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On the elastic stability of a strained solid and the localized soft-mode theory

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Abstract. We have studied the elastic stability of an arbitrary equilibrium state of a homogeneous solid when Lagrangian parameters are used. We first introduce the notion of subrepresentation (SR) and we show how the passage from one SR to another can be easily described by a 'passage matrix'. The equation determining the 'strain spinodal' is then obtained in terms of this passage matrix and it is demonstrated that an inflection point on the free-energy surface in Lagrangian parameter spaces does not necessarily correspond to an elastic instability of the solid. These results are finally applied to the localized soft-mode theory, showing the existence of an important harmonic contribution to the strain renormalization of the second-order elastic constants, which has been entirely neglected by Clapp and subsequent workers. For some alloys, the numerical values prove that this harmonic contribution tends to stabilize the lattice but not enough to compensate the anharmonic effects, and therefore Clapp's model is still likely to be valid.

1. Introduction

An equilibrium state of a solid (assumed to be without electric or magnetic properties) can be thermodynamically described by the temperature T and the Lagrangian strain parameters (LSPS) η_{ij} evaluated from a certain reference configuration, for instance that which is established at the temperature T and at zero applied stress. Associated with each equilibrium state there is then a pair (η_{ij}, T) and vice versa.

All such equilibrium states are not stable (or metastable) states. So their stability towards small additional deformations at a fixed temperature T (*mechanical stability*) can be questioned. Of course, the answer to this depends upon the type of additional deformations under consideration. Here, we restrict ourselves to homogeneous fluctuations (*elastic stability*). Furthermore, the types of configuration of the system to be dealt with in this paper are only those corresponding to homogeneous states of the solid. It is then possible to consider a geometrical representation in which all the states involved are represented by points in a six-dimensional space of LSPS.

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The purpose of the present article is to establish the equation determining the corresponding 'strain spinodal' in such space. We show how the peculiarities of the LSPs lead to a new equation in which not only the second-order derivatives matrix of the free energy but also a 'passage matrix' appear.

The paper is organized as follows. First, in section 2, we reformulate the finite-deformation thermodynamic theory of a stressed solid developed by Wallace (1967, 1970, 1972) in a somewhat more formal way by introducing the notion of subrepresentation (SR) (of the Helmholtz representation) and suitable matrix notation. The elastic stability criteria will then be formulated in section 3, first in a general case and next in two particular cases (namely the microscopic case developed by Milstein (1971) and the case using the Lagrangian macroscopic description) in order to emphasize the difference between them.

Finally, in the last section (section 4), we reconsider the localized soft-mode theory described by Clapp (1973) and further developed by other workers (Guénin and Gobin 1982a, b, Guénin and Clapp 1986, Verlinden and Delaey 1986) to explain the nucleation process in thermoelastic martensitic transformations. It is shown that the strain renormalization of the second-order elastic constants (SOECs) and the stability criteria used by these researchers are in disagreement with the equations developed in the previous sections. These equations are then applied to calculate this renormalization and the critical strains for a Bain distortion and a $(011)[0\bar{1}1]$ shear, and the new results are compared with those obtained using Clapp's method. In particular, the influence of harmonic terms on the elastic stability are accounted for. Numerical values are presented for some alloys, for which third-order elastic constants (TOECs) are available (Verlinden *et al* 1984, Swartz *et al* 1975, Nagasawa *et al* 1982).

2. Notion of subrepresentation and the passage matrix

Let us denote by $\{x\}$ an arbitrary configuration of the solid ($\{x\}$ represents the whole set of positions of all the particles) and by $F(\{x\}, T)$ the corresponding Helmholtz free energy in the state $(\{x\}, T)$ (Helmholtz representation). In fact, it is well known that F does not depend on the positions $\{x\}$ of all the particles. In particular, it can be seen (Wallace 1970) that, for a given reference configuration $\{x^r\}$ and whenever the deformation involved in the 'movement' $\{x^r\} \rightarrow \{x\}$ is homogeneous or at most weakly inhomogeneous, the free energy F is a function only of the LSPs $\eta_{ij}(\{x\})$ $(i, j = 1, 2, 3)$ of the configuration, defined as

$$\eta^r_{ij}(\{x\}) = \tfrac{1}{2}[\alpha^r_{ki}(\{x\})\alpha^r_{kj}(\{x\}) - \delta_{ij}] \qquad i, j = 1, 2, 3 \tag{1}$$

where

$$\alpha^r_{ij}(\{x\}) = \partial x_i / \partial x^r_j \tag{2}$$

and where we have used the superscript r to indicate the dependence on the configuration taken as reference†. Hence, for all $\{x\}$ satisfying the above condition, it can be written that

$$F(\{x\}, T) = F_r(\eta^r_{ij}(\{x\}), T). \tag{3}$$

In such a way, we may construct an infinite number of free energy *functions*

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† In this paper, we always make use of the Einstein summation convention, implying a sum over repeated indices. Moreover, we use complete notation as well as Voigt notation for the Lagrangian parameters and all the properties deduced from these.

$F_r(\eta^r_{ij}, T)$ (one for each reference configuration r) whose dependence on the respective η^r_{ij} will be different for different values of r. By analogy with the notion of representation in classical thermodynamics, we shall speak of the different *subrepresentations* SR r (of the Helmholtz representation). Thus, associated with the r SR there will be a LSP space $(\boldsymbol{\eta}^r)$ and a free-energy surface $F_r(\boldsymbol{\eta}^r, T)$ in such space. Particularly important for its extended use is the SR which we shall call $r = 0$ and define as that where the LSPs are referred to the equilibrium configuration $\{\boldsymbol{x}^0\}$ at zero applied stress (undeformed state).

It follows from equation (3) that the expression of all the properties of the solid in an arbitrary equilibrium state $(\{\boldsymbol{x}\}, T)$ as functions of the parameters $\boldsymbol{\eta}^r$ will lead once more to different results in each SR. Thus, if P denotes any such property, we shall have

$$P(\{\boldsymbol{x}\}, T) = P_r(\boldsymbol{\eta}^r(\{\boldsymbol{x}\}), T). \tag{4}$$

In particular, this is true for the stress 'vector' $\boldsymbol{\sigma}$ and the SOEC matrix $\mathbf{C}'$. For a fixed temperature T, the values of these properties in a given configuration $\{\boldsymbol{x}^i\}$[†] are usually obtained as the gradient and the curvature matrix, respectively, of the free-energy density[‡] surface at the corresponding point $\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\})$:

$$\boldsymbol{\sigma}(\{\boldsymbol{x}^i\}, T) = \boldsymbol{F}_r(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T) = \rho_r(T)\boldsymbol{f}_r(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T) \tag{5}$$

$$\mathbf{C}(\{\boldsymbol{x}^i\}, T) = \mathbf{F}_r(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T) = \rho_r(T)\mathbf{f}_r(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T) \tag{6}$$

where $\boldsymbol{f}_r(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T)$ and $\mathbf{f}_r(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T)$ are the gradient and the curvature matrix, respectively, of $f_r(\boldsymbol{\eta}^r, T)$ (Helmholtz free energy per unit mass) at $\boldsymbol{\eta}^r = \boldsymbol{\eta}^r(\{\boldsymbol{x}^i\})$ and $\rho_r(T) \equiv \rho(\{\boldsymbol{x}^r\}, T)$ is the volume density.

It should be emphasized, however, that this is not true in all SRs. Indeed, Wallace (1970, 1972) shows that, stated in our SR language, the expression in the r SR (whatever r) of the equilibrium stress tensor in the state $(\{\boldsymbol{x}^i\}, T)$ is

$$\begin{aligned}\sigma_{kl}(\{\boldsymbol{x}^i\}, T) &= \sigma^r_{kl}(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T)\\ &= \rho_i(T)\alpha^r_{km}(i)\alpha^r_{ln}(i)[\partial f_r(\boldsymbol{\eta}^r, T)/\partial \eta^r_{mn}]|_{\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\})} \qquad \forall r\end{aligned} \tag{7}$$

$(\alpha^r_{km}(i) \equiv \alpha^r_{km}(\{\boldsymbol{x}^i\}))$ and that this equation reduces to equation (5) when $r = i$, i.e. when the free-energy function used is precisely that which depends on the LSPs evaluated from the configuration $(\{\boldsymbol{x}^i\}, T)$. It follows then that *only* the form of the surface F_i[‡] in the neighbourhood of the origin provides *directly* the properties of the solid in the state $(\{\boldsymbol{x}^i\}, T)$. We shall call the corresponding SR the 'good' SR to study this state. In this SR, the SOEC matrix of the solid in the state $(\{\boldsymbol{x}^i\}, T)$ is directly equal to the curvature matrix of the corresponding surface F_i whereas in an arbitrary SR r it will be given by the equation (Wallace 1967)

$$\begin{aligned}C_{ijkl}(\{\boldsymbol{x}^i\}, T) &= C^r_{ijkl}(\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\}), T)\\ &= \rho_i(T)\alpha^r_{im}(i)\alpha^r_{jn}(i)\alpha^r_{kp}(i)\alpha^r_{lq}(i)[\partial^2 f_r(\boldsymbol{\eta}^r, T)/(\partial\eta^r_{mn}\,\partial\eta^r_{pq})]|_{\boldsymbol{\eta}^r(\{\boldsymbol{x}^i\})} \qquad \forall r.\end{aligned} \tag{8}$$

[†] In what follows, we shall distinguish the equilibrium configuration under study by the superscript i, whereas r will always refer to the arbitrary reference state. In particular, r may represent the same state i.

[‡] In this section, F stands for a Helmholtz free-energy density (per unit volume of a reference state). The reference state is taken as the state $(\{\boldsymbol{x}^r\}, T)$ when we deal with the r SR.

One can also write the above equations in matrix notation. Indeed, let us introduce the coefficients $A^{(r,s)}_{ijkl}$, defined by

$$A^{(r,s)}_{klij} = \tfrac{1}{2}[\alpha^{s}_{ki}(r)\alpha^{s}_{lj}(r) + \alpha^{s}_{kj}(r)\alpha^{s}_{li}(r)] \tag{9}$$

where $r \equiv \{\boldsymbol{x}^{r}\}$ and $s \equiv \{\boldsymbol{x}^{s}\}$ denote two arbitrary reference configurations. They have the symmetry properties

$$A^{(r,s)}_{klij} = A^{(r,s)}_{klji} = A^{(r,s)}_{lkij} = A^{(r,s)}_{lkji} \tag{10}$$

and therefore they may be written in Voigt notation according to the relations

$$\begin{aligned} A^{(r,s)}_{ijkl} &\equiv A^{(r,s)}_{IK} \qquad && \text{if } I = 1, \ldots, 6 \text{ and } K = 1, 2, 3 \\ 2A^{(r,s)}_{ijkl} &\equiv A^{(r,s)}_{IK} \qquad && \text{if } I = 1, \ldots, 6 \text{ and } K = 4, 5, 6. \end{aligned} \tag{11}$$

These new coefficients define a 6 × 6 and in general non-symmetric matrix which we shall denote by $\mathbf{A}(r, s)$. In terms of this matrix, the relation between the LSPs of a given configuration $\{\boldsymbol{x}\}$ in two arbitrary SRs r and s can be written as

$$\boldsymbol{\eta}^{s}(\{\boldsymbol{x}\}) = \mathbf{A}(r, s)\boldsymbol{\eta}^{r}(\{\boldsymbol{x}\}) + \boldsymbol{\eta}^{s}(\{\boldsymbol{x}^{r}\}) \qquad \forall\{\boldsymbol{x}\} \tag{12}$$

and then it may be called the 'passage matrix' from the r SR to the s SR; it describes the transformation to be applied to one LSP space to get the other and, consequently, the deformation relating both surfaces F_r and F_s. From the symmetry properties of the stress tensor and of the LSPs it then follows that both equation (7) and equation (8) can be written in terms of the 'passage matrix' $\mathbf{A}(i, r)$, leading to the relations

$$\begin{aligned} \boldsymbol{\sigma}(\{\boldsymbol{x}^{i}\},T) &= \rho_i(T)\mathbf{A}(i, r)\boldsymbol{f}_r(\boldsymbol{\eta}^{r}(\{\boldsymbol{x}^{i}\}), T) \\ &= [\rho_i(T)/\rho_r(T)]\mathbf{A}(i, r)\,\boldsymbol{F}_r(\boldsymbol{\eta}^{r}(\{\boldsymbol{x}^{i}\}), T) \qquad \forall r \end{aligned} \tag{13}$$

and

$$\begin{aligned} \mathbf{C}(\{\boldsymbol{x}^{i}\}, T) &= \rho_i(T)\mathbf{A}(i, r)\mathbf{f}_r(\boldsymbol{\eta}^{r}(\{\boldsymbol{x}^{i}\}), T)\mathbf{A}(i, r)^{\mathrm{T}} \\ &= [\rho_i(T)/\rho_r(T)]\mathbf{A}(i, r)\mathbf{F}_r(\boldsymbol{\eta}^{r}(\{\boldsymbol{x}^{i}\}), T)\mathbf{A}(i, r)^{\mathrm{T}} \qquad \forall r \end{aligned} \tag{14}$$

(the superscript T denotes the transposition matrix operation). Consequently, the SOEC matrix of the solid in the state $(\{\boldsymbol{x}^{i}\}, T)$ is obtained from the curvature matrix $\mathbf{F}_r(\boldsymbol{\eta}^{r}(\{\boldsymbol{x}^{i}\}), T)$ only after appropriate transformation via the passage matrix, which introduces also a dependence on the strain (from r to i). Note that equation (14), which is completely equivalent to equation (7), is exact. As done in section 4, however, approximations are usually necessary to evaluate the matrix $\mathbf{F}_r$ at $\boldsymbol{\eta}^{r}(\{\boldsymbol{x}^{i}\})$.

It is easy to verify that $\mathbf{A}(r, s)$ reduces to the identity matrix whenever $r = s$ and then, when $r = i$, equations (13) and (14) read

$$\boldsymbol{\sigma}(\{\boldsymbol{x}^{i}\}, T) = \rho_i(T)\boldsymbol{f}_i(\boldsymbol{\eta}^{i} = 0, T) \tag{15}$$

$$\mathbf{C}(\{\boldsymbol{x}^{i}\}, T) = \rho_i(T)\mathbf{f}_i(\boldsymbol{\eta}^{i} = 0, T) \tag{16}$$

in good agreement with the above-mentioned results.

In the following section, it will be seen how the use of the passage matrix not only simplifies the notation but also provides a simple test to determine whether or not all SRS are equivalent so far as the elastic stability of an arbitrary state is concerned.

3. Elastic stability of an arbitrary equilibrium state; determination of the 'strain spinodal'

Let us first consider the case of arbitrary configurational variables, denoted by the vector $X = (X_1, \ldots, X_n)$ and assumed to be independent of the point (homogeneous system). Obviously, $X = X(\{x\})$. The Helmholtz free energy is then $F = F(X, T)$. Related to such variables X, we have a set of conjugated forces $Y = (Y_1, \ldots, Y_n)$ which at equilibrium will be functions only of X and T and which represent the forces to be applied on the solid (by an external agency) in order to keep it at equilibrium in the configuration X and at temperature T. More precisely,

$$Y_0 \equiv Y^{\mathrm{eq}}(X_0, T) = F(X_0, T) \tag{17}$$

where $F(X_0, T)$ is the gradient of the surface $F(X, T)$ (for a fixed temperature T) at X_0.

The condition for the equilibrium state (X_0, T) to be elastically stable (at constant temperature and applied forces) is that the Gibbs free-energy functional surface $G(X; Y_0, T)$ (in the X-space) defined as

$$G(X, T) = F(X, T) - Y_0 \cdot X \tag{18}$$

has a minimum at X_0 (Y_0 and T remaining constants). As is well known, this condition is equivalent to the positive definite character of the curvature matrix $\mathbf{F}(X, T)$ of the (thermodynamic) Helmholtz free-energy surface $F(X, T)$ (for a fixed T) at X_0:

$$\mathbf{F}(X, T) = [\nabla_x \cdot (\nabla_x F)^{\mathrm{T}}](X, T). \tag{19}$$

So, if $\mathbf{F}$ (from now on called the stability matrix) is positive definite at a point X, the free-energy surface is convex in the neighbourhood of this point and the equilibrium state (X, T) is stable. Otherwise, it will be instable. Between both extreme cases, there are a set of points X where F has an inflection point (along one or probably various directions, called instability directions). The whole set of these points will constitute the 'elastic configurational spinodal' which will be obtained as the solution of

$$\det[\mathbf{F}(X, T)] = 0. \tag{20}$$

This equation divides X-space into different stability domains separated by instability regions. Inside each of the stability domains there will be a minimum of F corresponding to a stable (or metastable) phase at zero applied stress; equation (20) then determines the limiting stability surface (obviously a function of the temperature T) for each of such phases.

Let us now contemplate two particular cases of the above general formulation, corresponding to two sets of configurational variables X essentially different in nature.

In the first case (Milstein 1971), the variables X are taken to be the variables a_i ($i = 1, \ldots, 6$) that describe the unit cell of the solid. Furthermore, it is assumed that $T = 0$ K so that the interatomic potential energy $E(\boldsymbol{a})$ plays here the role of the Helmholtz free energy $F(X, T)$. The general equilibrium and stability conditions formulated above then reduce to those established by Milstein (equations (2) and (6), (7) in his paper), his F standing for our Y and his matrix $\mathbf{B}$ for our stability matrix $\mathbf{F}$. In this case, we have just one set of parameters $\boldsymbol{a}$, surface $E(\boldsymbol{a})$ describes properly all the states and the 'elastic configurational spinodal' is directly obtained as the solution of equation (20) when $\mathbf{F}(X, T)$ is substituted by $\mathbf{E}(\boldsymbol{a}) = \mathbf{B}(\boldsymbol{a})$. So, Milstein studies elastic stability along a particular path in the $\boldsymbol{a}$-space *by looking for inflection points on the surface* $E(\boldsymbol{a})$.

Now, let us consider the thermodynamical approach in terms of the LSP $\boldsymbol{\eta}$. As in section 2, F now stands for a free-energy density. The conjugated forces are then the stress vector components σ_I and the stability matrix $\mathbf{F}$ is the SOEC matrix $\mathbf{C}$. The condition for the state $(\{x\}, T)$ to be elastically stable therefore reduces to the positive character of $\mathbf{C}$. As pointed out in section 2, this matrix in the arbitrary r SR is not equal to $\mathbf{F}_r$, but it is related to this matrix after appropriate transformation, as stated in equation (14). Thus, the true stability matrix in the 0 SR, for example, which we shall denote by $\mathbf{F}'_0(\boldsymbol{\eta}^0, T)$, is†

$$\mathbf{F}'_0(\boldsymbol{\eta}^0(\{x^i\}), T) = \mathbf{A}(i, 0)\mathbf{F}_0(\eta^0(\{x^i\}), T)\mathbf{A}(i, 0)^{\mathrm{T}} \tag{21}$$

and so the 'elastic configurational spinodal' in the $\boldsymbol{\eta}^0$-space (usually called the 'strain spinodal') is not obtained as the solution of equation (20) with $\mathbf{F}(X, T) \rightarrow \mathbf{F}_0(\boldsymbol{\eta}^0, T)$ but as the solution of

$$\det[\mathbf{F}'_0(\boldsymbol{\eta}, T)] = \det[\mathbf{A}(i, 0)\mathbf{F}_0(\boldsymbol{\eta}^0, T)\mathbf{A}(i, 0)^{\mathrm{T}}] = 0 \tag{22}$$

where the matrix $\mathbf{A}$, like $\mathbf{F}_0$, is a function of the point in the $\boldsymbol{\eta}^0$-space.

Obviously, the difference between $\mathbf{F}'_0$ and $\mathbf{F}_0$ is unimportant, so far as the stability of a state is concerned, if the eigenvalues of both matrices are equal. From equation (22), the condition for this to be true reduces to the orthogonality property of the passage matrix $\mathbf{A}(i, 0)$ for all configurations $\{x^i\}$, i.e.

$$\mathbf{A}(i, 0)^{\mathrm{T}}\mathbf{A}(i, 0) = \mathbf{A}(i, 0)\mathbf{A}(i, 0)^{\mathrm{T}} = \mathbf{I} \tag{23}$$

where $\mathbf{I}$ is the 6 × 6 identity matrix. In this case, the free-energy functions f_i and f_0 would be simply related by a translation to a new origin followed by a rotation (see equation (12)). It may be verified in a simple case, however, that condition (23) is not always fulfilled, showing that the surface f_0 must actually be deformed to obtain the new surface f_i.

We conclude that, to study the elastic stability of a state in this approach, the 'good' SR must be used. Otherwise, if one works in a fixed but arbitrary SR, the corresponding passage matrix must be taken into account, relating the stability matrix to the curvature matrix of the corresponding free-energy function. In particular, the presence of this matrix makes it possible to have an inflection point on the surface $F_0(\boldsymbol{\eta}^0, T)$ which, however, *does not represent an elastic instability of the solid.*

In the next section, these results are applied to the localized soft-mode theory (Clapp 1973) and we discuss the inaccuracy of Clapp's method to calculate the strain spinodal.

4. Effect on the localized soft-mode theory

The localized soft-mode theory, first introduced by Clapp (1973), is a model which intends to render negligible the shape change contribution to the nucleation barrier in a thermoelastic martensitic transformation. The essential idea of the model lies in the fact that the elastic stability of a solid in a given state may be strongly influenced by the

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† Note that the factor $\rho_i(T)/\rho_0(T)$ will be important only when one calculates explicitly the values of the elastic constants.

existence of internal strains (such as internal defects or surfaces). Moreover, Clapp postulates that the 'strain spinodal' in the η^0-space (0 SR) is sufficiently close to the origin to make the existence of critical strains in the solid (beyond which it would become instable) energetically plausible. In order to verify this hypothesis, Clapp calculates the SOECs for the states $(\{x\}, T)$ lying near the origin $\eta^0 = \mathbf{0}$ in terms of the strain $\eta^0(\{x\})$ and the TOECs in the undeformed state and then proceeds to study the solutions of the equation

$$\det[\mathbf{C}_0(\eta^0, T)] = 0 \tag{24}$$

which indeed determines the strain spinodal in this space.

Nevertheless, Clapp and subsequent workers (Guénin and Gobin 1982a, b, Verlinden *et al* 1984, Verlinden and Delaey 1986) further assume *a priori* that the Helmholtz free-energy surface $F_0(\eta^0, T)$ in the 0 SR directly describes the character of all the states in the same way as the surface $E(\boldsymbol{a})$ of Milstein's treatment. Thus, the SOEC matrix of the solid in an arbitrary state $(\eta^0 = \boldsymbol{n}, T)$ is taken as the curvature matrix $\mathbf{F}_0(\eta^0, T)$ at this point:

$$\mathbf{C}_0(\eta^0 = \boldsymbol{n}, T) = \mathbf{F}_0(\eta^0 = \boldsymbol{n}, T) = \rho_0(T)\mathbf{f}_0(\eta^0 = \boldsymbol{n}, T). \tag{25}$$

As shown in the preceding section, however, this is true *only* when $\boldsymbol{n} = \mathbf{0}$, the correct general expression being that obtained from equation (14). This leads the above-mentioned workers to a wrong strain renormalization of the SOECs and consequently also to a wrong stability criterion.

In order to be explicit about the effect of the inaccurate treatment followed up to now, we have reconsidered both points, especially the stability criterion since it determines whether or not the model is plausible. Of course, the value of the critical strain depends on the direction in η^0-space that one takes. We have studied two cases: the case of a Bain strain, which according to Clapp (1973) turns out to be the most unstable type of strain, and a $(011)[0\bar{1}1]$ shear proposed by Guénin (1979) as the strain playing the most important role in the local softening of the solid when it undergoes a thermoelastic martensitic transformation. Here we shall develop only the latter case.

Let us then return to equation (14), with $r = 0$, and make $i = 1$ so that $\{x^1\}$ will denote the strained state. From equations (9) and (11), it follows that the passage matrix for a $(011)[0\bar{1}1]$ shear is given by

$$\mathbf{A}(1,0) = \mathbf{A}(\beta) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & (1-\beta)^2 & \beta^2 & -2\beta(1-\beta) & 0 & 0 \\ 0 & \beta^2 & (1+\beta)^2 & 2\beta(1+\beta) & 0 & 0 \\ 0 & \beta(1-\beta) & -\beta(1-\beta) & 1-2\beta^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1+\beta & \beta \\ 0 & 0 & 0 & 0 & -\beta & 1-\beta \end{bmatrix} \tag{26}$$

where $\beta = \beta'/2$ and β' denotes the shear amplitude. Now, we assume that the strain spinodal is indeed located near the origin so that all calculations are done to first order in the deformation parameter. Then, for a sufficiently small β, this matrix becomes

$$\mathbf{A}(\beta) \simeq \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1-2\beta & 0 & -2\beta & 0 & 0 \\ 0 & 0 & 1+2\beta & 2\beta & 0 & 0 \\ 0 & \beta & -\beta & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1+\beta & \beta \\ 0 & 0 & 0 & 0 & -\beta & 1-\beta \end{bmatrix}. \tag{27}$$

Furthermore, in order to evaluate the matrix $\mathbf{F}_0$ at $\boldsymbol{\eta}^0(\{\boldsymbol{x}^1\})$, we assume, following Clapp, that $F_0(\boldsymbol{\eta}^0, T)$ can be represented by a Taylor expansion in a neighbourhood of the origin and then $\mathbf{F}_0(\beta, T)$ is obtained in terms of the SOECs and TOECs of the solid in the undeformed state, higher-order terms being neglected because they give rise to second-order contributions in β. In this way, assuming that the crystal is cubic in the undeformed state, Guénin (1979) obtains the following coefficients for this matrix ($\beta \equiv -\varepsilon/2$):

$$\begin{aligned} F^0_{11} &= C^0_{11} \\ F^0_{12} &= F^0_{21} = C^0_{12} + (\varepsilon/2)(C^0_{112} - C^0_{123}) \\ F^0_{13} &= F^0_{31} = C^0_{12} - (\varepsilon/2)(C^0_{112} - C^0_{123}) \\ F^0_{22} &= C^0_{11} + (\varepsilon/2)(C^0_{111} - C^0_{112}) \\ F^0_{23} &= F^0_{32} = C^0_{12} \\ F^0_{33} &= C^0_{11} - (\varepsilon/2)(C^0_{111} - C^0_{112}) \\ F^0_{44} &= C^0_{44} \\ F^0_{55} &= C^0_{44} + (\varepsilon/2)(C^0_{144} - C^0_{166}) \\ F^0_{66} &= C^0_{44} - (\varepsilon/2)(C^0_{144} - C^0_{166}) \\ &\text{and all remaining coefficients equal to zero} \end{aligned} \tag{28}$$

which define a matrix with orthorhombic symmetry. In Clapp's method, this matrix would already be the SOEC matrix of the solid after the shear strain and so the strain renormalization is attributed to anharmonic terms. The critical strain ε_c would then be obtained as a solution of equation (24), yielding as the most critical condition (Guénin 1979)

$$(C^0_{11} - C^0_{12})^2(C^0_{11} + 2C^0_{12}) + (\varepsilon_c^2/4)[4abC^0_{12} - a^2C^0_{11} - 2(C^0_{11} + C^0_{12})b^2] = 0 \tag{29}$$

where $a \equiv C^0_{111} - C^0_{112}$ and $b \equiv C^0_{112} - C^0_{123}$.

Let us now consider separately the strain renormalization of the SOECs and the stability criterion as given by the present method.

4.1. *Strain renormalization of the second-order elastic constants*

From the equation of continuity (Wallace 1970) we have

$$\rho_1(T)/\rho_0(T) = 1/\det[\boldsymbol{\alpha}^0(\{\boldsymbol{x}^1\})] = 1 \tag{30}$$

which corresponds to the zero volume change of the shear. Then, to first order in ε, use of equations (14), (27) and (28) leads to the following elastic constants:

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\begin{aligned}
C_{11} &= C^0_{11} \\
C_{12} = C_{21} &= C^0_{12} + (\varepsilon/2)(2C^0_{12} + C^0_{112} - C^0_{123}) \\
C_{13} = C_{31} &= C^0_{12} - (\varepsilon/2)(2C^0_{12} + C^0_{112} - C^0_{123}) \\
C_{22} &= C^0_{11} + (\varepsilon/2)(4C^0_{11} + C^0_{111} - C^0_{112}) \\
C_{23} = C_{32} &= C^0_{12} \\
C_{24} = C_{42} &= (\varepsilon/2)(C^0_{11} - C^0_{12})(A - 1) \\
C_{33} &= C^0_{11} - (\varepsilon/2)(4C^0_{11} + C^0_{111} - C^0_{112}) \\
C_{34} = C_{43} &= -(\varepsilon/2)(C^0_{11} - C^0_{12})(A - 1) \\
C_{44} &= C^0_{44} \\
C_{55} &= C^0_{44} - (\varepsilon/2)(2C^0_{44} + C^0_{166} - C^0_{144}) \\
C_{66} &= C^0_{44} + (\varepsilon/2)(2C^0_{44} + C^0_{166} - C^0_{144}) \\
&\text{and all remaining coefficients equal to zero}
\end{aligned} \tag{31}
$$

where A is the anisotropy constant of the solid in the initial undeformed state.

Comparison between equations (28) and (31) shows immediately two differences. First, the SOEC matrix of the solid in the final strained state as it is defined by equation (31) has no special symmetry since the constants C_{24} and C_{34} are not zero†. This is a more reliable result as indeed the strained lattice will have no symmetry elements (except possibly for special values of ε). Second, and most important, contrary to Clapp's results, where strain renormalization (as temperature renormalization) is attributed uniquely to anharmonic terms, the present treatment yields an additional harmonic contribution. It follows then that, even for an ideally harmonic solid, its elastic properties change when it is submitted to external stresses. Such a result is in fact well understood if one takes into account that, contrary to temperature-induced deformations (which on the average are zero in the harmonic approximation), strains induced by an external stress involve changes in the atomic *equilibrium* positions and hence changes also in its elastic properties, although the force constants remain unchanged‡. This situation becomes extreme for the C_{24} and C_{34} constants, whose strain dependence is entirely due to the harmonic contribution (to first order in ε).

To appreciate properly the influence of the harmonic terms, numerical values for three different alloys are presented in table 1 as calculated from the SOECs and TOECs found in the literature (Verlinden *et al* 1984, Swartz *et al* 1975, Nagasawa *et al* 1982). In

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† It is worth noting here that the value of these constants as calculated from equation (8.20) of Wallace's (1970) paper are zero. In fact, this equation is obtained as a first approximation of the general equation (8.11) only for symmetric strains.

‡ In fact, there exists also a possible contribution to this strain renormalization coming from a change in the atomic force constants, even in the harmonic approximation. The existence of such a change can be easily understood if one takes into account the change in the crystal symmetry of the solid when it is deformed (for the restrictions that such symmetry imposes on the atomic force constants, see Brüesch (1982)).

Table 1. Strain renormalization of the second-order elastic constants for (011)[0$\bar{1}$1] shear ($T = 293$ K).

	SEOC (10^{11} Pa)	
Alloy	Present method	Clapp's method
Cu–Zn–Al	$C_{11} = 1.164$	$C_{11} = 1.164$
	$C_{12} = 1.023 + 0.323\varepsilon$	$C_{12} = 1.023 - 0.7\varepsilon$
	$C_{13} = 1.023 - 0.323\varepsilon$	$C_{13} = 1.023 + 0.7\varepsilon$
	$C_{22} = 1.164 - 2.772\varepsilon$	$C_{22} = 1.164 - 5.1\varepsilon$
	$C_{23} = 1.023$	$C_{23} = 1.023$
	$C_{24} = 0.773\varepsilon$	$C_{24} = 0$
	$C_{33} = 1.164 + 2.772\varepsilon$	$C_{33} = 1.164 + 5.1\varepsilon$
	$C_{34} = -0.773\varepsilon$	$C_{34} = 0$
	$C_{44} = 0.844$	$C_{44} = 0.844$
	$C_{55} = 0.844 - 0.844\varepsilon$	$C_{55} = 0.844$
	$C_{66} = 0.844 + 0.844\varepsilon$	$C_{66} = 0.844$
Cu–Zn	$C_{11} = 1.241$	$C_{11} = 1.241$
	$C_{12} = 1.042 + 1.002\varepsilon$	$C_{12} = 1.042 - 0.04\varepsilon$
	$C_{13} = 1.042 - 1.002\varepsilon$	$C_{13} = 1.042 + 0.04\varepsilon$
	$C_{22} = 1.241 - 1.403\varepsilon$	$C_{22} = 1.241 - 3.885\varepsilon$
	$C_{23} = 1.042$	$C_{23} = 1.042$
	$C_{24} = 0.709\varepsilon$	$C_{24} = 0$
	$C_{33} = 1.241 + 1.403\varepsilon$	$C_{33} = 1.241 + 3.885\varepsilon$
	$C_{34} = -0.709\varepsilon$	$C_{34} = 0$
	$C_{44} = 0.809$	$C_{44} = 0.809$
	$C_{55} = 0.809 - 0.754\varepsilon$	$C_{55} = 0.809 + 0.055\varepsilon$
	$C_{66} = 0.809 + 0.754\varepsilon$	$C_{66} = 0.809 - 0.055\varepsilon$
Cu–Au–Zn	$C_{11} = 1.206$	$C_{11} = 1.206$
	$C_{12} = 1.077 - 0.237\varepsilon$	$C_{12} = 1.077 - 0.84\varepsilon$
	$C_{13} = 1.077 + 0.237\varepsilon$	$C_{13} = 1.077 + 0.84\varepsilon$
	$C_{22} = 1.206 - 2.233\varepsilon$	$C_{22} = 1.206 - 4.645\varepsilon$
	$C_{23} = 1.077$	$C_{23} = 1.077$
	$C_{24} = 0.559\varepsilon$	$C_{24} = 0$
	$C_{33} = 1.206 + 2.233\varepsilon$	$C_{33} = 1.206 + 4.645\varepsilon$
	$C_{34} = -0.559\varepsilon$	$C_{34} = 0$
	$C_{44} = 0.624$	$C_{44} = 0.624$
	$C_{55} = 0.624 - 0.944\varepsilon$	$C_{55} = 0.624 - 0.32\varepsilon$
	$C_{66} = 0.624 + 0.944\varepsilon$	$C_{66} = 0.624 + 0.32\varepsilon$

particular, the change in sign in the strain-dependent term for some elastic constants should be noted. Analogous results for the Bain distortion are given in table 2.

4.2. Stability criteria and determination of the critical strain

From equations (22) and (31), one finds the following condition for the critical shear strain ε_c:

$$\begin{aligned}|\mathbf{C}| \equiv (C^0_{11} - C^0_{12})^2(C^0_{11} + 2C^0_{12}) + (\varepsilon_c^2/4)\,[4abC^0_{12} - a^2C^0_{11}\\ - 2(C^0_{11} + C^0_{12})b^2 - \Delta(C^0_{11}, C^0_{12}, A, a, b)] = 0 \qquad (32)\end{aligned}$$

where a and b are the above-defined constants and Δ is given by

$$\begin{aligned}\Delta = 8(C^0_{11} - C^0_{12})[(1/2A)(1 - A)^2(C^0_{11} - C^0_{12})(C^0_{11} + 2C^0_{12})\\ + (2C^0_{11})^2 + 2C^0_{11}C^0_{12} - (C^0_{12})^2 + a(C^0_{11} + C^0_{12}) - bC^0_{12})]. \qquad (33)\end{aligned}$$

Table 2. Strain renormalization of the second-order elastic constants for Bain distortion ($T = 293$ K).

	SEOC (10^{11} Pa)	
Alloy	Present method	Clapp's method
Cu–Zn–Al	$C_{11} = 1.164 + 2.772\tau$	$C_{11} = 1.164 + 5.1\tau$
	$C_{12} = 1.023 - 0.646\tau$	$C_{12} = 1.023 + 1.4\tau$
	$C_{13} = 1.023 + 0.323\tau$	$C_{13} = 1.023 - 0.7\tau$
	$C_{22} = 1.164 + 2.772\tau$	$C_{22} = 1.164 + 5.1\tau$
	$C_{23} = 1.023 + 0.323\tau$	$C_{23} = 1.023 - 0.7\tau$
	$C_{24} = 0$	$C_{24} = 0$
	$C_{33} = 1.164 - 5.544\tau$	$C_{33} = 1.164 - 10.2\tau$
	$C_{34} = 0$	$C_{34} = 0$
	$C_{44} = 0.844 + 0.844\tau$	$C_{44} = 0.844$
	$C_{55} = 0.844 + 0.844\tau$	$C_{55} = 0.844$
	$C_{66} = 0.844 - 1.688\tau$	$C_{66} = 0.844$
Cu–Zn	$C_{11} = 1.241 + 1.403\tau$	$C_{11} = 1.241 + 3.885\tau$
	$C_{12} = 1.042 + 2.004\tau$	$C_{12} = 1.042 + 0.08\tau$
	$C_{13} = 1.042 + 1.002\tau$	$C_{13} = 1.042 - 0.04\tau$
	$C_{22} = 1.241 + 1.403\tau$	$C_{22} = 1.241 + 3.885\tau$
	$C_{23} = 1.042 + 1.002\tau$	$C_{23} = 1.042 - 0.04\tau$
	$C_{24} = 0$	$C_{24} = 0$
	$C_{33} = 1.241 - 2.806\tau$	$C_{33} = 1.241 - 7.77\tau$
	$C_{34} = 0$	$C_{34} = 0$
	$C_{44} = 0.809 + 0.754\tau$	$C_{44} = 0.809 - 0.055\tau$
	$C_{55} = 0.809 + 0.754\tau$	$C_{55} = 0.809 - 0.055\tau$
	$C_{66} = 0.809 - 1.508\tau$	$C_{66} = 0.809 + 0.11\tau$
Cu–Au–Zn	$C_{11} = 1.206 + 2.233\tau$	$C_{11} = 1.206 + 4.645\tau$
	$C_{12} = 1.077 - 0.474\tau$	$C_{12} = 1.077 + 1.68\tau$
	$C_{13} = 1.077 + 0.237\tau$	$C_{13} = 1.077 - 0.84\tau$
	$C_{22} = 1.206 + 2.233\tau$	$C_{22} = 1.206 + 4.645\tau$
	$C_{23} = 1.077 + 0.237\tau$	$C_{23} = 1.077 - 0.84\tau$
	$C_{24} = 0$	$C_{24} = 0$
	$C_{33} = 1.206 - 4.466\tau$	$C_{33} = 1.206 - 9.29\tau$
	$C_{34} = 0$	$C_{34} = 0$
	$C_{44} = 0.624 + 0.944\tau$	$C_{44} = 0.624 + 0.32\tau$
	$C_{55} = 0.624 + 0.944\tau$	$C_{55} = 0.624 + 0.32\tau$
	$C_{66} = 0.624 - 1.889\tau$	$C_{66} = 0.624 - 0.64\tau$

Comparison between equations (29) and (32) shows that both stability conditions are equal except for the term Δ arising from the additional harmonic contribution. As shown in equation (33), this new term is proportional to $C_{11}^{0} - C_{12}^{0}$ and therefore the critical strains obtained in both methods will be similar as the difference between the elastic constants is negligible. In the case of a β-Cu–Zn–Al alloy, experimental results (Guénin 1979, Verlinden *et al* 1984) prove that this difference is small, further decreasing as the temperature decreases, so that the critical strains provided by both Clapp's method (ε_{c2}) and the present method (ε_{c1}) will be nearly equal. This is illustrated in figure 1(*a*), where we have plotted both stability conditions (equations (29) and (32), respectively) and also the stability condition obtained when only harmonic terms are taken into account (ε_{c3}). The corresponding plot for the Bain distortion is given in figure 1(*b*). In figure 2

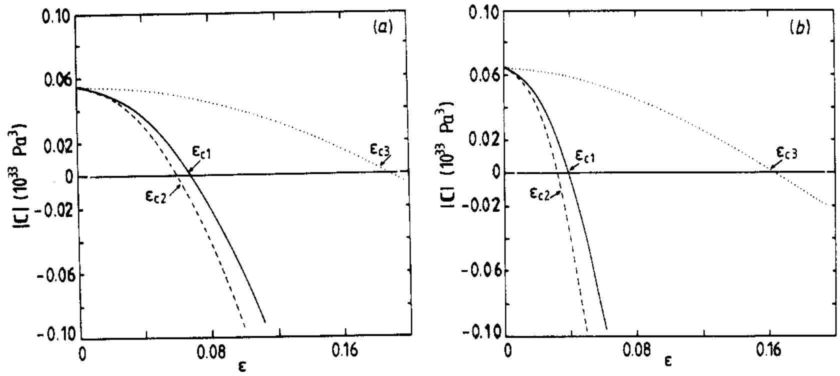

Figure 1. $|\mathbf{C}|$ as a function of the strain (*a*) for a (011)[0$\bar{1}$1] shear and (*b*) for a Bain distortion in a β-Cu–Zn–Al alloy at T = 293 K: ——, present calculations; – – –, Clapp's results; · · · ·, harmonic contribution.

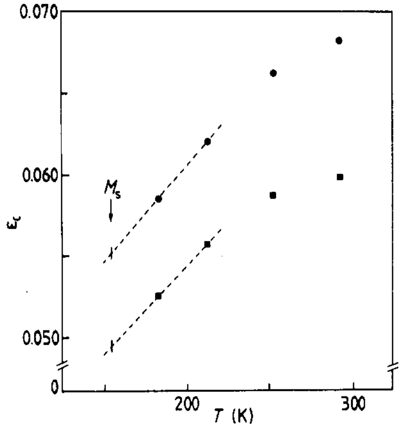

Figure 2. Temperature dependence of the critical strains ε_{c1} (●) and ε_{c2} (■) for the β-Cu–Zn–Al alloy. Extrapolated values at the martensitic transformation temperature M_s = 158 K are also shown.

the temperature dependence of the critical strains ε_{c1} and ε_{c2} is shown for (011)[0$\bar{1}$1] shear in the same alloy, which transforms martensitically at a temperature M_s = 158 K (Verlinden *et al* 1984). The extrapolated value of ε_c at this temperature differs in the two methods by 10% (at room temperature, this difference is 15%). Similar effects have been obtained for a Cu–Zn and a Au–Cu–Zn alloy. So, in the case of (011)[0$\bar{1}$1] shear, increments (at room temperature) of 15–18% in the critical strain are found relative to the values obtained using Clapp's method. Furthermore, the critical strain ε_{c3} when only harmonic terms are taken into account increases greatly too ($\varepsilon_{c3} \simeq 0.2$).

We thus draw the following conclusions.

(i) The critical strain remains small enough to render plausible the localized soft-mode theory (thus, $\varepsilon_{c1} \simeq \pm 0.07$ for shear strain in Cu–Zn–Al alloy).

(ii) The effect of the additional harmonic contribution is to increase the elastic stability of the solid ($\varepsilon_{c1} > \varepsilon_{c2}$).

(iii) According to Clapp's postulate, it is the anharmonic contribution which strongly reduces the elastic stability of the solid ($\varepsilon_{c3} \simeq 3\varepsilon_{c1}$).

Finally, it should be pointed out that the above results have been obtained for some alloys and particular types of strain. In such cases, we have verified that Clapp's method, although inaccurate, leads to well approximated results for the stability criteria (in spite of the fact that the effect on the strain renormalization of the SOECs is much more noticeable). There is no evidence, however, for this to be always true.

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