Finite-strain solitons of a ferroelastic transformation in two dimensions

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Interfaces in the $4mm$-$2mm$ ferroelastic transformation are treated to all orders in the nonlinearity of the Lagrangian strain tensor. The free-energy density has minimal form so that three of the six strains vanish identically, yielding a two-dimensional (square-rectangular) problem. The reduced form of the density contains no terms coupling the remaining strains; for free boundary conditions, a small volume decrease in the product state results from the geometrical nonlinearity of the strain tensor. An explicit procedure to obtain the displacement from the strains is given, and closed expressions for the displacements of the parent-product and product-product solitons are found. The extended form of the density includes a term coupling two strains, allowing a volume increase in the product state; the numerical solution of two second-order, ordinary differential equations followed by evaluation of two integrals gives the displacement. All three strains are nonzero in the wall region. For both densities, the displacements for solitons describing wall problems satisfy the two-dimensional wave equation (in the coordinates x_1 and x_2); the parent-product and product-product interfaces are parallel to the parent (110) and $(1\bar{1}0)$ planes, and the product-product walls are twin boundaries.

I. INTRODUCTION

Martensitic transformations are diffusionless solid-state transformations, usually first order, in which the strain is the primary order parameter; more generally, the term is used for transformations in which the strain energy dominates the morphology and the kinetics. A subclass of these transformations obeys the group-subgroup relation, and can be described by Landau theory (which expands the free-energy density in the strains and their gradients). Examples are the cubic-tetragonal transition (in Nb_3Sn, V_3Si, In-Tl alloys, and Fe-Pd alloys) and the tetragonal-orthorhombic transition, but not reconstructive transformations such as the fcc-bcc transition in Fe. The strain can play a major role also in transformations where it is the secondary order parameter; examples occur in displacive transitions (the cubic-tetragonal transition in $BaTiO_3$) and in some order-disorder transitions (the tetragonal-orthorhombic transition in the celebrated 92-K superconductor $YBa_2Cu_3O_{7-\delta}$, but not the transition in β-brass). The results of pure strain theories such as those presented in Refs. 1 and 2 may find application in the theory of these transformations.

This article treats wall problems, the simplest inhomogeneities, in the theory of the $4mm$-$2mm$ ferroelastic transformation, to all orders in the nonlinear term in the strain tensor; the results apply strictly only to the square-rectangular transformation, but should be qualitatively correct for the tetragonal-orthorhombic (T-O) case as well, and the latter terminology is adopted below. Unlike walls in incommensurate systems, the parent-product (here T-O) and product-product (here O-O') walls have positive energy; they are forced into the system by boundary conditions (to minimize macroscopic displacements), or occur due to multiple nucleation events. The results may be useful for wall problems in the cubic-tetragonal transformation, which is more important, but much more difficult.

Section II reviews finite-strain theory (a convenient reference is the book by Brillouin[3]) for the particular case of the tetragonal-orthorhombic (T-O) transformation. Section III obtains relations between the displacement and the strains, and suggests that the strains are simple if the components of the displacement satisfy the two-dimensional wave equation in the coordinates x_1 and x_2. Section IV considers the free-energy density, which has minimal form, with only three strains e_1, e_2, and e_6. The homogeneous part is standard except that it contains the coupling term $Ee_1e_2^2$; the nonlinear term in the strain tensor is essential if this term is included. The strain-gradient part is obtained to all orders in the nonlinearity of the strain tensor. Sections V and VI consider wall problems, with free boundary conditions; the strains are expected to be functions of a single coordinate, permitting analytical or simple numerical solutions. Section V considers the reduced version of the density (without the coupling term). Both homogeneous and inhomogeneous situations are described in terms of a single strain e_2, the strains e_1 and e_6 vanishing identically; an explicit procedure is given to find the displacement from e_2. Closed expressions for the displacements of T-O and O-O' solitons are found; the asymptotic forms of the inhomogeneous solutions are interpreted in terms of rotated homogeneous solutions. The dilatation is nonzero except for infinitesimal strains, and the volume decreases on going to the orthorhombic phase. Section VI considers the term coupling e_1 and e_2 (which can explain a volume increase), for both homogeneous and inhomogeneous (wall) problems. The latter cannot be solved analytically, but the displacement can be found by integration of the solutions of two ordinary differential equations; all three strains are nonvanishing in the wall region (which has monoclinic structure), even when the density contains no terms coupling e_6 to other strains. For both densities, both T-O and O-O' walls are parallel to the tetragonal (110) and (1$\bar{1}$0) planes, and the O-O' walls are twin boundaries, as in Ref. 2.

II. FINITE-STRAIN THEORY

The tetragonal state, with all strains zero, is the reference state for the tetragonal-orthorhombic (T-O) transformation. In the Lagrangian description, the components of the strain tensor η are

$$\eta_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i} + u_{k,i}u_{k,j}) \; ; \quad (2.1)$$

u_i is the ith component of the displacement vector relative to the undeformed state, $u_{i,j} = \partial_j u_i$, and repeated indices are summed from 1 to 2. The square of distance between two nearby points is $ds^2 = (dx_i)^2$ in the undeformed state, and $dS^2 = (dx_i + du_i)^2$ in the deformed state; the two are related by $dS^2 - ds^2 = 2\eta_{ij}\,dx_i\,dx_j$. The free-energy density describing the transformation is an expansion in the components of η and their derivatives. Although the strains are usually small (less than a few %), the nonlinear term in Eq. (2.1) is important. If an arbitrarily deformed state with displacement $\bar{\mathbf{u}} = (\bar{u}_1, \bar{u}_2)$ is rotated by an angle θ, then the new displacement (relative to the fixed space axes) has components

$$u_1(x_1,x_2) = -x_1 + c[x_1 + \bar{u}_1(x_1,x_2)] + s[x_2 + \bar{u}_2(x_1,x_2)] \; , \quad (2.2a)$$

$$u_2(x_1,x_2) = -x_2 - s[x_1 + \bar{u}_1(x_1,x_2)] + c[x_2 + \bar{u}_2(x_1,x_2)] \; , \quad (2.2b)$$

where $c = \cos\theta$ and $s = \sin\theta$. The tensor η_{ij} obtained from the displacement $\mathbf{u}$ is identical to the tensor $\bar{\eta}_{ij}$ obtained from the displacement $\bar{\mathbf{u}}$, and the free energy is unchanged. Equations (2.2) are useful in interpreting solutions for inhomogeneous strains.

For the free-energy density of Sec. IV, the problem is two dimensional; the parent phase has $4mm$ (tetragonal) symmetry, with the three-axis the fourfold axis, and the 1-3 and 2-3 planes the mirror planes. Then the component u_3 is identically zero and the other components are independent of x_3; the appropriate combinations are the strains

$$e_1 = (\eta_{11} + \eta_{22})/\sqrt{2} \; , \quad (2.3a)$$

$$e_2 = (\eta_{11} - \eta_{22})/\sqrt{2} \; , \quad (2.3b)$$

$$e_6 = \eta_{12} \; , \quad (2.3c)$$

the other three strains vanishing identically. The orthorhombic (O) state has two variants, $e_2 = \pm e_{20}$. If the strains are homogeneous, e_6 must vanish; otherwise the deformed state is monoclinic, not orthorhombic. Explicitly, the vectors $(1,0)$ and $(0,1)$ in the undeformed state transform to $(1 + u_{1,1}\, , u_{2,1})$ and $(u_{1,2}\, , 1 + u_{2,2})$, which are orthogonal if $e_6 = 0$.

e_1, e_2, and e_6 are usually called the dilatational, deviatoric, and shear strains, respectively, but these terms are misleading, and avoided in the following. e_1 is not the true dilatational strain, except for infinitesimal strains; for example, the displacement $\mathbf{u} = (b-1)(x_1, -x_2/b)$ conserves the volume, but gives nonzero e_1. The true dilatational strain, which vanishes if the volume is conserved, is $e_0 = \Delta - 1$, where (in two dimensions) the local ratio $\Delta(x_1,x_2)$ of the final to initial volumes is the Jacobian of the transformation $x_i \rightarrow x_i + u_i$:

$$\Delta = (1 + u_{1,1})(1 + u_{2,2}) - u_{1,2}u_{2,1} \; ; \quad (2.4a)$$

another useful form expresses Δ in terms of the strains[3]

$$\Delta = [(1 + \sqrt{2}e_1)^2 - 2e_2^2 - 4e_6^2]^{1/2} \; . \quad (2.4b)$$

III. DISPLACEMENT AND STRAINS

This section shows that the strains e_1 and e_6 are simply related if the components of the displacement satisfy the two-dimensional wave equation. These strains are secondary to the T-O transformation which is driven by an instability to nonzero e_2, as discussed in Sec. IV; in the absence of terms coupling e_2 to the other strains, one expects the minimum-energy solutions to have both $e_1 = 0$ and $e_6 = 0$, since the instability is in the e_2 part of the free energy, not in the e_1 or e_6 parts. This section is related to Sec. IV as kinematics to dynamics.

It is always possible to obtain the displacement for arbitrary homogeneous strains, but not for arbitrary inhomogeneous strains. For example, even if the equations of motion allow solutions with $e_1 = 0$ and $e_6 = 0$, such solutions in inhomogeneous situations are allowed only for special orientations of the walls, as discussed in Refs. 1 and 2. Some guesswork is required to find forms for the strains which both can be obtained from a displacement and also minimize the free energy.

The basic results are obtained after obvious manipulations of Eqs. (2.1) and (2.3):

$$u_{1,11} - u_{1,22} + u_{k,1}(u_{k,11} - u_{k,22}) = \sqrt{2}e_{1,1} - 2e_{6,2} \; , \quad (3.1a)$$

$$u_{2,11} - u_{2,22} + u_{k,2}(u_{k,11} - u_{k,22}) = -\sqrt{2}e_{1,2} + 2e_{6,1} \; . \quad (3.1b)$$

If the u_i $(i = 1,2)$ satisfy the wave equation $u_{i,11} - u_{i,22} = 0$, that is, if

$$u_i(x_1,x_2) = U_i(x_1 + x_2) + V_i(x_1 - x_2) \; , \quad (3.2)$$

then

$$e_{1,1} = \sqrt{2}e_{6,2} \;\; \text{and} \;\; e_{1,2} = \sqrt{2}e_{6,1} \; ; \quad (3.3)$$

the full "geometrical" nonlinearity (that of the strain tensor) has been retained in deriving these results. Then both e_1 and e_6 satisfy the wave equation. Such solutions are appropriate for wall problems, with strains translationally invariant in the tetragonal [110] or [1$\bar{1}$0] directions; but e_2 is also translationally invariant only if constraints are imposed on the functions U_i and V_i, which are further constrained by the "physical" nonlinearity [see, for example, Eq. (5.1c) below].

Section VI discusses the general case of Eqs. (3.3). The important special case $e_1 = 0$ and $e_6 = 0$ is the basis of other work,[1,2,4–6] and is discussed in Sec. V; the relations $U_1' + U_2' + (U_1')^2 + (U_2')^2 = 0$ and $V_1' - V_2' + (V_1')^2 + (V_2')^2 = 0$ are easily derived. The importance of functions of $x_1 \pm x_2$ was recognized by Barsch and Krumhansl,[1] who found the product-product soliton of the cubic-tetragonal transformation at a single temperature; the strains e_1 and e_6 vanish for walls parallel to the cubic {110} planes. The T-O (more properly the square-rectangular) transformation was studied by Jacobs,[2] who found the strains e_2 (at all temperatures) for the T-O and O-O' solitons; e_1 and e_6 vanish if the walls are parallel to the tetragonal (110) and (1$\bar{1}$0) planes. Further developments were made by Barsch and Krumhansl,[4] Ericksen,[5] and Kartha *et al.*[6] References 2 and 5 considered the full strain tensor, while the others linearized it. The development leading to Eq. (3.2) is an independent and further contribution. The one-dimensional case has only one strain, and so similar considerations did not enter perhaps the earliest application of Landau theory to wall problems in martensitic transformations.[7]

IV. FREE ENERGY

Sections V and VI describe the T-O transformation in terms of the free-energy density

$$\mathcal{F} = \frac{1}{2}A_1 e_1^2 + \frac{1}{2}A_2 e_2^2 + \frac{1}{4}B_2 e_2^4 + \frac{1}{6}C_2 e_2^6 + \frac{1}{2}A_6 e_6^2 + E e_1 e_2^2 + \Psi(e_{\alpha,i}) , \tag{4.1a}$$

$$\begin{aligned}\Psi(e_{\alpha,i}) = {} & \frac{1}{2}d_1(e_{1,1}^2 + e_{1,2}^2) + \frac{1}{2}d_2(e_{2,1}^2 + e_{2,2}^2) + \frac{1}{2}d_3(e_{6,1}^2 + e_{6,2}^2) \\ & + d_4(e_{1,1}e_{2,1} - e_{1,2}e_{2,2}) + d_5(e_{1,1}e_{6,2} + e_{1,2}e_{6,1}) + d_6(e_{2,1}e_{6,2} - e_{2,2}e_{6,1}) .\end{aligned} \tag{4.1b}$$

In Eq. (4.1a), the terms in e_1^2, e_2^2, and e_6^2 are the usual contributions for a linear, homogeneous, elastic medium; A_1 and A_6 are positive, while A_2 vanishes at a temperature T_0 and is negative below. All coefficients but A_2, including those in Ψ, are assumed independent of temperature. The term in e_2^6 (with $C_2 > 0$ for stability) is necessary if B_2 is negative (first-order transition). The strain-gradient part Ψ of Eq. (4.1b) gives the contribution from inhomogeneous strains; this expression (quoted in Ref. 4) is derived and discussed in the Appendix.

Equation (4.1) is minimal in that it omits many terms allowed by symmetry; only essential terms are retained. Particularly troublesome are terms which couple e_2 to other strains, and which can induce these parasitic strains in the presence of nonvanishing e_2. Equation (4.1) includes only one coupling term, $Ee_1e_2^2$, plus coupling terms in Ψ. Other coupling terms (which may be numerically important, and would be considered in a full solution) are omitted, first because they might destroy the two-dimensional character, and second because strains other than e_2 can develop for other reasons (for example, boundary conditions). The more tractable "reduced" density, without the term $Ee_1e_2^2$, is considered in Sec. V; but it cannot explain a volume increase in the orthorhombic state. Section VI considers the full ("extended") density which allows a volume increase. A more general treatment would include also terms coupling the strains e_1, e_2, and e_6 to the other three strains, and therefore the results obtained below apply strictly only to the square-rectangular transformation.

The first variation in the density of Eq. (4.1) is

$$\delta\mathcal{F} = \partial_1 S_1 + \partial_2 S_2 + H_1\delta e_1 + H_2\delta e_2 + H_6\delta e_6 , \tag{4.2}$$

where the functionals H_1, H_2, and H_6 are

$$H_1 = A_1e_1 - d_1\nabla^2 e_1 - d_4 e_{2,11} + d_4 e_{2,22} - 2d_5 e_{6,12} + Ee_2^2 , \tag{4.3a}$$

$$\begin{aligned}H_2 = {} & A_2e_2 + B_2e_2^3 + C_2e_2^5 - d_2\nabla^2 e_2 - d_4 e_{1,11} \\ & + d_4 e_{1,22} + 2Ee_1e_2 ,\end{aligned} \tag{4.3b}$$

$$H_6 = A_6e_6 - d_3\nabla^2 e_6 - 2d_5 e_{1,12} . \tag{4.3c}$$

The terms $\partial_1 S_1$ and $\partial_2 S_2$ are surface terms and do not appear below; for completeness,

$$S_1 = (d_1e_{1,1} + d_4e_{2,1} + d_5e_{6,2})\delta e_1 + (d_2e_{2,1} + d_4e_{1,1} + d_6e_{6,2})\delta e_2 + (d_3e_{6,1} + d_5e_{1,2} - d_6e_{2,2})\delta e_6 ,$$

$$S_2 = (d_1e_{1,2} - d_4e_{2,2} + d_5e_{6,1})\delta e_1 + (d_2e_{2,2} - d_4e_{1,2} - d_6e_{\epsilon,1})\delta e_2 + (d_3e_{6,2} + d_5e_{1,1} + d_6e_{2,1})\delta e_6 .$$

The condition that the free energy be stationary with respect to variations in the u_i yields the equations of motion as

$$\partial_1[(H_1+H_2)(1+u_{1,1})+H_6u_{1,2}/\sqrt{2}]+\partial_2[(H_1-H_2)u_{1,2}+H_6(1+u_{1,1})/\sqrt{2}]=0\ , \tag{4.4a}$$

$$\partial_1[(H_1+H_2)u_{2,1}+H_6(1+u_{2,2})/\sqrt{2}]+\partial_2[(H_1-H_2)(1+u_{2,2})+H_6u_{2,1}/\sqrt{2}]=0\ . \tag{4.4b}$$

These coupled, fourth-order, partial differential equations for the components u_i retain the full geometrical and physical nonlinearities, and are valid for any density with variation of the form (4.2). But their solution is a formidable problem in general. Sections V and VI develop analytical techniques for wall problems, but the solutions are not proved to be global minima of the energy. The geometrically linearized versions of Eqs. (4.4) are much simpler, but still difficult to solve:

$$H_{1,1}+H_{2,1}+H_{6,2}/\sqrt{2}=0\ , \tag{4.5a}$$

$$H_{1,2}-H_{2,2}+H_{6,1}/\sqrt{2}=0\ . \tag{4.5b}$$

V. DISPLACEMENTS FOR THE REDUCED DENSITY

Using the reduced density of Sec. IV (without the term $Ee_1e_2^2$), this section obtains closed expressions for the parent-product and product-product solitons, to all orders in the nonlinear term in the strain tensor. Expressions for the components u_i, consistent with $e_1=0$ and $e_6=0$, are given in Sec. V A. The homogeneous solution is obtained in Sec. V B, and inhomogeneous solutions in Secs. V C–V F. The true dilatational strain e_0 does not vanish for these solutions, and the volume decreases in the orthorhombic phase, as seen from Eq. (2.4b).

A. Basic equations

Trial solutions of Eqs. (4.4) are $H_1=0$, $H_2=0$, and $H_6=0$; in turn, trial solutions of these are (recall that $E=0$)

$$e_1=0\ , \tag{5.1a}$$

$$e_{2,11}-e_{2,22}=0\ , \tag{5.1b}$$

$$A_2e_2+B_2e_2^3+C_2e_2^5-d_2\nabla^2e_2=0\ , \tag{5.1c}$$

$$e_6=0\ . \tag{5.1d}$$

Equation (5.1b) is satisfied if e_2 is a function of $x_1\pm x_2$ (or is independent of x_1 and x_2). Equations (5.1) are identical to Eqs. (10)–(12) of Ref. 2, which omitted the terms involving d_4, d_5, and d_6 in Eq. (4.1b); these terms are necessary both in principle and in practice, for they enter the determination of the coefficients d_i from phonon dispersion curves.[4] The above shows, however, that they have no consequences for solutions with $e_1=0$ and $e_6=0$, and all results of Ref. 2 are unchanged.

A procedure follows to obtain the components u_1 and u_2. These are assumed to be functions of $x_1\pm x_2$ alone, corresponding to a particular setting of the deformed structure relative to the fixed space axes; then $e_1=\pm\sqrt{2}e_6$, and both vanish if one does. As suggested by the results of Ref. 2, the components are written as

$$u_1(x_1,x_2)=\ f_1(x_1\pm x_2)-f_2(x_1\pm x_2), \tag{5.2a}$$

$$u_2(x_1,x_2)=\mp f_1(x_1\pm x_2)\mp f_2(x_1\pm x_2), \tag{5.2b}$$

where f_1 and f_2 represent the linear and higher-order terms, respectively. Forms satisfying all requirements are

$$f_1(x_1\pm x_2)=\int^{x_1\pm x_2}dX\,e_2(X)/\sqrt{2}\ , \tag{5.3}$$

$$f_2(x_1\pm x_2)=\int^{x_1\pm x_2}dX\ [1-\Delta(X)]/2\ , \tag{5.4}$$

where $\Delta(X)=[1-2e_2^2(X)]^{1/2}$; the lower limits of the integrals are taken to be zero, except for T-O solitons. Equations (5.2)–(5.4) extend the fourth-order results of Ref. 2 to all orders in the homogeneous strain e_{20}, consistent with $e_1=0$ and $e_6=0$. The only requirements are that the strain e_2 be a function of $x_1\pm x_2$, and that $|e_2|\le 1/\sqrt{2}$; the explicit form of the free-energy density affects only details of the function e_2.

Equations (5.2)–(5.4) can also be obtained by following the procedure of Ericksen.[5] With $\sqrt{2}e_2=\sin\alpha$ (to avoid a sign problem), one finds that α has the form

$$\alpha(x_1,x_2)=\alpha_+(x_1+x_2)+\alpha_-(x_1-x_2)\ ; \tag{5.5a}$$

a solution for the components u_i in terms of the functions α_+ and α_- is

$$u_1=-x_1+(s_1/\sqrt{2})\left[\int^{x_1+x_2}\sin\alpha_+(X)\,dX+\int^{x_1-x_2}\cos\alpha_-(X)\,dX\right]\ , \tag{5.5b}$$

$$u_2=-x_2+(s_2/\sqrt{2})\left[\int^{x_1+x_2}\cos\alpha_+(X)\,dX+\int^{x_1-x_2}\sin\alpha_-(X)\,dX\right]\ , \tag{5.5c}$$

where s_1 and s_2 are independently ± 1. The special cases $\alpha_- = \pi/2$ and $\alpha_+ = 0$, rotated by $\pi/4$, reproduce Eqs. (5.2)–(5.4). Obviously u_1 and u_2 satisfy the wave equation.

If the lower limits of the integrals in Eqs. (5.3) and (5.4) are zero, then f_1 and f_2 are, respectively, even and odd functions of their arguments; for $X = x_1 + x_2$,

$$u_1(-x_2, -x_1) = -u_2(x_1, x_2) \; , \qquad u_2(-x_2, -x_1) = -u_1(x_1, x_2) \; , \tag{5.6}$$

and the O-O' walls $X = 0$ are twin boundaries, as in Ref. 2. This is a general result, independent of the details of the free-energy density; it is not sufficient that the u_i be functions of $x_1 \pm x_2$ — the signs in Eqs. (5.2) and the evenness or oddness are crucial.

B. Homogeneous strains

The strains are $e_1 = 0$, $e_2 = \pm e_{20}$, and $e_6 = 0$, where e_{20} is the larger positive solution of $A_2 + B_2 e_{20}^2 + C_2 e_{20}^4 = 0$; the true dilatational strain is $e_0 = \Delta_0 - 1$, where $\Delta_0 = (1 - 2e_{20}^2)^{1/2} \leq 1$. If the orthorhombic axes are parallel to the fixed space axes, the components of $\mathbf{u}$ are

$$\bar{u}_1 = \left[(1+\sqrt{2}e_2)^{1/2} - 1\right]x_1 \; , \quad \bar{u}_2 = \left[(1-\sqrt{2}e_2)^{1/2} - 1\right]x_2 \; , \tag{5.7}$$

representing an expansion in the one-direction and a contraction in the two-direction, or vice versa. But a direct transition between the two variants $e_2 = \pm e_{20}$ involves prohibitively large energies, since both dilatational and shear strains are generated. Rather, the O-O' walls discussed below connect two oppositely rotated variants, as shown in Figs. 1 and 2 of Ref. 2, and described by Eqs. (5.9) below.

The components for other settings of the orthorhombic axes relative to the fixed space axes are obtained by rotating the above solution; from Eqs. (2.2), the choice

$$c = \left[(1 + \sqrt{2}e_2)^{1/2} + (1 - \sqrt{2}e_2)^{1/2}\right]/2 \tag{5.8}$$

gives components which are functions of $X = x_1 \pm x_2$:

$$u_1 = (e_2 + e_0/\sqrt{2})X/\sqrt{2} \; , \qquad u_2 = \mp(e_2 - e_0/\sqrt{2})X/\sqrt{2} \; . \tag{5.9}$$

This displacement represents a shear in the tetragonal [110] or [1$\bar{1}$0] directions (explicitly, with vanishing component in the orthogonal direction); this remarkable result (another reason for avoiding the terms dilatational, deviatoric, and shear) is due to the special form of the displacement when both e_1 and e_6 vanish. It is this property which allows the analytical solution of the form $u_i(x_1 \pm x_2)$.

C. Second-order transition; O-O' soliton

For a second-order tetragonal-orthorhombic (T-O) transition, the coefficient B_2 is greater than zero, and C_2 can be taken to be zero. The T solution $e_2 = 0$ minimizes the energy for $A_2 > 0$. The transition occurs at $A_2 = 0$. For $A_2 < 0$, the minimum in the free energy is at $e_2 = \pm e_{20}$. There is no parent-product (T-O) soliton because the T solution is a local maximum of the free-energy density below the transition.

The strain of the soliton connecting the two orthorhombic variants O and O' with $e_2 = e_{20}$ and $e_2 = -e_{20}$ is[2] $e_2(X) = e_{20}\tanh(\kappa X/\sqrt{2})$, where $X = x_1 \pm x_2$, $e_{20} = (-A_2/B_2)^{1/2}$, and $\kappa = (-A_2/2d_2)^{1/2}$; this form is familiar from the mean-field theory of many problems (e.g., the domain wall in an Ising ferromagnet). The components of $\mathbf{u}$ are given by Eqs. (5.2) from the functions f_1 and f_2:

$$f_1(X) = (e_{20}/\kappa)\ln\cosh(\kappa X/\sqrt{2}) \; , \tag{5.10a}$$

$$f_2(X) = \frac{X}{2} - \frac{1}{\kappa\sqrt{2}}\left(\sqrt{2}e_{20}\arcsin\left[\sqrt{2}e_2(X)\right] + \Delta_0 \operatorname{arcsinh}\left[\Delta_0 \sinh(\kappa X/\sqrt{2})\right]\right) \; . \tag{5.10b}$$

These solutions can be rotated to produce trivially different solutions. Reference 2 gives expansions and figures of deformed regions for these results and also those of Secs. V E and V F below.

In the asymptotic region $|X| \to \infty$, the functions f_1 and f_2 are

$$f_1(X) = e_{20}|X|/\sqrt{2} - (e_{20}/\kappa)\ln 2 \; , \tag{5.11a}$$

$$f_2(X) = (1 - \Delta_0)X/2 - \{(e_{20}/\kappa)\arcsin(\sqrt{2}e_{20}) + [\Delta_0/(\sqrt{2}\kappa)]\ln\Delta_0\}\operatorname{sgn}(X) \; , \tag{5.11b}$$

plus exponentially small terms. To fix ideas, let $X = x_1 + x_2$. Equations (5.11) are reproduced by the following sequences of operations. In the region $X \to \infty$, the tetragonal state is first deformed as described by Eqs. (5.7) with $e_2 = e_{20} > 0$, then rotated clockwise by the angle $|\theta|$ from Eq. (5.8), and finally translated by the vector $\mathbf{a} + \mathbf{b}$, where

$$\mathbf{a} = -(e_{20}/\kappa)\ln 2\;(1, -1) \; , \tag{5.12a}$$

$$\mathbf{b} = \{(e_{20}/\kappa)\arcsin(\sqrt{2}e_{20}) + [\Delta_0/(\sqrt{2}\kappa)]\ln\Delta_0\}\;(1, 1) \; . \tag{5.12b}$$

In the region $X \to -\infty$, the tetragonal state is first deformed as described by Eq. (5.7) with $e_2 = -e_{20}$, then rotated counterclockwise by the angle $|\theta|$ from Eq. (5.8), and finally translated by the vector $\mathbf{a} - \mathbf{b}$. The asymptotic solutions in Secs. V E and V F below can also be discussed in terms of rotations.

D. Second-order transition; chain of O-O' solitons

The solution of Eq. (5.1c) for a chain of O-O' solitons is well known from the mean-field theory of inhomogeneous systems:

$$e_2(X) = e_{20}[2m/(1+m)]^{1/2}\,\mathrm{sn}(u|m) \ . \qquad (5.13)$$

Here and in the following, the notation of Ref. 8 is used for elliptic integrals (K, E, and Π) and Jacobian elliptic functions (sn, dn, ...). The argument above is $u = \kappa X/\sqrt{1+m}$, with $\kappa = (-A_2/2d_2)^{1/2}$, the parameter is m, and the spatial period in u is $4K(m)$; the previous subsection considers the degenerate case $m = 1$. The functions f_1 and f_2 are

$$f_1(X) = (e_{20}/\kappa)\ln\{[\mathrm{dn}(u|m) - k\,\mathrm{cn}(u|m)]/(1-k)\} \ , \qquad (5.14a)$$

$$f_2(X) = e_{20}^2\,[u - E(u|m)]/(\kappa\sqrt{1+m}) + O(e_{20}^4) \ , \qquad (5.14b)$$

where $k = \sqrt{m}$ is the modulus; the function f_2 cannot be obtained in closed form.

E. First-order transition; T-O soliton

For a first-order tetragonal-orthorhombic (T-O) transition $B_2 < 0$ and $C_2 > 0$ (for stability). Depending on the parameter A_2, there are several possibilities. (a) $A_2 > B_2^2/4C_2$: the T state is stable; there is no O state. (b) $B_2^2/4C_2 > A_2 > 3B_2^2/16C_2$: the T state is stable; the O state is metastable. (c) $A_2 = 3B_2^2/16C_2$: the T and O states have the same energy. (d) $3B_2^2/16C_2 > A_2 > 0$: the T state is metastable; the O state is stable. (e) $0 > A_2$: there is no T state; the O state is stable. The two-strain in the O regions (in the range $A_2 < B_2^2/4C_2$ where the O state exists) is $e_2 = \pm e_{20}$, where $e_{20} = [(-B_2/2+\gamma)/C_2]^{1/2}$, with $\gamma = (B_2^2/4 - A_2C_2)^{1/2}$.

The T-O soliton strictly exists only at the transition temperature (defined by $A_2 = 3B_2^2/16C_2$). The strain is[2]

$$e_2(X) = e_{20}/(1+e^{-\sqrt{2}\kappa X})^{1/2} \ , \qquad (5.15)$$

where $\kappa = [3B_2^2/(16C_2d_2)]^{1/2}$; Eq. (5.15), which occurs also in one-dimensional problems,[7,9] couples the T parent ($e_2 = 0$, $X \to -\infty$) to one of the O products ($e_2 = e_{20}$, $X \to \infty$). The functions f_1 and f_2 are

$$f_1(X) = (e_{20}/\kappa)\,\ln(\sqrt{1+w} + \sqrt{w}) \ , \qquad (5.16a)$$

$$f_2(X) = \frac{1}{\kappa\sqrt{2}}\left[\ln\left(\frac{\sqrt{1+\Delta_0^2 w} + \sqrt{1+w}}{2}\right) - \Delta_0\,\ln\left(\frac{\sqrt{1+\Delta_0^2 w} + \Delta_0\sqrt{1+w}}{1+\Delta_0}\right)\right] \ , \qquad (5.16b)$$

where $w = \exp(\sqrt{2}\kappa X)$, and the constants of integration have been chosen so that u_1 and u_2 vanish deep inside T material ($X \to -\infty$, $w \to 0$).

F. First-order transition; O-O' soliton

The two-strain of the O-O' soliton is[2]

$$e_2(X) = e_{20}\sinh(\kappa' X/\sqrt{2})/[\cosh^2(\kappa' X/\sqrt{2}) + \alpha]^{1/2} \ ; \qquad (5.17)$$

this form occurs also in one-dimensional problems.[7,9,10] Here κ' and α are defined by $\kappa' = e_{20}(\gamma/d_2)^{1/2}$ and $\alpha = (-B_2 + 2\gamma)/(B_2 + 4\gamma)$, with $\gamma = (B_2^2/4 - A_2C_2)^{1/2}$. Equation (5.17) is valid in the range $A_2 < 3B_2^2/16C_2$ where the O state has lower energy than the T state; the parameter α diverges as A_2 approaches $3B_2^2/16C_2$ from below, and the O-O' soliton splits into two T-O solitons.[2,9] The functions f_1 and f_2 are

$$f_1(X) = \frac{e_{20}}{\kappa'}\ln\left(\frac{\cosh(\kappa' X/\sqrt{2}) + [\cosh^2(\kappa' X/\sqrt{2}) + \alpha]^{1/2}}{1+\sqrt{1+\alpha}}\right) \ , \qquad (5.18a)$$

$$f_2(X) = \frac{X}{2} - \frac{1}{\kappa'\sqrt{2}}\left(\sqrt{n}u - p_1\Delta_0\Pi(N;u|m) + \frac{\Delta_0}{2}\ln\left[\frac{\mathrm{dn}(u|m) + p_1\mathrm{sc}(u|m)}{\mathrm{dn}(u|m) - p_1\mathrm{sc}(u|m)}\right]\right) \ , \qquad (5.18b)$$

where $N = \alpha/(\alpha+1)$, $m = \alpha/(\alpha+2e_{20}^2)$, $n = (\alpha+1)/(\alpha+2e_{20}^2)$, $p_1 = [(n-1)(1-N)]^{1/2}$, and $\mathrm{sn}(u|m) = n^{-1/2}\tanh(\kappa' X/\sqrt{2})$. A simpler expression is available in terms of $\Pi(n;u|m)$, but $n > 1$ (hyperbolic case); see Ref. 8, Eq. (17.7.8).

VI. DISPLACEMENTS FOR THE EXTENDED DENSITY

This section considers the free-energy density of Eq. (4.1), including the coupling term $Ee_1e_2^2$; it is essential here to include the nonlinear term in the strain tensor, since $e_1 = O(e_2^2)$. Wall problems are reduced to the solution of two second-order, ordinary differential equations for the strains, followed by the evaluation of integrals to find the displacement.

For homogeneous strains, the free energy is stationary if $e_1 = e_{10}(= -Ee_{20}^2/A_1)$, $e_2 = \pm e_{20}$, and $e_6 = 0$, where e_{20} is found from $A_2 + (B_2 - 2E^2/A_1)e_{20}^2 + C_2e_{20}^4 = 0$. For orthorhombic axes parallel to the space axes, the components are

$$\bar{u}_1 = [(S\pm\sqrt{2}e_{20})^{1/2}-1]x_1 , \quad \bar{u}_2 = [(S\mp\sqrt{2}e_{20})^{1/2}-1]x_2 , \tag{6.1}$$

where $S = 1+\sqrt{2}e_{10}$. The ratio of final to initial volumes is $\Delta_0 = (S^2 - 2e_{20}^2)^{1/2}$; the volume increases in the orthorhombic state if $E < -A_1/\sqrt{2}$, for small $|e_2|$. Most experimental results are for cubic-tetragonal systems: V_3Si (Ref. 11) and Nb_3Sn (Ref. 12) have small strains ($\sim 10^{-3}$ and $\sim 2\times10^{-3}$), and experiments detect no volume change; the strain is larger (~ 0.02) for $In_{79}Tl_{21}$ (Ref. 13), but the change in volume is "very small"; for $Mn_{85}Ni_9C_6$ (Ref. 14), the volume increases in the tetragonal state, by about 3 parts in 10^3 (comparable to the strains themselves), presumably because of a large coefficient for the term $e_1(e_2^2+e_3^2)$ — the strains are defined in Ref. 1.

For inhomogeneous strains, the components are assumed to have the form

$$u_1(x_1,x_2) = a(x_1 \mp x_2) + U_1(x_1 \pm x_2) , \tag{6.2a}$$

$$u_2(x_1,x_2) = \mp d(x_1 \mp x_2) \pm U_2(x_1 \pm x_2) , \tag{6.2b}$$

consistent with Eq. (3.2). In terms of the unknown parameters a and d and the unknown functions U_1 and U_2, the strains are given by

$$\sqrt{2}e_1 = (a+d+a^2+d^2) + U_1' + U_2' + (U_1')^2 + (U_2')^2 , \tag{6.3a}$$

$$\sqrt{2}e_2 = (a-d) + (1+2a)U_1' - (1+2d)U_2' , \tag{6.3b}$$

$$\pm 2e_6 = \sqrt{2}e_1 - 2(a+d+a^2+d^2) ; \tag{6.3c}$$

e_6 is a linear function of e_1, as in Eqs. (3.3). If a and d are related by

$$a+d+a^2+d^2 = e_{10}/\sqrt{2} , \tag{6.4}$$

then $e_6 \neq 0$ only in the wall region (where the structure is monoclinic). The components are then given by Eqs. (6.2), with

$$U_1(X) = S^{-1}[\,(d - e_{10}/\sqrt{2})X + (1+2a)f_1(X) - (1+2d)f_2(X)] , \tag{6.5a}$$

$$U_2(X) = S^{-1}[\,(a - e_{10}/\sqrt{2})X - (1+2d)f_1(X) - (1+2a)f_2(X)] , \tag{6.5b}$$

where $X = x_1 \pm x_2$; f_1 and f_2 are given by Eqs. (5.3) and (5.4), but here

$$\Delta(X) = [1 - 2e_{10}^2 - 2e_2^2(X) + 2\sqrt{2}Se_1(X)]^{1/2} . \tag{6.6}$$

These results reduce to those of Sec. V for $E = 0$ (and zero e_{10}, a, and d).

Equations (6.2) plus (6.5) for homogeneous strains are of course rotated versions of Eqs. (6.1). To fix ideas, let $e_2 = e_{20}$, and take $X = x_1 + x_2$; then $f_1(X) = e_{20}X/\sqrt{2}$, $f_2(X) = (1-\Delta_0)X/2$, and application of Eqs. (2.2)–(6.1) gives

$$1+2a = \cos\theta\, g_+ - \sin\theta\, g_- , \quad 1+2d = \cos\theta\, g_- + \sin\theta\, g_+ , \tag{6.7}$$

with $g_\pm = (S \pm \sqrt{2}e_{20})^{1/2}$; Eqs. (6.7) determine the parameters a and d in terms of the arbitrary rotation angle θ. For the O-O' wall, with $e_2(X \to \pm\infty) = \pm e_{20}$, the leading term in f_1 is instead $e_{20}|X|/\sqrt{2}$. From Eqs. (6.7), the rotation angles have the same magnitude in the two asymptotic regions for $d = a = (\sqrt{S}-1)/2$, with θ found from $\sqrt{S}\cos\theta = (g_+ + g_-)/2$; this reduces to Eq. (5.8) when $E = 0$. The discussion at the end of Sec. V C applies (except that the translation vectors **a** and **b** are not determined here). Also, Eqs. (5.5) are satisfied (for $X = x_1 + x_2$ and $d = a$), and the O-O' walls are twin boundaries. Solutions for $d \neq a$ correspond merely to rotations of the structure with $d = a$; explicitly, rotation of the latter by the angle θ found from $\cos\theta = (1+a+d)/S^{1/2}$ gives Eqs. (6.2) and (6.5).

It remains to determine the strains e_1 and e_2. The variation of the density is

$$\begin{aligned}\delta\mathcal{F} = {} & [(1+u_{1,1})(H_1+H_2 \pm H_6/\sqrt{2}) \pm u_{1,2}(H_1-H_2 \pm H_6/\sqrt{2})]\,\delta U_1'/\sqrt{2} \\ & + [(1+u_{2,2})(H_1-H_2 \pm H_6/\sqrt{2}) \pm u_{2,1}(H_1+H_2 \pm H_6/\sqrt{2})]\,\delta U_2'/\sqrt{2} \\ & + [(1+2a)\delta a + (1+2d)\delta d]\,(H_1/\sqrt{2} \mp H_6/2) \\ & + [(1+2U_1')\delta a - (1+2U_2')\delta d]\,H_2/\sqrt{2} .\end{aligned} \tag{6.8}$$

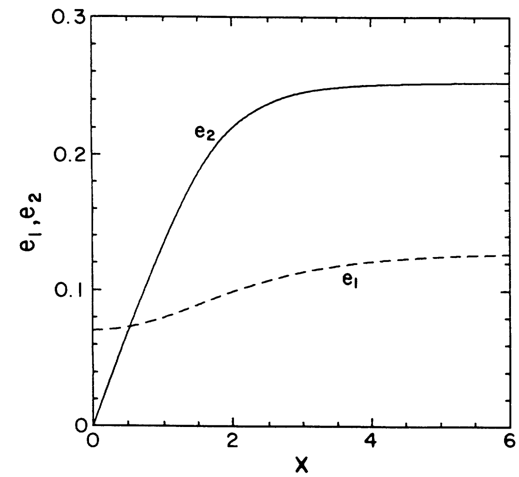

FIG. 1. Strains e_1 (dashed line) and e_2 (solid line) as functions of $X = x_1 \pm x_2$ near the center of an O-O' wall. The parameter E is -2; other parameter values are given in the text.

The third of the four square brackets vanishes because of Eq. (6.4), and $\mathcal{F}$ is stationary if $H_1 \pm H_6/\sqrt{2} = 0$ and $H_2 = 0$. For the extended density, e_1 and e_2 satisfy the coupled, ordinary differential equations

$$-(2d_1+d_3+2\sqrt{2}d_5)e_1''+A_1e_1+Ee_2^2-A_6(e_{10}-e_1)/2 = 0\ , \tag{6.9a}$$

$$-2d_2e_2'' + A_2e_2 + B_2e_2^3 + C_2e_2^5 + 2Ee_1e_2 = 0\ . \tag{6.9b}$$

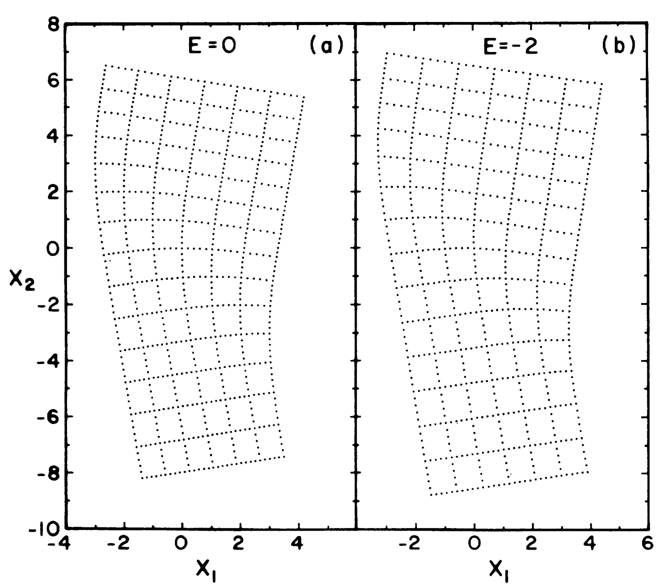

FIG. 2. Deformed regions, for $E = 0$ and $E = -2$; other parameter values are given in the text. The undeformed region was the rectangle $|x_1| \leq 3$, $|x_2| \leq 7$. The shear strain e_6 vanishes in part (a), and also asymptotically in part (b), but is nonzero in the wall region for the latter.

Note that the inhomogeneity in e_2 generates nonzero e_6, even when the only term coupling e_6 to the other strains [the d_5 term in Eq. (4.1b)] is omitted.

Equations (6.9) are easily solved numerically; but the coefficients A_1, etc., are unknown, and comparison with experiment is not possible. Figure 1 plots the strains e_1 and e_2, and Fig. 2 shows two deformed regions, both for an O-O' wall. Unrealistic parameter values are used, for display purposes: $A_1 = 1$, $A_2 = 0$, $A_6 = 1$, $B_2 = -40$, $C_2 = 750$, $d_1 + d_3/2 + \sqrt{2}d_5 = 1$, $d_2 = 1$, and $E = 0$ or -2.

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APPENDIX: STRAIN-GRADIENT ENERGY

This appendix derives and discusses the expression of Eq. (4.1b) for the strain-gradient contribution Ψ to the free-energy density. The strains are assumed to vary slowly over atomic distances, and only the lowest-order invariants are retained. The six forms $\eta_{ij,k}\eta_{lm,n} + \cdots$ which are invariant under rotation by $\pi/2$ about the three-axis and under reflection in the 2-3 plane are

$$I_1 = (\eta_{11,1})^2 + (\eta_{22,2})^2\ , \quad I_2 = (\eta_{11,2})^2 + (\eta_{22,1})^2\ ,$$
$$I_3 = (\eta_{12,1})^2 + (\eta_{12,2})^2\ , \quad I_4 = \eta_{11,1}\eta_{22,1} + \eta_{11,2}\eta_{22,2}\ , \tag{A1}$$
$$I_5 = \eta_{11,1}\eta_{12,2} + \eta_{12,1}\eta_{22,2}\ , \quad I_6 = \eta_{11,2}\eta_{12,1} + \eta_{12,2}\eta_{22,1}\ .$$

Then Ψ is the linear combination $\Psi = \sum_{l=1}^{6} \alpha_l I_l$. A little algebra yields Eq. (4.1b), in which the coefficients d_i are the following combinations of the α_i:

$$d_1 = \alpha_1 + \alpha_2 + \alpha_4\ , \quad d_2 = \alpha_1 + \alpha_2 - \alpha_4\ ,$$
$$d_3 = 2\alpha_3\ , \quad d_4 = \alpha_1 - \alpha_2\ , \tag{A2}$$
$$d_5 = (\alpha_5 + \alpha_6)/\sqrt{2}\ , \quad d_6 = (\alpha_5 - \alpha_6)/\sqrt{2}\ .$$

Equation (4.1b), which retains the full nonlinearity of the strain tensor, is identical to Eq. (2.18) of Ref. 4 (which considered only the linearized tensor).

But Eq. (4.1b) contains redundant terms, because Ψ is a density, and there exist two relations involving the invariants I_l. The first relation,

$$I_6 = I_5 + \partial_1(\eta_{11,2}\eta_{12} + \eta_{12,2}\eta_{22}) - \partial_2(\eta_{11,1}\eta_{12} + \eta_{12,1}\eta_{22})\ , \tag{A3}$$

is an identity to all orders in the geometrical nonlinearity. Therefore the free energy depends only on the sum $\alpha_5 + \alpha_6$, not on the difference, and terms involving d_6 are absent in Eqs. (4.3) for the functionals H_i appearing in the equations of motion, Eqs. (4.4). Explicitly, the last (d_6) term in Eq. (4.1b) is a surface term and can be discarded:

$$e_{2,1}e_{6,2} - e_{2,2}e_{6,1} = \partial_2(e_{2,1}e_6) - \partial_1(e_{2,2}e_6) = \partial_1(e_2 e_{6,2}) - \partial_2(e_2 e_{6,1}) \; . \quad \text{(A4)}$$

Further reduction of Eq. (4.1b) is possible in the approximation (almost certainly valid in practical cases) of a linearized strain tensor; the second relation is

$$2I_5 - I_2 - I_4 = \partial_1[\eta_{11}(u_{1,22} + u_{k,1}u_{k,22}) - \eta_{22}(u_{2,12} + u_{k,2}u_{k,12})] + \partial_2[\eta_{22}(u_{2,11} + u_{k,2}u_{k,11}) - \eta_{11}(u_{1,12} + u_{k,1}u_{k,12})] + \sqrt{2}e_1(u_{k,12}^2 - u_{k,11}u_{k,22}) \; ; \quad \text{(A5)}$$

the first two terms on the right-hand side are surface terms, and the last is of third order in derivatives of the u_i. Correspondingly, the term in Eq. (4.1b) involving d_5 is

$$e_{1,1}e_{6,2} + e_{1,2}e_{6,1} = (e_{1,1}^2 + e_{1,2}^2)/\sqrt{2} - (e_{1,1}e_{2,1} - e_{1,2}e_{2,2})/\sqrt{2} + e_1(u_{k,12}^2 - u_{k,11}u_{k,22}) + \partial_1[e_1(\eta_{12,2} - \eta_{22,1})] + \partial_2[e_1(\eta_{12,1} - \eta_{11,2})] \; ; \quad \text{(A6)}$$

in this identity, the first two terms are proportional to the first and fourth terms in Eq. (4.1b), the third is of third order, and the last two are surface terms. Then the geometrically linearized theory contains only four strain-gradient coefficients. With the help of Eq. (A6), Eq. (4.1b) can be rewritten in several forms, one of which is (with surface and third-order terms discarded)

$$\Psi(e_{\alpha,i}) = \frac{1}{2}d_1'(e_{1,1}^2 + e_{1,2}^2) + \frac{1}{2}d_2(e_{2,1}^2 + e_{2,2}^2) + \frac{1}{2}d_3(e_{6,1}^2 + e_{6,2}^2) + d_4'(e_{1,1}e_{2,1} - e_{1,2}e_{2,2}) \; . \quad \text{(A7)}$$

In this expression, and also in the equations of motion [Eqs. (4.5)], d_6 is absent (as mentioned above), and d_1, d_4, and d_5 appear only in the combinations $d_1' = d_1 + \sqrt{2}d_5$ and $d_4' = d_4 - d_5/\sqrt{2}$. Reference 4 also found four strain-gradient coefficients; a difference is that no relations between the coefficients d_i are obtained here.

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