# Landau theory of a constrained ferroelastic in two dimensions

A. E. Jacobs*
*Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7* †
*and Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo 152, Japan*
(Received 10 March 1995)

The Landau expansion of the elastic energy in powers of the strains and their derivatives is applied to the ferroelastic transformation of a grain constrained so that the displacement vanishes on the boundaries of the grain; the model applies strictly only to the square-rectangular transformation, but some results may apply also to the tetragonal-orthorhombic transformation. The displacement and the strains are obtained by numerical minimization of the elastic energy (with respect to the displacement) for a square column with edges parallel to the (100) and (010) planes of the tetragonal phase. The structure obtained is a sequence of twin boundaries [parallel to the (110) planes of the parent phase] with nonzero dilatational and shear strains near the boundaries. The mean-field transformation temperature $T_c(L)$ is depressed from the bulk value due to the finite width $L$ of the grain, behaving roughly as $T_c(L) = T_c(\infty) - \text{const}/L$.

## I. INTRODUCTION

Ferroelastic transformations (a subclass of martensitic transformations) are shape-changing solid-state phase transformations; the space group of the product phase is a subgroup of that of the parent phase, and the transformation can, in principle, be described by Landau theory. Examples are the cubic-tetragonal transformation (in $Nb_3Sn$, $V_3Si$, and In-Tl alloys and Fe-Pd alloys) and the tetragonal-orthorhombic transformation, but not reconstructive transformations such as the fcc-bcc transformation in Fe. The Landau expansion of the elastic energy in powers of the strains and their gradients requires that the strains be slowly varying so that a continuum description can be used; this is a weak point of the analysis, but one expects the results to be qualitatively correct even if the parent-product and product-product walls are only a few atomic spacings wide. Another limitation of the expansion is that the Landau parameters are not well known from experiment; at the moment, one can expect only qualitative predictions. Although the Landau theory applies strictly only to proper ferroelastic transformations (in which the strains are the primary order parameters) some of the results may apply also to some improper ferroelastic transformations (in which the strains are secondary order parameters) such as the tetragonal-orthorhombic transformation in $YBa_2Cu_3O_{7-\delta}$.

The product-product and parent-product interfaces have been considered in several articles.[1–7] In agreement with experiment, the continuum theory predicts that the elastic energy is minimized if the product-product walls in the cubic-tetragonal[2] and tetragonal-orthorhombic[3,7] transformations are parallel to the (110) planes of the parent phase. This previous work is deficient in several respects. First, the product-product walls (which originate, in effect, because of multiple nucleation events) have positive energy and are not present in equilibrium. Second, because free boundary conditions are employed at the surfaces, macroscopic displacements are generated, which are forbidden in polycrystalline samples; grain boundaries limit displacements (otherwise of order 100 Å for a strain of $10^{-3}$ and a grain size of 10 $\mu$m) to roughly the interatomic spacing. Third, again because of the free boundary conditions, previous work cannot explain why ferroelastic transformations typically occur over a range of temperatures.

That previous results are inapplicable to polycrystalline samples is the main motivation for this study of a constrained ferroelastic. The elastic energy of a single grain is minimized subject to the constraint that the displacement vanish on the surface of the grain; the purpose of the study is to determine how the elastic energy is minimized in a single grain. Informally, the question is "How does a system, which gains energy by changing its shape, gain energy when its shape cannot change?" Part of the answer is well known in physical metallurgy: twin walls enter the system, forming more or less periodic bands of product variants to limit the displacement near the boundary of each grain. Though the twin walls have positive energy, they are equilibrium structures in polycrystalline material. Like grain boundaries, they will anneal out eventually, but likely twin-wall removal is no faster (and perhaps much slower) than grain growth. The following shows that the continuum theory yields a sequence of twin walls; it also determines the strains and the displacement near the boundaries, and shows that the transformation is spread over a range of temperatures.

## II. ELASTIC ENERGY

The following analysis applies strictly only to the square-rectangular transformation, but many results apply also to the tetragonal-orthorhombic transformation, and the terminology of the latter is used. The tetragonal (T) state, the parent or undeformed state stable at high

 

temperature, has $4mm$ symmetry; the 3-axis of the coordinate system is along the fourfold axis, and the 1-3 and 2-3 planes are mirror planes. A point $\mathbf{x}$ in the parent goes to the point $\mathbf{x}' = \mathbf{x} + \mathbf{u}$ in the product, $\mathbf{u}$ being the displacement vector. It is assumed that the component $u_3$ vanishes (or is constant) and that the other components are independent of $x_3$; then a two-dimensional description is possible.

In the Lagrangian description, the components of the strain tensor $\eta$ are[8]

$$\eta_{ij} = \tfrac{1}{2}(u_{i,j} + u_{j,i} + u_{k,i}u_{k,j}) \ , \tag{2.1}$$

where $u_i$ is the $i$th component of $\mathbf{u}$, $u_{i,j} = \partial_j u_i = \partial u_i/\partial x_j$, and repeated indices are summed; the nonlinear term in Eq. (2.1) ensures that the energy is invariant with respect to the definition of the coordinate axes. The strain tensor relates $ds^2 = (dx_i)^2$ and $dS^2 = (dx_i + du_i)^2$, the squares of the distance between two nearby points in the undeformed and deformed states, by $dS^2 - ds^2 = 2\,\eta_{ij}\,dx_i\,dx_j$. The elastic-energy density describing the transformation is an expansion in the components of $\eta$ and their derivatives.

The appropriate combinations of the strain tensor are the strains

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

$$e_2 = (\eta_{11} - \eta_{22})/\sqrt{2} \ , \tag{2.2}$$

$$e_6 = \eta_{12} \ ,$$

the other three strains vanishing identically. The strains $e_1$, $e_2$, and $e_6$ are usually called the dilatational, deviatoric, and shear strains, respectively, but $e_1$ is not the true dilatational strain $e_0$; the latter, which vanishes if the volume is conserved, is defined by $e_0 = \Delta - 1$, where[8] (in two dimensions)

$$\Delta(x_1, x_2) = [(1 + \sqrt{2}e_1)^2 - 2e_2^2 - 4e_6^2]^{1/2} \tag{2.3}$$

is the local ratio of the final to initial volumes (the Jacobian of the transformation $x_i \to x_i + u_i$).

The elastic-energy density is taken to be[3,5,7]

$$\mathcal{F} = \tfrac{1}{2}A_1e_1^2 + \tfrac{1}{2}A_2e_2^2 + \tfrac{1}{4}B_2e_2^4 + \tfrac{1}{6}C_2e_2^6 + \tfrac{1}{2}A_6e_6^2 + \Psi(e_{\alpha,i}) \ , \tag{2.4a}$$

$$\Psi(e_{\alpha,i}) = \tfrac{1}{2}d_1(e_{1,1}^2 + e_{1,2}^2) + \tfrac{1}{2}d_2(e_{2,1}^2 + e_{2,2}^2) + \tfrac{1}{2}d_3(e_{6,1}^2 + e_{6,2}^2) \ . \tag{2.4b}$$

All coefficients but $A_2$ are independent of temperature; for stability, $A_1$, $A_6$, $d_1$, $d_2$, and $d_3$ are positive. All strains vanish in the T state. The coefficient $A_2 = a(T - T_0)$ (with $a > 0$) is negative below a temperature $T_0$, yielding the orthorhombic (O) product at lower $T$; in the O state, $e_1 = 0$, $e_2 = \pm e_{20}$ (corresponding to the two O variants), and $e_6 = 0$. From Eq. (2.3), a small volume decrease (of order $e_2^2$) accompanies the T→O transformation, but this is easily remedied[7] by adding a term in $e_1e_2^2$ to Eq. (2.4a). The coefficient $B_2$ can be either positive or negative. The former case describes a second-order transition at $A_2 = 0$ in the bulk, and the term in $e_2^6$ is not necessary. In the latter case, the transition is first-order (as is usual in ferroelastics), and the term in $e_2^6$ (with $C_2 > 0$) must be included for stability; the bulk transition temperature ($> T_0$) is found from $A_2 = 3B_2^2/(16C_2)$, while the bulk strains in the two O variants are $\pm e_{20}$ with $e_{20} = [(-B_2/2 + \gamma)/C_2]^{1/2}$ and $\gamma = (B_2^2/4 - A_2C_2)^{1/2}$. The expansion in powers of $e_2^2$ is, of course, limited to temperatures $T$ close to the transformation temperature; nonpolynomial terms are required to remedy an unphysical result of the expansion, that the strain $e_{20}$ does not saturate at low $T$. The terms in $e_1^2$ and $e_6^2$ in Eq. (2.4a) are the usual contributions for a linear, homogeneous, elastic medium.

The strain-gradient part $\Psi$ of Eq. (2.4b) gives the contribution from inhomogeneous strains. Contrary to statements in the literature, Eq. (2.4b) (which was used in Ref. 3) has the proper rotational invariance; it merely omits several invariants, terms coupling the derivatives of the strains,[5,7] as discussed below. The strain-gradient terms give nonzero width to the parent-product and product-product interfaces; in fact, they are necessary to define the length scale. Other approaches,[9–13] which omit these terms, have, however, been used successfully.

Equation (2.4) contains only essential terms. Of the many terms allowed by symmetry and of the same order as those retained, those that couple $e_2$ to other strains are particularly troublesome, for they can induce strains $e_1$ and $e_6$ parasitically in the presence of non-vanishing $e_2$ or its derivatives; examples are terms like $e_1e_2^2$ in Eq. (2.4a) and $e_{1,1}e_{2,1} - e_{1,2}e_{2,2}$ (see Refs. 5 and 7) in Eq. (2.4b), and higher-order combinations like $e_6^2(e_{2,1}^2 + e_{2,2}^2)$. These 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, and it is desired that there be no confusion about their origin; in fact, the following shows that nonzero strains $e_1$ and $e_6$ develop as a result of the boundary conditions, even though the energy density contains no terms coupling $e_1$ and $e_6$ to $e_2$.

Some of the Landau coefficients appearing in the expression for the free energy are known for some materials, but a complete set appears to be unavailable for any material. This article is then necessarily qualitative and exploratory. I have chosen a set of coefficients believed to be representative: $A_1 = 1$, $A_6 = 1$, $B_2 = -3$, and $C_2 = 10^6$; the unit of length is fixed by the choice $d_2 = 1$; $d_1$ and $d_3$ are also taken to be 1 (since there is no reason to take them different from $d_2$). The coefficient $d_2$ determines the width parameter $\xi$ for the product-product soliton[3,7]

$$e_2(X) = e_{20}\sinh(X/\sqrt{2}\xi)/[\cosh^2(X/\sqrt{2}\xi) + \alpha]^{1/2} \tag{2.5}$$

[where $X = x_1 \pm x_2$ and $\alpha = (-B_2 + 2\gamma)/(B_2 + 4\gamma)$] according to $\xi = e_{20}^{-1}(d_2/\gamma)^{1/2}$; the width of the wall de-

creases with decreasing $T$: at low $T$, $\xi \approx \sqrt{-d_2/A_2}$. The choices for $B_2$ and $C_2$ give a weakly first-order transition in the bulk at $A_2 \approx 2\times10^{-6}$, with strain $e_{20} = 1.5\times10^{-3}$; the strains $e_{20}$ are rather large at low $T$, about 0.03 at $A_2 = -1$. Other choices for the parameters were investigated, with no qualitative change in the results.

## III. CONSTRAINED SQUARE

The strain energy $F = \int \mathcal{F} dV$ was minimized with respect to the components $u_1(x_1, x_2)$ and $u_2(x_1, x_2)$ using a conjugate-gradient method, subject to the conditions $\mathbf{u} \equiv 0$ on (and outside) the surface of a square of side $L$ with edges parallel to the (010) and (100) planes of the parent phase. This procedure guarantees that the compatability equations are satisfied, unlike other approaches; it is less accurate but far simpler than solving the partial differential equations (which are fourth-order in derivatives of the displacement). The full (nonlinear) strain tensor was used (although the strains are only a few percent at most). The components of the displacement were found on a square grid of points equally spaced at intervals $L/192$, and the strains from numerical differ-

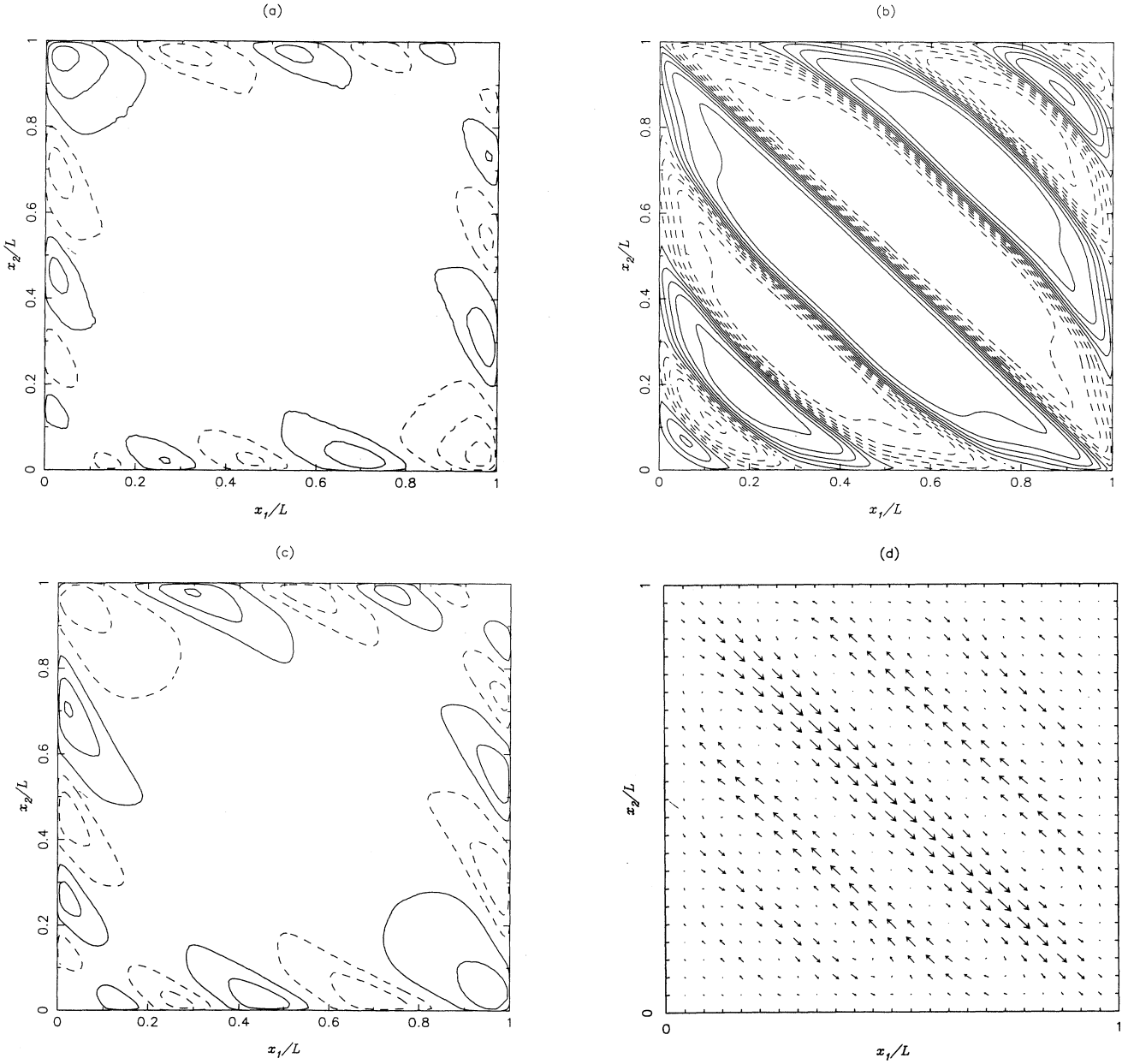


FIG. 1. Parts (a), (b), and (c): contour plots of the normalized strains $e_1/e_{20}$, $e_2/e_{20}$, and $e_6/e_{20}$; part (d): displacement field $\mathbf{u}$. The linear dimension of the square grain is $L = 96$, and the temperature corresponds to $A_2 = -0.5$. In parts (a) – (c), contour lines are drawn at $e_j/e_{20} = 0.1$, 0.3, etc., (solid lines), and $-0.1$, $-0.3$, etc. (dashed lines). In part (d), the magnitude of the displacement field is not to scale.

entiation of the displacement. Because a centered, five-point, finite-difference approximation was used for the derivatives, the strains do not vanish at the boundary and at the first grid point outside the boundary (recall that the displacement vanishes on and outside the boundary). The nonvanishing of the strains at these points is entirely due to the finite spacing of the grid points; in the figures discussed below, the strains are plotted only on and inside the square. Starting values for the minimization were obtained by hand nucleation of an orthorhombic region embedded in tetragonal material or from converged values at other parameter values ($T$, $L$, etc.). Final values were independent of the starting values with the same symmetry; that is, walls are not pinned but enter and exit freely at the corners. Solutions were of two symmetries, $e_2$ odd about a diagonal of the square or $e_2$ even; the first had the lower energy in all cases investigated. Of course there are many other solutions; further work might examine twin walls in both directions.

Figure 1 shows the strains and the displacement at $A_2 = -0.5$ for a square of side $L = 96$ (the length scale is defined by the choice $d_2 = 1$ in the strain-gradient energy $\Psi$). The dilatational and shear strains are localized near the boundary of the square; the deviatoric strain forms a twin wall along the diagonal and several other walls, which become less well defined near the corners. The walls are parallel, and the displacement is zero between the walls, except near the boundaries. The change in the wall orientation near the boundary is reminiscent of the tapering of twins at the interface between orthogonally oriented twins in $YBa_2Cu_3O_{7-\delta}$ (Ref. 14 and references therein).

Figure 2 shows the deviatoric strain for $L = 96$ (as in Fig. 1) at a lower temperature $A_2 = -1$. As discussed below Eq. (2.5), the walls narrow with decreasing $T$; the widths in Figs. 1(b) and 2 are comparable to those expected from the analytical solution for a single wall (which gives the $\pm 50\%$ widths as 1.32 and 0.93 at $A_2 = -0.5$ and $-1$). The walls are better defined at the lower temperature, particularly toward the corners; their positions change by only 10% with the decrease in $T$.

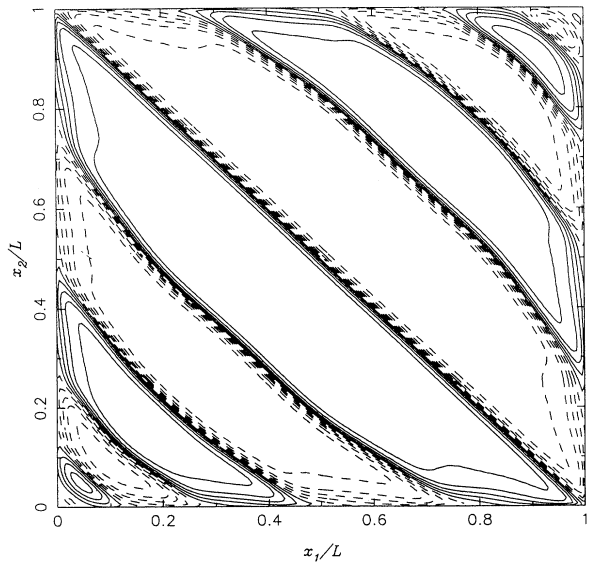


FIG. 2. Contour plot of the normalized strain $e_2/e_{20}$ for the grain of Fig. 1, but at a temperature corresponding to $A_2 = -1$.

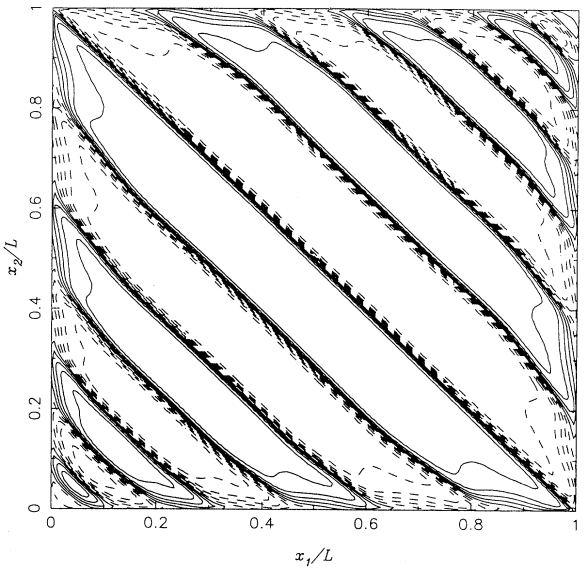


FIG. 3. Contour plot of the normalized strain $e_2/e_{20}$ for a grain of linear dimension $L = 192$, at a temperature corresponding to $A_2 = -0.5$.

Figure 3 shows the deviatoric strain for a larger square ($L = 192$), at $A_2 = -0.5$. The distance between walls is about 50% greater than in Fig. 1. From Figs. 1(b), 2, and 3, the wall spacing is roughly independent of $T$, does not scale with the system size $L$, and (for given $T$ and $L$) decreases with the length of the wall.

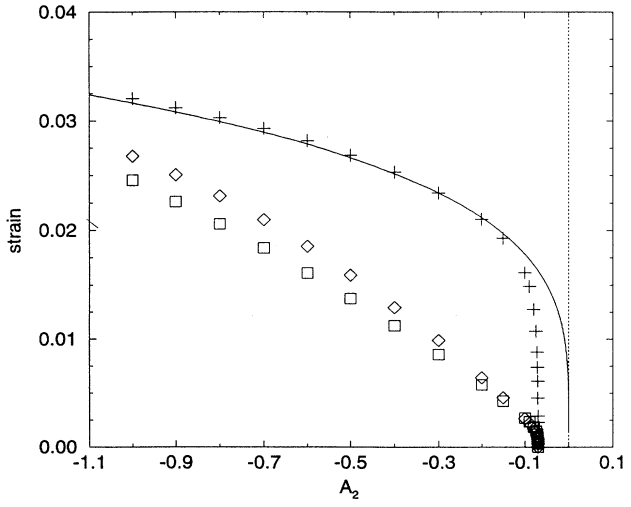


FIG. 4. Strain $e_{20}$ in bulk material (solid line) as a function of the Landau parameter $A_2$; maximum values of $|e_1|$ (diamonds), $|e_2|$ (pluses), and $|e_6|$ (squares) for a grain of linear dimension $L = 96$ as functions of $A_2$.

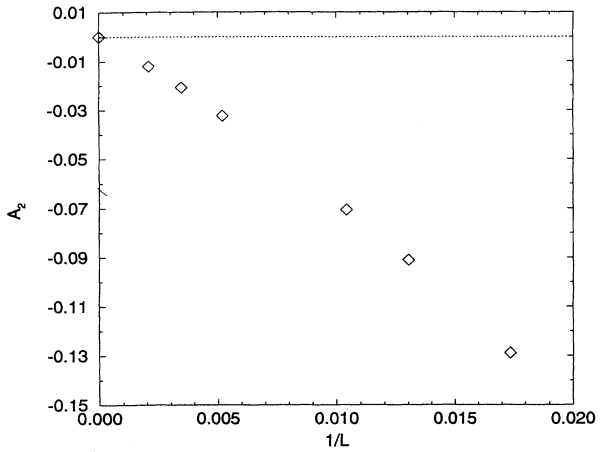


FIG. 5. Dependence of the Landau parameter $A_2$ at the mean-field transformation temperature $T_c$ on the reciprocal of the grain size $L$.

Figure 4 shows the maximum values of $|e_1(x_1, x_2)|$, etc., as functions of the Landau parameter $A_2$ for $L = 96$, and also the strain $e_{20}$ in bulk orthorhombic material. Near the transformation temperature, the deviatoric strain $e_2$ is, of course, much less than the bulk value, and the walls are poorly defined near the corners. The maximum deviatoric strain is about 1% larger than the bulk value at low $T$, perhaps due to incomplete convergence. The dilatational and shear strains are small near the transformation temperature; they increase in magnitude with decreasing $T$ and become of the same order as the deviatoric strain.

Figure 5 shows the mean-field transformation temperature (more precisely, the value of the Landau coefficient $A_2$ below which the twinned product phase has lower energy than the tetragonal phase) as a function of $1/L$; of course a true phase transition occurs only in the limit $L \to \infty$. The results apply only to a grain embedded in a matrix of other grains, not to grains with free surfaces. The transformation temperature of a single grain decreases with the size of the grain, and so the ferroelastic transformation in a polydisperse, polycrystalline sample occurs over a range of temperatures. In terms borrowed from the martensite literature, the transformation starts at $T = M_S$ and finishes at $T = M_F$, corresponding to the transformation temperatures of the largest and smallest grains.

The continuum theory then predicts correctly the twin-wall orientation in constrained systems. It also predicts that the transformation temperature decreases with the grain size, so that ferroelastic transformations occur over a range of temperatures. The observed narrowing at the collision of twinned regions may also find an explanation in the continuum theory, but further work is required for confirmation.

## ACKNOWLEDGMENTS

This research was supported by the Natural Sciences and Engineering Research Council of Canada and by the Japan Society for the Promotion of Science. I am grateful to R. J. Gooding, V. Heine, M. Luskin, H. Shiba, and Y. Yamada for discussions and correspondence.

* Electronic address: jacobs@physics.utoronto.ca
† Present address.

[1] F. Falk, Z. Phys. B **51**, 177 (1983).
[2] G. R. Barsch and J. A. Krumhansl, Phys. Rev. Lett. **53**, 1069 (1984).
[3] A. E. Jacobs, Phys. Rev. B **31**, 5984 (1985).
[4] J. L. Ericksen, Int. J. Solids Struct. **22**, 951 (1986).
[5] G. R. Barsch and J. A. Krumhansl, Metall. Trans. **19A**, 761 (1988).
[6] S. Kartha, T. Castán, J. A. Krumhansl, and J. P. Sethna, Phys. Rev. Lett. **67**, 3630 (1991).
[7] A. E. Jacobs, Phys. Rev. B **46**, 8080 (1992).
[8] L. Brillouin, *Tensors in Mechanics and Elasticity* (Academic, New York, 1964).
[9] C. Collins and M. Luskin, in *Partial Differential Equations and Continuum Models of Phase Transitions*, Lecture Notes in Physics, Vol. 344, edited by M. Rascle, D. Serre, and M. Slemrod (Springer-Verlag, New York, 1989), p. 34.
[10] M. Luskin, in *Progress in Partial Differential Equations: the Metz Surveys*, Pitman Research Notes in Mathematics, Vol. 249, edited by M. Chipot and J. Saint Jean Paulin (Longman House, London, 1991), p. 156.
[11] C. Collins, M. Luskin, and J. Riordan, in *Microstructure and Phase Transitions*, IMA Volumes in Mathematics and Its Applications, Vol. 54, edited by R. James, D. Kinderlehrer, and M. Luskin (Springer-Verlag, New York, 1993), p. 51.
[12] P. Klouček and M. Luskin, Continuum Mech. Thermodynamics **6**, 209 (1994).
[13] P. Klouček and M. Luskin, Math. Comput. Modelling **20**, 101 (1994).
[14] A. H. King and Y. Zhu, Philos. Mag. A **67**, 1037 (1993); Y. Zhu, M. Suenaga, and J. Tafto, *ibid.* **67**, 1057 (1993).