered enters in accommodating interaction with its neighbor variants (these remain static, since we are ignoring correlations between events in different cells). The situation is depicted in Fig. 1: As the local temperature  $\tau$  decreases quasistatically,  $x$  increases in thermoelastic equilibrium from  $a$  to  $b$ . From  $b$  onwards the stability condition ceases from being satisfied, and an increase of  $x$  only can take place out of equilibrium, ending in some point of the  $c'$ - $d$  branch such as  $c$ . Further growth between  $c$  and  $d$  is again thermoelastic. Increasing the temperature between  $d$  and  $c'$ , on reversion, causes the transformed fraction  $x$  to decrease in thermoelastic equilibrium. Between  $c'$  and  $b'$  the system reverts out of equilibrium and finally, from  $b'$  to  $a$ , the system evolves in thermoelastic equilibrium again. As a consequence of the instability the system follows noncoincident forward ( $a$ - $d$ ) and reverse ( $d$ - $a$ ) transformation paths. In each of the two nonequilib-

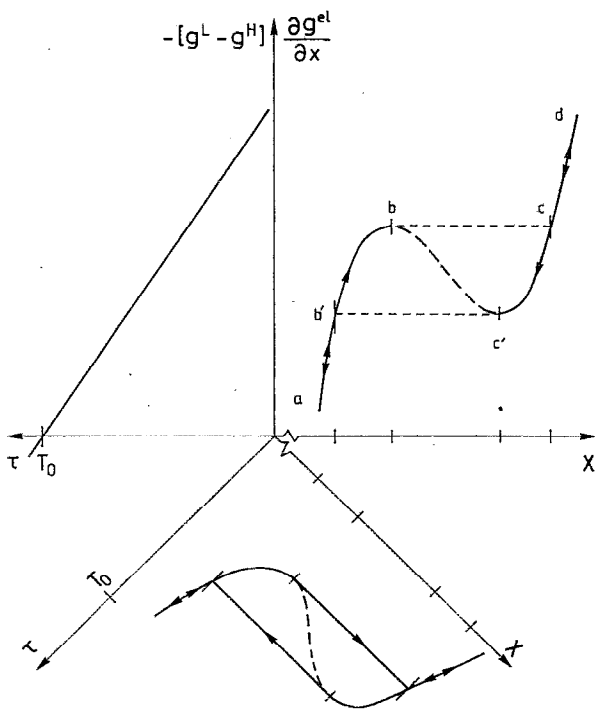


FIG. 1. Schematic diagram representing a generic elastic instability. The left-hand side shows the chemical free energy of the transformation,  $g^L - g^H$ , as a function of the local temperature  $\tau$ . The right-hand side shows a local evolution of  $\partial g^{\text{el}}/\partial x$  ( $g^{\text{el}}$  is the elastic strain energy) with the local transformed fraction  $x$ : The function grows monotonically from  $a$  to  $b$ , decreases from  $b$  to  $c'$  (the heavy dashed portion) and increases again from  $c'$  to  $d$ . This behavior corresponds to a nonconvex shape of  $g^{\text{el}}(x)$ . Thus, between  $b$  and  $c'$  a thermoelastic balance cannot be satisfied, and growth from  $b$  onwards takes place out of equilibrium, following the fine discontinuous line until point  $c$  if the temperature remains constant. Equivalently, on heating, reversion from  $c'$  backwards follows the fine discontinuous line until point  $b'$ . The bottom part of the diagram shows the resulting hysteresis loop, traced by the transformed fraction  $x$  as a function of temperature  $\tau$ , when the condition of thermoelastic equilibrium [Eq. (4)] is imposed.

rium evolutions the system dissipates energy and consequently the overall process exhibits hysteresis.<sup>17</sup>

The dissipated energy can be computed in the following way:

$$\begin{aligned}
 g^{\text{diss}} &= - \oint \left( \frac{\partial g}{\partial x} \right)_{\tau} dx \\
 &= - \oint \left( (g^L - g^H) + \frac{\partial g^{\text{el}}}{\partial x} \right) dx \\
 &= - \int_{b'}^b \frac{\partial g^{\text{el}}}{\partial x} dx - (c - b) \left( \frac{\partial g^{\text{el}}}{\partial x} \right)_b - \int_c^{c'} \frac{\partial g^{\text{el}}}{\partial x} dx \\
 &\quad - (c' - b') \left( \frac{\partial g^{\text{el}}}{\partial x} \right)_{c'} \\
 &= [h(c) - h(b)] + [h(b') - h(c')], \quad (7)
 \end{aligned}$$

where  $h(x)$  is defined as

$$h(x) = g^{\text{el}}(x) - x \frac{\partial g^{\text{el}}}{\partial x}. \quad (8)$$

It is worth noting that only the states joining nonequilibrium jumps appear in the final result for  $g^{\text{diss}}$ . Further insight into the meaning of the function  $h(x)$  is obtained searching for a hypothetical transformation path, at a given temperature, that would not give rise to energy dissipation (equilibrium path). This is achieved by a Maxwell construction,

$$0 = \oint x d \left( \frac{\partial g^{\text{el}}}{\partial x} \right). \quad (9)$$

An integration by parts leads to the result  $h(x) = \text{const}$ , showing that  $h(x)$  is the thermodynamic potential characterizing the equilibrium between two states of different transformed fraction  $x$  at the same temperature. In addition, it is clear from Eq. (7) that the equivalent of Eq. (4) for a nonequilibrium situation reads

$$(g^L - g^H) + \frac{\partial g^{\text{el}}}{\partial x} + \frac{\partial g^{\text{diss}}}{\partial x} = 0, \quad (10)$$

if one accepts a continuous formalism for the energy dissipation. A balance equation of this same form, though applying to the whole system, has been the usual starting point of different studies on the thermodynamics of the martensitic transformation.<sup>18,19</sup>

### III. TIME EVOLUTION

#### A. Evolution in thermoelastic equilibrium

When the system follows an evolution in thermoelastic equilibrium described by Eq. (4), with the temporal derivative  $\dot{\tau} = d\tau/dt$  tending to zero, we have

$$\frac{\partial (g^L - g^H)}{\partial \tau} d\tau + \frac{\partial^2 g^{\text{el}}}{\partial x^2} dx = 0. \quad (11)$$

In this equation  $\tau$  represents the temperature  $T$  of the whole system because the two temperatures coincide in pure thermoelastic equilibrium. Since each term in the equation can be integrated independently,  $x$  is only a function of  $\tau$ , independent of  $\dot{\tau}$  and hence of time. For the complete system as a whole this result predicts that  $X$  as a function of  $T$  does not depend on  $T$ , for low enough  $T$  values, if the transformation takes place in thermoelastic equilibrium.

#### B. Relaxation dynamics

When, from point  $b$  in Fig. 1, the system continues being cooled (even very slowly) a relaxation process takes place out of equilibrium. We consider the temporal evolution of  $x$  during the process given by the following dynamic equation:

$$\frac{dx}{dt} = -\kappa \left( (g^L - g^H) + \frac{\partial g^{\text{el}}}{\partial x} \right), \quad (12)$$

where, as seen before,  $[(g^L - g^H) + \partial g^{\text{el}}/\partial x]$  is the thermodynamic force and  $\kappa$  is a mobility.

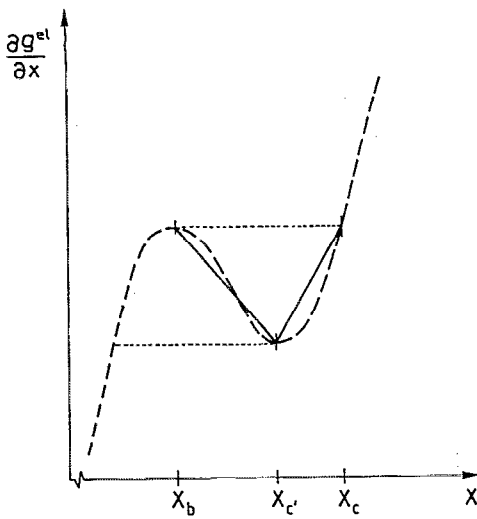


FIG. 2. Schematic diagram showing an approximation by straight lines to the function  $\partial g^{\text{el}}/\partial x$  in the region of elastic instability, useful to perform analytic calculations.

When the system is in thermodynamic equilibrium the second member of the equation above, according to Eq. (4), vanishes and hence  $dx/dt = 0$ . This does not mean that growth arrests, since in thermoelastic equilibrium  $d\tau/dt \rightarrow 0$  as well and hence it is possible that  $dx/d\tau$  remains finite. The situation is equivalent to a quasistatic evolution of a thermodynamic system in classical equilibrium thermodynamics.

Suppose now that the system has been brought to point  $b$  in thermoelastic equilibrium, i.e., with  $\dot{\tau} \rightarrow 0$ , so that  $\tau$  can be considered to remain constant during the relaxation process. This assumption, additionally, takes for granted that the latent heat released or absorbed during the process does not modify substantially the temperature of the system. The more general situation will be discussed later.

For the sake of being able to integrate the dynamic equation (12) explicitly, we simplify the behavior of the elastic energy to the following form, shown in Fig. 2:

$$\frac{\partial g^{\text{el}}}{\partial x} = -\alpha(x - x_b) + \beta, \quad x_b < x < x_{c'},$$

$$\frac{\partial g^{\text{el}}}{\partial x} = \alpha'(x - x_{c'}) + \beta', \quad x_{c'} < x < x_c, \quad (13)$$

where  $\beta \equiv (\partial g^{\text{el}}/\partial x)_{x_b}$  and  $\beta' \equiv (\partial g^{\text{el}}/\partial x)_{x_{c'}}$ . On the other hand, since the entropy change of the transformation is practically independent of temperature,

$$g^L - g^H = a(\tau - T_0), \quad (14)$$

where  $a \equiv \Delta S$  is the entropy change and  $T_0$  is the temperature of chemical equilibrium between the two phases. Between  $x_b$  and  $x_{c'}$  the differential equation (12) takes now the form

$$\frac{dx}{dt} = \bar{\alpha}(x - x_b) - [\bar{\beta} + \kappa a(\tau - T_0)], \quad (15)$$

where  $\bar{\alpha} = \alpha\kappa$  and  $\bar{\beta} = \beta\kappa$ . Note that if the system reaches the point  $x_b$  in pure thermoelastic equilibrium, the second member of the equation vanishes (as it should) at this point. For the system to be able to relax from  $x_b$  one needs an arbitrarily small difference between driving and resistive forces at  $x_b$ ; the difference is measured by the second term in the right-hand side of Eq. (15). Solution of the equation (with  $\tau$  constant) reads

$$x - x_b = (1/\bar{\alpha})[\bar{\beta} + \kappa a(\tau - T_0)](1 - e^{\bar{\alpha}t}). \quad (16)$$

A similar solution can be found between  $x_{c'}$  and  $x_c$ . A characteristic relaxation time  $t_c$  will be given by

$$t_c = \bar{\alpha}^{-1} \approx \left( \kappa \left| \frac{\partial^2 g^{\text{el}}}{\partial x^2} \right| \right)^{-1}, \quad (17)$$

and is therefore inversely proportional to the mean slope of the function  $(\partial g^{\text{el}}/\partial x)$  in the unstable region (Fig. 1). Experimental estimates of  $t_c$  for noble-metal-based alloys can be found in Ref. 20 and estimates of interface velocities and jump distances in Refs. 10 and 21–23.

It is important to note that a change of variables  $d\tau = \dot{\tau}dt$  in Eq. (15) leads this time to a transformed fraction  $x$  dependent on  $\tau$  and on  $\dot{\tau}$  as well. Thus, growth in thermoelastic equilibrium should be experimentally recognizable from growth out of equilibrium: In thermoelastic equilibrium we expect the curves of  $X$  to scale with  $|T|$  (for small enough  $T$ ), but this will not be the case out of equilibrium.

#### IV. GENERAL TREATMENT

The oversimplified way of dealing with the growth problem in the previous paragraphs is only valid if actually  $\dot{\tau} \rightarrow 0$  and if temperature changes due to the latent heat exchanged in the transformation can be neglected.

In this section we face a more general situation where  $\tau = \tau(t)$  and therefore the role of the latent heat of transformation, whose relevance has been pointed out in Refs. 24 and 25, is amenable to study. We only give results for the  $b \rightarrow c'$  relaxation stage since results for the other stages go along the same lines.

The dynamic differential equation, generalization of Eq. (15), to consider in the  $b \rightarrow c'$  stage of relaxation out of equilibrium reads

$$\frac{dx}{dt} = \bar{\alpha}(x - x_b) - \{\bar{\beta} + \kappa a[\tau(t) - T_0]\}, \quad (18)$$

where  $\tau(t)$  gives the evolution of local temperature with time. To evaluate  $\tau(t)$ , we take the region (a cell in our grid) where the relaxation process occurs as a domain of heat capacity  $C$  connected to its surroundings at a temperature  $T_{\text{ext}}$  through a thermal contact resistance  $P^{-1}$  (Fig. 3). The thermal power  $dq/dt$  released in the domain considered is

$$\frac{dq}{dt} = L \frac{dx}{dt}, \quad (19)$$

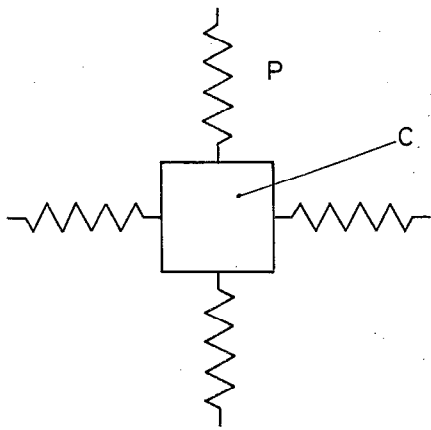


FIG. 3. Symbolic representation of one cell in the system as an element of infinite thermal conductivity, heat capacity  $C$ , and thermal coupling to the ambiance  $P$ .

where  $L$  is the absolute value of the latent heat of transformation. Hence, the temperature evolution in the domain considered is given by

$$L \frac{dx}{dt} = C \frac{d\tau}{dt} + P[\tau - T_{\text{ext}}(t)]. \quad (20)$$

This equation couples to Eq. (18) to give the solutions  $x(t)$  and  $\tau(t)$ .

To calculate the behavior of the local temperature  $\tau(t)$  for a general form of dissipation, assume a linear temperature variation  $T_{\text{ext}}(t) = T(t - t_0) + T_{\text{ext}}(t_0)$ , with  $T$  constant, and consider an impulsional (infinitely short in time) power dissipation at  $t = t_0$ . For any  $t > t_0$ , the differential equation for  $\tau(t)$  is

$$\frac{d\tau}{dt} + \frac{P}{C} [\tau - T_{\text{ext}}(t_0)] = \frac{P}{C} \left( \frac{dT}{dt} \right) (t - t_0). \quad (21)$$

Solution of this equation with the initial condition

$$C[\tau(t_0) - T_{\text{ext}}(t_0)] = 1 \quad (22)$$

determines the Green function for heat conduction in our problem. The solution reads

$$G(t - t_0) = \left( \frac{1}{C} + \frac{C}{P} \dot{T} \right) \exp\left( -\frac{P}{C} (t - t_0) \right) - \frac{C}{P} \dot{T}, \quad (23)$$

and the thermal relaxation time is  $\mu = C/P$ . The solution for an arbitrary dissipation  $L(dx/dt)$  is then

$$\tau(t) - T_{\text{ext}}(t) = L \int_{t_0}^t \frac{dx}{dt'} G(t' - t_0) dt'. \quad (24)$$

This equation shows that, in general, the drift in local temperature  $\tau(t)$  of the cell considered with respect to the temperature  $T_{\text{ext}}(t)$  of the neighbor cells depends on the transformation rate  $dx/dt$  in the cell, solution of the dynamic differential Eq. (18), which in turn depends on the local temperature  $\tau(t)$  of the cell. Solution of the two coupled equations appears to be simpler in the two limiting cases of interest: isothermal growth and adiabatic growth.

## A. Isothermal limit

In the isothermal limit, which will apply to a system with very large thermal diffusivity or very slow kinetics of nonthermoelastic relaxation,  $\mu \rightarrow 0$  and therefore

$$t' - t_0 \gg \mu, \quad \forall t', \quad (25)$$

which leads to

$$G \simeq -\frac{TC}{P} = -\dot{T}\mu \rightarrow 0, \quad (26)$$

so that, obviously,

$$\tau(t) \simeq T_{\text{ext}}(t). \quad (27)$$

This means that, due to its large thermal diffusivity, the cell considered follows the temperature of the neighbor cells in this limit. Now we can explore the consequences of such behavior on the relaxation kinetics.

Putting this result into Eq. (18) for the evolution between  $b$  and  $c'$  (Fig. 1) we obtain

$$\frac{dx}{dt} = \bar{\alpha}(x - x_b) - \{\bar{\beta} + \kappa a [T_{\text{ext}}(t) - T_0]\}, \quad (28)$$

and considering a linear temperature variation  $T_{\text{ext}}(t) = T(t - t_0) + T_{\text{ext}}(t_0)$ , with  $T$  constant, we obtain

$$\begin{aligned} \frac{dx}{dt} = & -\kappa a \dot{T}(t - t_0) + \bar{\alpha}(x - x_b) \\ & + \kappa a \left( [T_0 - T_{\text{ext}}(t_0)] - \frac{\beta}{a} \right). \end{aligned} \quad (29)$$

If we consider the system to be in thermoelastic equilibrium at point  $b$ , remembering that  $x(t_0) = x_b$ , we obtain

$$[T_0 - T_{\text{ext}}(t_0)] - (\beta/a) = 0 \quad (30)$$

and the resulting equation of motion reads therefore

$$\frac{dx}{dt} = -\kappa a \dot{T}(t - t_0) + \bar{\alpha}(x - x_b). \quad (31)$$

It has for solution

$$x - x_b = (\kappa a \dot{T} / \bar{\alpha}) [(t - t_0) + (1/\bar{\alpha})(1 - e^{-\bar{\alpha}(t-t_0)})]. \quad (32)$$

The first term in the square bracket arises from a linear variation assumed for  $T_{\text{ext}}(t)$ , which implies a continuous increase in chemical driving force and hence in transformed fraction  $x$ ; the second term shows that the relaxation kinetics in the isothermal limit is dominated by the same characteristic time previously found in Eq. (16).

## B. Adiabatic limit

In the adiabatic limit, corresponding to a small thermal diffusivity of the system or very fast relaxation kinetics,  $\mu = C/P \rightarrow \infty$  and therefore

$$t' - t_0 \ll \mu, \quad \forall t'. \quad (33)$$

Expanding the exponential of Eq. (23) in series and cutting to first order leads to

$$G(t - t_0) \approx (1/C) - (t - t_0)\eta, \quad (34)$$

where

$$\eta = (1/C\mu) + \dot{T}. \quad (35)$$

Then,

$$\begin{aligned} \tau(t) - T_{\text{ext}}(t) &\approx L \int_{t_0}^t \frac{dx}{dt'} \left( \frac{1}{C} - (t' - t_0)\eta \right) dt' \\ &= L \left( \frac{1}{C} [x(t) - x(t_0)] \right. \\ &\quad \left. - \eta [x(t) - \bar{x}] (t - t_0) \right), \end{aligned} \quad (36)$$

where

$$\bar{x} = \frac{1}{t - t_0} \int_{t_0}^t x dt' \quad (37)$$

is the mean value of  $x$  in the time interval  $(t - t_0)$ . If we accept that, approximately,

$$\bar{x} \approx \frac{1}{2} [x(t) + x(t_0)], \quad (38)$$

we obtain

$$\tau(t) - T_{\text{ext}}(t) \approx \frac{L}{C} [x(t) - x(t_0)] \left( 1 - \eta C \frac{t - t_0}{2} \right), \quad (39)$$

and in the purely adiabatic limit ( $\eta = 0$ ),

$$\tau(t) - T_{\text{ext}}(t) \approx (L/C) [x(t) - x(t_0)]. \quad (40)$$

Thus, we find that in the adiabatic limit the temperature of the cell where the relaxation takes place is highly affected by the latent heat released in the transformation.

Inserting this result now into Eq. (18) leads to

$$\frac{dx}{dt} = \left( \bar{\alpha} - \kappa a \frac{L}{C} \right) (x - x_b) - \{ \bar{\beta} + \kappa a [T_{\text{ext}}(t) - T_0] \}, \quad (41)$$

having taken into account that  $x(t_0) = x_b$ . If again we take  $T_{\text{ext}}(t) = \dot{T}(t - t_0) + T_{\text{ext}}(t_0)$  with  $\dot{T}$  constant, we arrive at an equation that looks exactly the same as in the isothermal case [Eq. (31)] replacing  $\bar{\alpha}$  by  $\bar{\alpha} - \kappa a L/C$ . From the solution (32) we see that the consequence is an increase in the characteristic relaxation time, which now reads

$$t_c \sim [\bar{\alpha} - \kappa a (L/C)]^{-1}. \quad (42)$$

This means that a temperature lag between the cell considered and its neighbor cells, characteristic of the adiabatic limit, slows down the relaxation process and hence the overall growth of the  $L$  phase.

### C. Energy dissipation

The energy dissipated in the relaxation process can be written in the general form

$$\frac{dE^{\text{diss}}}{dt} = - \sum_i X_i J_i, \quad (43)$$

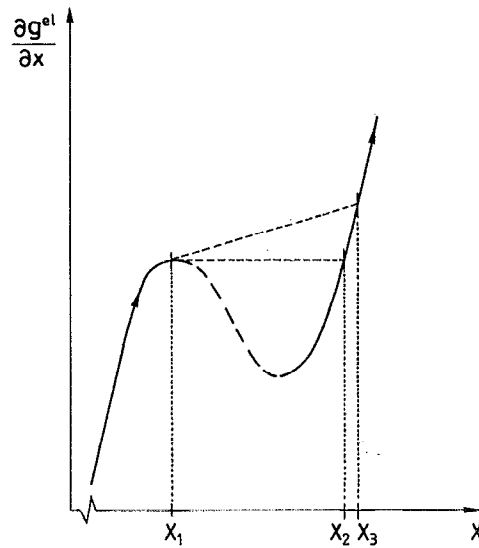


FIG. 4. Schematic diagram showing the evolution of  $\partial g^{\text{el}}/\partial x$  with the local transformed fraction  $x$  and two trajectories in the instability region. The horizontal discontinuous straight line corresponds to an out-of-equilibrium evolution at constant temperature; the ascending discontinuous straight line corresponds to an out-of-equilibrium evolution with a constant temperature rate.

where  $X_i$  are generalized forces and  $J_i$  the corresponding conjugate fluxes acting during the process. In our case the equation reads

$$\frac{dg^{\text{diss}}}{dt} = - \left( a[\tau(t) - T_0] + \frac{\partial g^{\text{el}}}{\partial x} \right) \frac{dx}{dt}. \quad (44)$$

In the isothermal approximation  $\tau(t) \approx T_{\text{ext}}(t)$  and taking  $T_{\text{ext}}(t) = \dot{T}(t - t_0) + T_{\text{ext}}(t_0)$  we obtain

$$\frac{dg^{\text{diss}}}{dt} = - \left( a[T_{\text{ext}}(t_0) - T_0] + \frac{\partial g^{\text{el}}}{\partial x} \right) \frac{dx}{dt} - a\dot{T}(t - t_0) \frac{dx}{dt}. \quad (45)$$

Hence the energy dissipated will be given by

$$\begin{aligned} g^{\text{diss}} &= - \int_{x_1}^{x_2} \left( a[T_{\text{ext}}(t_0) - T_0] + \frac{\partial g^{\text{el}}}{\partial x} \right) dx \\ &\quad - \int_{x_2}^{x_3} \left( a[T_{\text{ext}}(t_0) - T_0] + \frac{\partial g^{\text{el}}}{\partial x} \right) dx \\ &\quad - \int_{x_1}^{x_3} a\dot{T}(t - t_0) dx. \end{aligned} \quad (46)$$

Here, as shown in Fig. 4,  $x_1$  is the point where  $\partial^2 g^{\text{el}}/\partial x^2 = 0$ ,  $x_2$  is the value that  $x$  would reach if  $\dot{T} = 0$ , and  $x_3$  is the actual final point in the relaxation process.

The first term in the second member of Eq. (46) is the dissipation of elastic energy, i.e.,  $h(x_2) - h(x_1)$  according to Eq. (7). The other two terms give an additional dissipative effect due to the fact that  $T$  is not constant. In the purely adiabatic limit Eq. (41) shows that

$$\tau(t) \approx T_{\text{ext}}(t) + [x(t) - x(t_0)]L/C.$$

Substituting into Eq. (44), and following the same argument than above, one finds

$$\begin{aligned}
 g^{\text{diss}} = & - \int_{x_1}^{x_2} \left( a[T_{\text{ext}}(t_0) - T_0] + \frac{\partial g^{\text{el}}}{\partial x} \right) dx \\
 & - \int_{x_2}^{x_3} \left( a[T_{\text{ext}}(t_0) - T_0] + \frac{\partial g^{\text{el}}}{\partial x} \right) dx \\
 & - \int_{x_1}^{x_3} a\dot{T}(t - t_0) dx \\
 & - \int_{x_1}^{x_3} \frac{aL}{C} [x(t) - x(t_0)] dx, \quad (47)
 \end{aligned}$$

which looks the same as Eq. (46) with the addition of a new last term.

Both Eqs. (46) and (47) show that the energy dissipation can actually be written as the sum of two contributions<sup>26</sup>:

$$g_{\text{diss}} = W_i + \langle T \rangle S_i. \quad (48)$$

$W_i$  is the elastic energy dissipation which, in principle, does not give rise to entropy production in the system, and  $\langle T \rangle S_i$  is the dissipation associated with entropy production,  $\langle T \rangle$  being an average temperature in the process. For small enough  $\dot{T}$ , since  $x_2$  will be very close to  $x_3$ , we can neglect the second integral in the second member of any of the two equations. Hence, in the isothermal limit

$$\langle T \rangle S_i \simeq - \int_{x_1}^{x_3} a\dot{T}(t - t_0) dx \sim - \frac{1}{2} a \dot{T} t_c \Delta x, \quad (49)$$

where  $t_c$  is the characteristic relaxation time of Eq. (17) and  $\Delta x \equiv x_3 - x_1$ . In the adiabatic limit we have an additional integral, which leads to

$$\int_{x_1}^{x_3} \frac{aL}{C} [x(t) - x(t_0)] dx = \frac{aL}{2C} (\Delta x)^2, \quad (50)$$

where we have used that  $x(t_0) \equiv x_1$ . Thus, in this limit

$$\langle T \rangle S_i \simeq - \frac{1}{2} a [\dot{T} t_c + (L/C) \Delta x] \Delta x. \quad (51)$$

It is worth noting that  $\dot{T}$  and  $\Delta x$  always have opposite signs, so that the new contribution in the adiabatic limit favors a smaller entropy production. This is understood when one considers that self-heating of the cell (because of the latent heat of transformation  $L$ ) keeps the system closer to the thermoelastic equilibrium temperature for the transformed fraction  $x_1$ .

## V. DISCUSSION AND CONCLUSIONS

In this work we have faced the possibility of local elastic instabilities during thermoelastic growth in a first-order phase transition, which are at the origin of the energy dissipation manifested by hysteresis phenomena. In thermoelastic martensitic systems the instability is typically expected to appear as a result of shape change accommodation by groups of self-accommodating crystallographic variants. Another example, that has been theoretically demonstrated,<sup>27</sup> is the elastic instability experimented by a

spherical inclusion that grows anisotropically to become an ellipsoid in an infinite elastic medium. Our work deals with the consequences of such instabilities on the growth kinetics and does not depend on the particular features of the instability mechanism.

We adopt a phenomenological approach where the instability appears as the result of representing the elastic energy by a nonconvex function. In this sense the treatment has some points in common with the study of the hysteresis during pseudoelastic behavior by Müller and Xu.<sup>28,29</sup>

The first prediction of our work is the existence of scaling of the transformed fraction  $X$  with temperature if growth was purely thermoelastic. On the contrary, growth out of equilibrium introduces an explicit dependence of the transformed fraction on the temperature rate  $\dot{T}$ . This suggests that a measure of the influence of  $\dot{T}$  on the  $X$ - $T$  curves would give information on the relative importance of nonequilibrium growth during transformation. The experimental studies of the thermoelastic martensitic transformation in several copper-based alloy systems seem to validate our prediction: A representation of  $X$  vs  $T$  (once a good reproducibility of the hysteresis cycle has been achieved by cycling) is independent of the temperature rate, at least for temperature rates small enough to guarantee the proximity of the system to a condition of equilibrium at any time. Unfortunately, however, to our knowledge there are not systematic experiments designed specifically to check our prediction.

We have also considered the role of heat conduction in the system: One expects the latent heat of transformation to hinder the interface motion during both forward and reverse transformations. In our treatment this appears as an increase in the characteristic relaxation time when the transforming cell is supposed to behave adiabatically rather than isothermally. In addition, the effect of the latent heat is to keep the system closer to thermoelastic equilibrium during relaxation.

The energy dissipated in the relaxation process appears as the sum of two contributions of a different origin: first, the elastic energy release that one would expect associated with the local elastic instability considered; and second, an energy dissipation related to heat conduction in the system because of both  $\dot{T} \neq 0$  and the need of evacuation of the latent heat. We associate the first contribution with the generation and propagation of elastic waves inside the material, usually detected experimentally as acoustic emission, and the second contribution with entropy production in the system. The latter appears to be comparatively small for small temperature rates  $\dot{T}$ . This is in agreement with all the calorimetric experiments on copper-based thermoelastic systems analyzed to this purpose, where we have found a negligible entropy production.<sup>30,31</sup>

The approach presented applies locally to one cell, at scales of the order of a self-accommodating group in thermoelastic transformations. The individual behavior of one cell that we have isolated in our treatment will actually depend on the behavior of neighboring cells. Thus, the overall transformation behavior will be determined by the

elastic and thermal interaction between cells. A detailed analysis of the complete problem appears to be a very complex task.

A first approach to the interaction problem could be the following: We pay attention only to states of thermoelastic equilibrium. Since we know that an applied stress shifts the equilibrium transformation temperature, the modification of the stress field on each cell following a relaxation process in some part of the system can be modeled as a change in the equilibrium temperature  $T_0$  of the cells. The change is different from cell to cell, depending on their mutual interactions. Work along these lines is currently in progress, with the ultimate goal of modeling the hysteretic behavior in thermoelastic martensitic systems.

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<sup>1</sup>H. C. Tong and C. M. Wayman, *Acta Metall.* **22**, 887 (1974).  
<sup>2</sup>G. B. Olson and M. Cohen, *Scr. Metall.* **9**, 1247 (1975).  
<sup>3</sup>G. V. Kurdjumov, *Tech. Phys. USSR* **18**, 999 (1948).  
<sup>4</sup>G. V. Kurdjumov and L. C. Khandros, *Dokl. Akad. Nauk. USSR* **66**, 211 (1949).  
<sup>5</sup>Z. S. Basinski and J. W. Christian, *Acta Metall.* **2**, 148 (1954).  
<sup>6</sup>H. C. Ling and W. S. Owen, *Acta Metall.* **29**, 1721 (1981).  
<sup>7</sup>J. W. Christian, *Metall. Trans. A* **13**, 509 (1982).  
<sup>8</sup>L. Kauffman and M. Cohen, *Prog. Met. Phys.* **7**, 165 (1958).  
<sup>9</sup>R. J. Salzbrenner and M. Cohen, *Acta Metall.* **27**, 739 (1979).

<sup>10</sup>L. C. Chang, *J. Appl. Phys.* **23**, 725 (1952).  
<sup>11</sup>A. Planes, J. L. Macqueron, M. Morin, and G. Guénin, *Phys. Status Solidi A* **66**, 717 (1981).  
<sup>12</sup>A. G. Khachatryan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983), pp. 408–430.  
<sup>13</sup>H. Tas, L. Delaey, and A. Deruyttere, *Metall. Trans.* **4**, 2833 (1973).  
<sup>14</sup>J. de Vos, L. Delaey, and E. Aernoudt, *Z. Metallkde.* **69**, 511 (1978).  
<sup>15</sup>T. Saburi and C. M. Wayman, *Acta Metall.* **27**, 979 (1979).  
<sup>16</sup>L. Delaey and E. Aernoudt, in *Proceedings of the International Conference on Martensitic Transformations* (The Japan Institute of Metals, Nara, 1986), pp. 926–933.  
<sup>17</sup>L. Delaey, J. Ortín, and J. Van Humbeeck, in *Proceedings of Phase Transformations '87*, edited by G. W. Lorimer (The Institute of Metals, Cambridge, 1988), pp. 60–66.  
<sup>18</sup>G. B. Olson and M. Cohen, *Scripta Metall.* **11**, 345 (1977).  
<sup>19</sup>A. Planes, T. Castán, J. Ortín, and L. Delaey, *J. Appl. Phys.* **66**, 2342 (1989).  
<sup>20</sup>Ll. Mañosa, A. Planes, D. Rouby, and J. L. Macqueron, *J. Phys. F* **18**, 1725 (1988).  
<sup>21</sup>F. C. Lovey, J. Ortín, and V. Torra, *Phys. Lett. A* **121**, 352 (1987).  
<sup>22</sup>A. Amengual, F. Garcías, F. Marco, C. Seguí, and V. Torra, *Acta Metall.* **36**, 2329 (1988).  
<sup>23</sup>Ll. Mañosa, A. Planes, D. Rouby, and J. L. Macqueron, *Acta Metall. Mater.* **38**, 1635 (1990).  
<sup>24</sup>R. J. Wasilewski, *Metall. Trans. A* **6**, 1405 (1975).  
<sup>25</sup>S.-K. Chan, *J. Chem. Phys.* **67**, 5755 (1978).  
<sup>26</sup>J. Ortín and A. Planes, *Acta Metall.* **37**, 1433 (1989).  
<sup>27</sup>M. Buisson and M. Berveiller, (private communication).  
<sup>28</sup>I. Müller, *Continuum Mech. Thermodyn.* **1**, 125 (1989).  
<sup>29</sup>I. Müller and H. Xu, *Acta Metall. Mater.* **39**, 263 (1991).  
<sup>30</sup>A. Planes, J. L. Macqueron, and J. Ortín, *Philos. Mag. Lett.* **57**, 291 (1988).  
<sup>31</sup>J. Ortín and A. Planes, *Mater. Sci. Forum* **56–58**, 139 (1990).