Interaction Energy in some Phenomenological Modelings of Phase Transitions in Crystalline Solids

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Abstract. Some phenomenological and macroscopic modelings of solid/solid phase transitions involve a so-called interaction term which may imply the nonconvexity of the strain energy function. Nevertheless, it is shown that, if this term is not too large, these modelings are valuable and account for some experimental facts.

1 Introduction

I will present some remarks on a category of phenomenological modelings of phase transition in crystalline solids. These modelings involve a so-called interaction term which may imply the nonconvexity of the strain energy density function of the medium. This lack of sacrosanct convexity generates some controversy, warning, or nonuse (see some comments in [2], [8], [9], [13], [19]).

I will show that, if this term is not too large, the modeling is valuable. Certainly, the stored energy density function is not convex but *quasiconvex* and, consequently, inherits a double-well like structure which may account for some experiments.

From a technical, say mathematical, standpoint, this study is nothing but a slight variant of the beautiful papers [11], [12]... Nevertheless, I hope it may interest people concerned with the modeling of shape memory alloys.

2 Setting the problem

First, the phenomenological modelings, that I will discuss, describe the state of the medium by a triple (ϵ, x, T) ; ϵ, T stand respectively for the linearized strain tensor and the temperature, while $0 \leq x \leq 1$ denotes a volume fraction. Since a volume fraction is put forward, note that this modeling operates at a large, say macroscopic, scale. Moreover, x being a scalar, I will consider only two phases; indeed considering more phases implies some substantial difficulties (except in obvious symmetry related phases). Thus this modeling concerns the detwining of two variants of martensite (martensite may present *two* variants in the case of soda, neodynium pentaphosphate, wolfram, ...) or is appropriate to polycristalline alloys where the variants of martensite

are not told apart in the austenite-martensite mixture. Next, a free energy density function is defined by a function W of the state variables. At last, the phase transitions are assumed nondissipative, which seems rather realistic, so that the medium has a thermoelastic behavior with a stored energy density function

$$\overline{W}(\epsilon, T) \;=\; Inf\,\{\, W\,(\epsilon, T, x)\;,\; 0 \leq x \leq 1\,\}$$

Of course, the whole point is the choice of W ; at least two approaches lead to the category of modelings that I consider. The first approach, which models the medium as a generalized standard medium [10], splits the free-energy into three terms:

$$W(\epsilon, x, T) \;=\; W^e(\epsilon - xa, T) \;+\; xW^{ch}(T) \;+ W^{\phi}(x, T) \tag{1}$$

The first term is the thermoelastic one, xa being the phase transformation part of the total strain ϵ , while the second one concerns the latent heat exchange. The last one is the stored part due to internal changes, it is affected by the interactions between phases thus it has to be minimal and equal to 0 at $x = 0$ or $x = 1$. Obviously $x \in [0, 1] \;\longmapsto\; x(1-x)$ is a simple and smooth function which satisfies the previous conditions, so a proposal for W^{ϕ} is:

$$W^{\phi}(x, T) \;=\; \phi(T)\, x\,(1 - x) \quad,\; \phi \geq 0$$

Note that in [14], [15], [16], it is reported that $x\,(1 - x)$ is proportional to the expectation value of the interfacial area, if the phases are randomly distributed over the specimen ... Moreover, this modeling implicitly assumes that the elastic coefficients of the phase are equal, so this modeling confines to detwining.

The second approach regards the medium as a mixture such that the free energy may be a x-weighted combination of the energies $W^i,\; i = 1, 2$, of each phase. But, referring to homogenization, subtracting a term W^c , minimal and equal to 0 at $x = 0$ or $x = 1$, yields a better estimate:

$$W(\epsilon, x, T) \;=\; x\, W^1(\epsilon, T) \;+\; (1 - x)\, W^2(\epsilon, T) \;-\; W^c(x, T) \tag{2}$$

Once again, a convenient choice is

$$W^c(x, T) \;=\; c(T)\, x\,(1 - x) \quad,\; c \geq 0$$

Note that this approach does not assume the identity of the elastic laws of the two phases. From the mixture standpoint, another approach, which will be detailed in remark 3.1, leads to an expression like (1) in the case of two linearly elastic phases with identical elastic moduli. More deeply, this last assumption, *which will stand for all the sequel*, implies the identity of the two approaches. More precisely, I assume

$$W^i(\epsilon,T) = 1/2\alpha(\varepsilon - a_i(T)).(\varepsilon - a_i(T)) + w_i \qquad ,i = 1,2$$

where a_i is the stress-free strain of the i-th phase, w_i the associated minimum energy and α the tensor of elastic moduli, a positive symmetric linear map on the space S^3 of symmetric matrices. Then the obvious identity

$$x\,W^1(\epsilon,T) \;+\; (1-x)\;W^2(\epsilon,T) - \;c(T)\,x\,(1-x) \;\;=\;\; (3)$$

$$1/2\;\alpha\,(\epsilon - \bar{a}(T))\;\cdot\;(\epsilon - \bar{a}(T)) \;+\; \bar{w}(x,T) \;+\; \phi(T)\,x\,(1-x)$$

where

$$\bar{a} \;=\; x\,a_1 \;+\; (1-x)\,a_2 \quad , \quad \bar{w} \;=\; x\,w_1 \;+\; (1-x)\,w_2$$
$$\phi \;=\; 1/2\;\alpha\,a\cdot a \;-\; c \quad , \; a = a_2 \;-\; a_1$$

yields a single modeling where two equivalent expressions of the free energy are given by the two members of this identity!

It is not my purpose to list all the authors who, specifically or vaguely, proposed or discussed this modeling. Due to the many studies devoted to Shape Memory Alloys, it is impossible to be exhaustive. Generally, some information may be found in [2], [6]-[9], [13]-[17], [19] and in the references therein. My main thrust is to decide on the value of a nondissipative modeling where the free energy and the strain energy functions are :

$$W_\phi(\epsilon,x,T) = 1/2\alpha(\epsilon - \bar{a}(T))\cdot(\epsilon - \bar{a}(T)) + \bar{w}(T) + \phi(T)x(1-x)$$

$$= xW^1(\epsilon,T) + (1-x)W^2(\epsilon,T) - c(T)x(1-x), c = 1/2\alpha a.a - \phi \qquad (4)$$

and

$$\overline{W}_\phi(\,\epsilon,T\,) \;=\; Inf\,\{\,W_\phi\,(\epsilon,T,x)\;,\;0 \le x \le 1\,\} \qquad (5)$$

Clearly, from the first expression, ϕ non positive implies that W_ϕ is a convex function of the couple (ϵ,x) and, consequently, that $\overline{W}_\phi$ is a convex function of ϵ . But, as previously noted, ϕ negative does not seem plausible! ... Moreover, it is not difficult to see that $\overline{W}_\phi$ is a convex function in ϵ if ϕ is positive. In fact, it is not a disaster. I will show that if ϕ is positive, *but not too large*, the modeling is valuable... In the following technical discussions, temperature will only play a role of parameter, thus temperature dependence is suppressed hereafter.

3 (Quasi)convexity properties of $\overline{W}_\phi$

A mechanical interpretation of the mathematical theory of quasiconvexification [5], [18] may be : "at the macroscopic scale the behavior of a hyperelastic material is not governed by the true stored energy function but by an apparent one : its quasiconvexification, which is the infimum of those average energies that can be attained in deformations with a given average". Hence a first criterion of a good macroscopic modeling is the quasiconvexity property of the stored energy density function $\overline{W}$ which, in our case, may be read as :

$$\overline{W}(E) \;=\; Inf\left\{ 1/|U| \int_U \overline{W}(E+\epsilon(u))\,dy \;;\; u(y) \;=\; 0\, on\, \partial U \right\} \;,\; \forall\, E \in\; S^3$$

where the choice of the domain U is unimportant. Note that convexity implies quasiconvexity but the converse is generally false. Here are some (quasi)convexity properties of the strain energy function $\overline{W}_\phi$:

Theorem 3.1. *Let*

$$h = Min\left\{1/2\alpha(z-a)\cdot(z-a); z = k\otimes v + v\otimes k, k, v \in R^3\right\} \in [0, 1/2\alpha a\cdot a]$$

then

$\phi \leq 0$ *implies* $\overline{W}_\phi$ *is convex,*

$h > 0$ *and* $0 \leq \phi \leq h$ *implies* $\overline{W}_\phi$ *is not convex but quasiconvex,*

$h < \phi$ *implies* $\overline{W}_\phi$ *is not quasiconvex.*

Moreover, $\overline{W}_\phi$ *equals* $\overline{W}_{1/2\;\alpha a\cdot a}$ *if* $\phi \geq\; 1/2\,\alpha\, a\cdot a$.

As noted in [11], h differs from 0 if and only if the full transformation strain a is not a symmetrized tensor product, in other words if the two stress-free strains are not compatible. Thus if $h > 0$, it can be claimed that the modeling with $\phi \in [0, h]$, is a "good" macroscopic modeling, whereas only $\phi = 0$ yields a good modeling if $h = 0$!

Proof of theorem 3.1. Several arguments of [11] pp 201-203 are used without giving details. First, in the definition of quasiconvexity, a unit cell Y and periodicity conditions may be used in place of U and Dirichlet conditions. Standard results on mesurable selections imply :

$$\begin{aligned} I &:= Inf\left\{ \int_Y \overline{W}_\phi(E+\epsilon(u))\,dy \;;\; u \in C^1_{per}(\bar{Y}) \right\} \\ &= Inf\left\{ \int_Y W_\phi(E+\epsilon(u),\theta(y))\,dy; u \in C^1_{per}(\bar{Y}), \theta \in B(Y) \right\} \end{aligned}$$

where $B(Y) := \{\theta \in L^\infty(Y); 0 \le \theta \le 1\}$. An elementary calculation using the second expression of W_ϕ in (4) gives

$$I = Inf\left\{ m\,W^1(E) + (1-m)\,W^2(E) - cm + J(m)\ ;\ 0 \le m \le 1 \right\},$$

$$J(m) = Inf\{ \int_Y c\theta^2 + 1/2\,\alpha\,\epsilon(u)\cdot\epsilon(u) + \theta\,\alpha\,\epsilon(u)\cdot a\,;$$
$$u \in C^1_{per}(\bar{Y}), \theta \in B(Y), \int_Y \theta = m\}.$$

As in [11] p. 202, Fourier analysis yields

$$J(m) \ge Inf\{ cm^2 + (h-\phi)\sum_{k\neq 0}\hat{\theta}(k)^2;$$
$$y \in Y \mapsto \theta(y) = \sum_{k\in Z^3}\hat{\theta}(k)\,e^{2i\pi k\cdot y} \in B(Y)\}$$

which proves the quasiconvexity of $\overline{W}_\phi$ if $0 \le \phi \le h$.

Clearly, (4), (5) imply that $\overline{W}_{\phi_1} \ge \overline{W}_{\phi 2}$ if $\phi_1 > \phi_2$, and that $\overline{W}_\phi = \overline{W}_{1/2\alpha a.a} = Min\,(W^1, W^2)$ if $\phi \ge 1/2\alpha a\cdot a$. Moreover, it is shown in [11] that the quasiconvexification and the convexification of $Min\,(W^1, W^2)$ are respectively $\overline{W}_h$ and $\overline{W}_0$. Thus, $\overline{W}_\phi$ is not convex if $0 < \phi$ and is not quasiconvex if $h < \phi$, because quasiconvexification and convexification preserve the order.

Remark 3.1. A rough way to define the strain energy function of a mixture of two phases described by the energy density functions W^i , in proportions x and (1-x), is to consider

$$W_a^{mix}(\epsilon, x) = Inf\left\{ x\,W^1(\epsilon^1) + (1-x)\,W^2(\epsilon^2)\ ;\ x\,\epsilon^1 + (1-x)\,\epsilon^2 = \epsilon \right\}$$

With W^i as in (3), it is shown in [11] that

$$W_a^{mix}(\epsilon, x) = W_0(\epsilon, x) = 1/2\ \alpha\,(\epsilon - \bar{a}(x))\cdot(\epsilon - \bar{a}(x)) + \bar{w}(x)$$

Thus, as announced previously, in order to account for interactions at a macroscopic level, some modelings ([6]-[9], [13]-[16], [19]) add a term depending on x, vanishing at x = 0,1. Their common proposal is $\phi\,x\,(1-x)$, hence they get W_ϕ as free energy density function for the medium! However, the previous definition W_a^{mix} presupposes constant and compatible strains in each phase, which is open to criticism. A better definition is

$$W_b^{mix}(\varepsilon, x) = Inf\ \{1/|Y| \int_Y \chi_x(y) W^1(\varepsilon(u)) + (1-\chi_x(y)) W^2(\varepsilon(u)) dy;$$
$$\chi_x\ characteristic\ function\ \int_Y \chi_x(y)dy = x|Y|, u(y) = \varepsilon y\ on\ \partial Y\}$$

It is proved in [11] that $W_b^{mix} = W_h$. Hence, adding a macroscopical term of interaction $Ix(1-x)$ yields a free energy equal to W_{h+I}. Then the quasiconvexity criterion of good modeling implies that I must be non positive. This sign, which is the opposite of what is widely used in the literature, corresponds exactly to what in [4] is termed, through microscopic considerations, mismatch energy.

4 Double-well like structure of $\overline{W}_\phi$ and experiments

From now on, I confine to the more interesting case $0 < \phi \leq h$ and will show that the lack of convexity of $\overline{W}_\phi$ accounts for some experimental results, which also guarantees a good modeling. Let

$$w = w_1 - w_2 \ , \ H_1 = \{e \in S^3; \ \ \alpha(e - a_1).a = w\}$$

Some elementary manipulations, as in [11] pp. 205-207, provide the following geometric properties of the graph of $\overline{W}_\phi$:

Proposition 4.1. *$\overline{W}_\phi$ is piecewise quadratic and differentiable on* S^3. *If $|w| > \phi$, $\overline{W}_\phi$ has only one absolute minimizer: a_1 (resp. a_2) if $w > \phi$ (resp. $w < -\phi$), and no other relative minimizers. If $|w| \leq \phi$, $\overline{W}_\phi$ has exactly two relative minimizers a_1 and a_2 : a_1* (resp. a_2) *is an absolute minimizer if and only if $w \geq 0$ (resp. $w \leq 0$).*

Proposition 4.2. *For each e_1 of H_1 , the function $\overline{W}_\phi - \Sigma_1 \cdot$, with $\Sigma_1 = \alpha\,(e_1 - a_1)$, has exactly two absolute minimizers e_1 and $e_2 = e_1 + a$.*

Since $\overline{W}_\phi$ is differentiable, the previous properties can be interpreted in terms of stress and strain. First, it appears that along all straight paths ϵ_Δ in the strain space S^3, $t \in R \longmapsto \epsilon_\Delta(t) = \epsilon_0 + t\,a$, *parallel to a*, the derivative of the energy $\overline{W}_\phi(\epsilon_\Delta(t))$ is not monotone. In other words, "the stress-strain relation is not monotone along ϵ_Δ ". Thus it should be of interest to do such strain controlled tests which must be *isothermal and biaxial* (in this direction see [6], [14], [15]). These hard device tests seem difficult to do, conversely it is easier to do isothermal and biaxial loading experiments [3]. Leaving hysteresis considerations aside, it seems clear that two different equilibrium configurations may occur when a specimen of shape memory alloy is subjected to certain uniform biaxial extension loadings. The present modeling may account for this fact. If Ω is a reference configuration of the specimen and n the unit outward normal to $\partial\Omega$, the total energy read as

$$I_\Sigma(v) = \int_\Omega \overline{W}_\phi(\epsilon(v))\,dx - \int_{\partial\Omega} \Sigma n.v\,ds = \int_\Omega \overline{W}_\phi(\epsilon(v)) - \Sigma \cdot \epsilon(v)\ dx$$

The previous propositions make it possible to use the arguments in [12] pp 82-83 and to prove the following *metastability* theorem :

Theorem 5.1. *For every $e_1 \in H_1$, there exists $\delta > 0$ such that for every Σ in a ball in S^3 of center $\Sigma_1 = \alpha\,(e_1 - a_1)$ and radious δ , the*

functional I_Σ has two distinct L^1 -local minimizers (one of them being an absolute minimizer in $H^1(\Omega)^3$). As Σ goes to Σ_1 , they converge strongly in L^1 towards "$x \longmapsto e_1 x$" and "$x \longmapsto (e_1 + a)\, x$" , absolute minimizers of I_{Σ_1} in $H^1(\Omega)^3$.

The L^1 topology is rough : in L^1 neighborhoods the displacements are near in the mean, but their strains may be very remote. These local, but non absolute, minimizers may be observed, they correspond to metastable equilibrium configurations : experimentalists [3] report that specimen can undergo large deformations from an equilibrium configuration to another one only by slightly hitting the strings of the device or through a small disturbance in the room. A similar metastability analysis, in the more difficult framework of finite strains, may be found in [1].

5 Conclusion

I believe that all the foregoing arguments clearly show that the considered modeling is coherent and able to account some phenomena involved by phase transitions in crystalline solids. According to remark 3.1, a nice introduction of this phenomenological and macroscopic modeling is adding a rational micro-macro definition of the energy function of a mixture to a woolly termed function, $I\, x\, (1 - x)$, $I \leq 0$, of the volume fraction x of one phase. It should be interesting to derive this last term through a rational scale transition that, for instance, takes into account micro-scale surface interactions.

Eventually, I thank my friend C. Lexcellent who told me about some pertinent earlier works.

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