Elasticity models for crystal microstructure

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1 Phase transformations and microstructure

Suppose that we cool a single crystal (e.g. of InTl, NiMn or CuAlNi) below a temperature θ_c at which a phase transformation involving a change of symmetry occurs. On examining the crystal in an optical or electron microscope we typically observe a characteristic pattern of *microstructure*, consisting locally of a large number of planar and parallel *interfaces* separating layers of the crystal. The orientation of the interfaces (or *twins*) can vary from one part of the crystal to another, and other interfaces (sometimes but not always planar) separate regions in which the twin orientations differ. The scale of the microstructure, as measured by the average layer thickness, varies considerably from material to material, and can be as small as a few interatomic distances.

In trying to understand this microstructure, two questions immediately arise:

1. What do the interfaces represent?
2. Why is the microstructure so fine?

To answer the first question we need to understand what occurs at the atomic level during the phase transformation. Consider as an example the case of the binary alloy Indium-Thallium (InTl), which for temperatures $\theta > \theta_c$ has a face-centred cubic structure termed *austenite*. Thus the unit cell of the crystal lattice consists for $\theta > \theta_c$ of a cube with an atom at each vertex and in the middle of each face. InTl is a *solid solution*, so that the atom at any particular lattice site can be either Indium or Thallium, and the value of θ_c depends on the overall concentration of Thallium (e.g. $\theta_c = 57°C$ for 20.73 mass % Tl).

For $\theta < \theta_c$ the crystal prefers for energetic reasons a face-centred tetragonal structure termed *martensite*, in which the cubic cell (of original side-length 1, say) extends in the direction of one of the three cubic axes to form a tetragon with sides of lengths η_1, η_2 and η_2, where for InTl $\eta_1 < 1 < \eta_2$. In fact $\eta_1 = \eta_1(\theta)$ and $\eta_2 = \eta_2(\theta)$ vary slightly with temperature, but we ignore this for simplicity. Now suppose that the crystal chooses to deform so that in one region the longer side of the tetragon corresponds to the (1,0,0) cubic

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axis, say, while in the remainder of the crystal the longer side of the tetragon corresponds to the (0,1,0) cubic axis. How can this occur while preserving the integrity of the lattice? The answer is for the two regions to be rotated with respect to one another, the interface between them being planar with a specific orientation, namely that corresponding to the (1,1,0) plane in the cubic lattice. In this way the only unit cells of the crystal not having the preferred tetragonal form are those intersecting the interface, and the distortion of each of these cells remains bounded, so that the total energy of the crystal is very nearly minimized.

To answer the second question is not so easy, and it is one of the virtues of the elasticity model in [9, 10] (see also Chipot & Kinderlehrer [14]) and described in the next section that a very convincing answer can be given in terms of an associated problem of the calculus of variations.

2 A model based on nonlinear elasticity

Following Ericksen [17] the theory of Ball & James [9, 10] models a crystal as a nonlinear elastic continuum. The total elastic energy of the crystal is assumed to have the form

$$I(y) = \int_\Omega W(Dy(x), \theta) dx, \tag{2.1}$$

where $\Omega \subset \mathbf{R}^3$ is a bounded open set with boundary $\partial\Omega$ occupied by the crystal in a reference configuration, Dy denotes the gradient of y, θ is the temperature, and W is the *stored-energy function* (or *free energy*) of the material. We will suppose that θ is a constant, and for simplicity suppress the dependence of W on θ, writing $W = W(\cdot)$. However it is important to keep in mind that W depends on θ, since it is this dependence that describes the phase transformation.

We neglect all other contributions to the energy of the crystal, and in particular any energy associated with interfaces. The neglect of interfacial energy is justified by the very large interfacial area observed in typical microstructures, which indicates that interfacial energy must be very small in comparison to the bulk elastic energy. In neglecting interfacial energy we are of course not denying its existence, but merely taking advantage of its smallness to develop a more tractable theory in which interfaces and microstructure appear naturally as singularities of energy-minimizing deformations. The procedure is analogous to the neglect of viscosity in gas dynamics, the resulting advantage there being the mathematically natural description of vortices and shock-waves as singularities of solutions. We will see that the zero interfacial energy theory leads to a number of interesting predictions that are experimentally verified; however, some more detailed aspects of microstructure morphology can only be understood within the context of a theory incorporating interfacial energy.

Given a boundary displacement $\overline{y} : \partial\Omega \to \mathbf{R}^3$ we consider the following problem:

$$\text{Minimize } I(y) \tag{2.2}$$

subject to

$$y|_{\partial\Omega} = \overline{y}. \tag{2.3}$$

In terms of this minimization problem the explanation given in [9, 10] for the fineness of observed microstructures is the following:

(a) In general I does not attain a minimum subject to (2.3).

(b) Let $y^{(j)}$ be a minimizing sequence for I subject to (2.3), i.e. $y^{(j)}|_{\partial\Omega} = \overline{y}$ and

$$\lim_{j\to\infty} I(y^{(j)}) = \inf_{y|_{\partial\Omega}=\overline{y}} I(y).$$

Then $y^{(j)}$ necessarily develops finer and finer microstructure as $j \to \infty$.

It is instructive to compare the situation described by (a),(b) with elasticity models of rubber, for example with the Mooney-Rivlin theory which in its compressible form has the corresponding stored-energy function

$$W(A) = c_1|A|^2 + c_2|\mathrm{cof}A|^2 + h(\det A), \tag{2.4}$$

where $c_1 > 0$, $c_2 > 0$, cof$A$ denotes the matrix of cofactors of A and $h : (0,\infty) \to \mathbf{R}$ is smooth, convex and bounded below. For this W it is known (*cf.* [3]) that

(a)′ I attains a minimum subject to (2.3).

(b)′ Minimizing sequences $y^{(j)}$ converge to minimizers (after possible extraction of a subsequence) and do not develop microstructure.

It is believed, but has not been proved, that minimizers are smooth, at least off a small set; certainly (see [4]) interfaces of the type observed in crystal microstructure are not possible, in accordance with observation. The reason that the same mathematical theory of nonlinear elasticity can lead to such dramatically different predictions for different materials lies in the properties of W. For example, W given by (2.4) is strongly elliptic, while the W corresponding to InTl is not. The question of exactly which stored-energy functions W lead to an attained minimum is open, but has been illuminated by an important counterexample discovered recently by Šverák [44].

In terms of the continuum theory interfaces are surfaces across which the deformation gradient jumps. Consider the case of a planar interface $x \cdot n = k$ having unit normal n. Suppose that y is continuous with $Dy = A$ for $x \cdot n < k$ and $Dy = B$ for $x \cdot n > k$, where A, B are given 3×3 matrices. Applying the continuity of y across the interface we see that

$$A - B = a \otimes n \tag{2.5}$$

for some $a \in \mathbf{R}^3$, where $(a \otimes n)_{i\alpha} := a_i n_\alpha$. Thus nontrivial interfaces correspond to pairs $A, B \in M^{3\times3}$ (where we denote by $M^{m\times n}$ the set of real $m \times n$ matrices) differing by a matrix of rank one.

3 Two, three and four gradients

3.1 The two-gradient problem

Let $A, B \in M^{3\times3}$ with $A \neq B$, and suppose that $W : M^{3\times3} \to \mathbf{R}$ with

$$W(A) = W(B) = 0,\ W(F) > 0 \text{ for } F \neq A, B. \tag{3.1}$$

(As we explain later, such a W cannot correspond to a real elastic material, but the example is instructive.) For $y : \Omega \to \mathbf{R}^3$ we write as before the total energy

$$I(y) = \int_\Omega W(Dy)dx. \tag{3.2}$$

Case 1

$$A - B = a \otimes n \quad \text{for some } a, n.$$

In this case we can form an interface with normal n separating the constant gradients A, B. Let $0 < \lambda < 1$. Repeating this construction we can define for each $j = 1, 2, \ldots$ a piecewise affine mapping $y^{(j)} : \mathbf{R}^3 \to \mathbf{R}^3$ such that $Dy^{(j)} = A$ in alternate layers normal to n of thickness $\frac{\lambda}{j}$ and $Dy^{(j)} = B$ in alternate layers of thickness $\frac{1-\lambda}{j}$. By adding a suitable constant vector to $y^{(j)}$ we can suppose that $y^{(j)}(0) = 0$. Note that by (3.1)

$$I(y^{(j)}) = 0. \tag{3.3}$$

As $j \to \infty$, $y^{(j)}(x) \to Cx$ uniformly in Ω, where

$$C = \lambda A + (1 - \lambda)B. \tag{3.4}$$

The $y^{(j)}$ so defined form a *simple laminate zero-energy microstructure.* Note that the limiting deformation $y = Cx$ does not have zero energy. In fact we can prove

Theorem 3.1 *The minimum of I in $W^{1,1}(\Omega; \mathbf{R}^3)$ subject to $y|_{\partial\Omega} = Cx$ is not attained.*

(Here $W^{1,p} = W^{1,p}(\Omega; \mathbf{R}^3)$, $1 < p < \infty$, denotes the usual Sobolev space of mappings $y : \Omega \to \mathbf{R}^3$ with y, Dy both p^{th}-power integrable.)

Proof. Define $\tilde{y}^{(j)}$ to equal $y^{(j)}$ except in a boundary layer E_j near $\partial\Omega$ of thickness $\frac{1}{j}$, in which we interpolate between $y^{(j)}$ and the boundary condition Cx in such a way that $\tilde{y}^{(j)}|_{\partial\Omega} = Cx$ and $D\tilde{y}^{(j)}(x)$ remains uniformly bounded independently of j. Then

$$I(\tilde{y}^{(j)}) = \int_{E_j} W(D\tilde{y}^{(j)})dx \to 0 \tag{3.5}$$

as $j \to \infty$. But it is easily checked that there does not exist a y with $I(y) = 0$ and $y|_{\partial\Omega} = Cx$. □

3.2 Description of microstructure via Young measures

Suppose we are given a sequence $y^{(j)}$ which is bounded in $W^{1,1}(\Omega; \mathbf{R}^3)$. Fix $x \in \Omega$, j and a number $\delta > 0$. Denote by $\nu^{(j)}_{x,\delta}$ the probability measure on $M^{3\times3}$ giving the distribution of the values of $Dy^{(j)}(z)$ as z is chosen uniformly at random from the ball centre x and radius δ. Then

$$\nu_x = \lim_{\delta \to 0} \lim_{j \to 0} \nu^{(j)}_{x,\delta} \tag{3.6}$$

defines the *Young measure* $(\nu_x)_{x\in\Omega}$ corresponding to $Dy^{(j)}$. The limit in (3.6) is understood in the sense of weak * convergence of probability measures. In general we need to extract a subsequence of $y^{(j)}$ for the limit to exist. The reader is referred for details to Tartar [40, 41], and to [5] (where the above intuitive definition is justified). For our purposes the key point is that ν_x is for a.e. $x \in \Omega$ a probability measure on $M^{3\times 3}$ giving the limiting distribution of the values of $Dy^{(j)}$ as $j \to \infty$ near the point x.

Example
Suppose $y^{(j)}$ is the simple laminate defined above. Intuitively, near any point x we have a probability λ of finding the value $Dy^{(j)} = A$ and a probability $1 - \lambda$ of finding the value $Dy^{(j)} = B$. Hence ν_x is independent of x and is given by

$$\nu_x = \lambda\delta_A + (1-\lambda)\delta_B$$

Suppose that $Dy^{(j)}$ is bounded in L^p for p sufficiently large ($p \geq 3$ will do), with Young measure $(\nu_x)_{x\in\Omega}$. Then ν_x satisfies the *minors relations*

$$< \nu_x, J >= J(< \nu_x, id >) \tag{3.7}$$

for any minor (i.e. subdeterminant) $J : M^{3\times 3} \to \mathbf{R}$, where

$$< \nu_x, f >:= \int_{M^{3\times 3}} f(A)\, d\nu_x(A) \tag{3.8}$$

and in particular

$$< \nu_x, id >= \int_{M^{3\times 3}} A\, d\nu_x(A). \tag{3.9}$$

The minors relations transcribe into the language of Young measures the results of Reshetnyak [34] on the sequential weak continuity of Jacobians on Sobolev spaces. They are a key technical tool in the analysis of microstructure.

3.3 The two-gradient problem (continued)

Suppose that W is given as in (3.1) but now that

Case 2

$$\text{rank}(A - B) > 1. \tag{3.10}$$

Thus we can no longer make an interface between A and B.

Question: Is there a zero-energy microstructure?

To answer this, suppose that $y^{(j)}$ satisfies

$$I(y^{(j)}) = \int_\Omega W(Dy^{(j)})\, dx \to 0 \tag{3.11}$$

as $j \to \infty$. Suppose that W grows sufficiently fast at infinity, for example

$$W(F) \geq c + d|F|^3 \tag{3.12}$$

where $d > 0$ and c are constants. From (3.11), the fact that W is zero only at A and B, and the definition of Young measures, it follows that the Young measure $(\nu_x)_{x\in\Omega}$ corresponding to (a suitable subsequence of) $Dy^{(j)}$ is supported for a.e. $x \in \Omega$ in the set $\{A, B\}$, i.e.

$$\nu_x = \lambda(x)\delta_A + (1 - \lambda(x))\delta_B, \tag{3.13}$$

where $0 \leq \lambda(x) \leq 1$ a.e.. To simplify the calculation we assume without loss of generality that $B = 0$. Then rank $A > 1$, so that there exists a 2×2 minor J with $J(A) \neq 0$. By the minors relations

$$< \nu_x, J >= J(< \nu_x, id >),$$

and substituting $\nu_x = \lambda(x)\delta_A + (1 - \lambda(x))\delta_0$ we obtain

$$\lambda(x)J(A) = J(\lambda(x)A) = \lambda(x)^2 J(A).$$

Hence $\lambda(x) = 0$ or 1 a.e.. It is not hard to deduce from this (for the details see [9]) that either $Dy^{(j)} \to A$ in measure or $Dy^{(j)} \to B$ in measure, so that there is *no microstructure.*

If rank $(A - B) > 1$ then if $Dy(x)$ takes both the values A and B on sets of positive measure it must take some other values as well. A quantitative expression of this fact is given in [8], where it is applied to study hysteretic phenomena induced by incompatible phases.

3.4 Three and four gradients

For the case of three gradients we have the following deep result.

Theorem 3.2 (Šverák [42]) *Let A_1, A_2, $A_3 \in M^{m\times n}$ with rank $(A_i - A_j) > 1$ for $i \neq j$. Let $y^{(j)}$ be bounded in $W^{1,p}(\Omega; \mathbf{R}^m)$, $p > 1$, where $\Omega \subset \mathbf{R}^n$ is bounded and open, and let $Dy^{(j)}$ have Young measure $(\nu_x)_{x\in\Omega}$ satisfying*

$$supp\ \nu_x \subset \{A_1, A_2, A_3\},\ a.e.\ x \in \Omega,$$

i.e. $\nu_x = \sum_{i=1}^3 \lambda_i(x)\delta_{A_i}$, where $\lambda_i(x) \geq 0$, $\sum_{i=1}^3 \lambda_i(x) = 1$. Then $\nu_x = \delta_{A_i}$ a.e. for some i.

Thus if $W(A_i) = 0$, $W(F) > 0$ for $F \notin \{A_1, A_2, A_3\}$, then no zero-energy microstructure is possible when the A_i have no rank-one connection. It is remarkable that this result does not extend to the case of four matrices.

Example (Bhattacharya *et al* [13], exploiting an idea of Tartar [39]). There exist four matrices A_1, A_2, A_3, $A_4 \in M^{2\times 2}$ with rank $(A_i - A_j) > 0$ for $i \neq j$, and a sequence of gradients $Dy^{(j)}$ with Young measure

$$\nu_x = \sum_{i=1}^4 \lambda_i \delta_{A_i},\quad \lambda_i > 0, \sum_{i=1}^4 \lambda_i = 1.$$

The idea of the example is to construct an '∞-laminate' (layers within layers within layers ...).

4 Predictions of the theory for crystal microstructure

The stored-energy functions W considered in the previous section were minimized on a finite number of matrices, and thus do not apply to real crystals. This is because of the requirement that W be frame-indifferent (invariant to superposed rotations), i.e.

$$W(QA) = W(A) \text{ for all } A \in M^{3\times 3},\ Q \in SO(3). \tag{4.1}$$

Thus if A minimizes W so do the infinite number of matrices QA, $Q \in SO(3)$.

As an example, consider the cubic to tetragonal transformation for InTl described in Section 1. Let us suppose that the temperature θ equals θ_c. We take as the reference configuration the cubic phase at $\theta = \theta_c$, which is consequently represented by the identity deformation $y(x) = x$ which has gradient $\mathbf{1}$. In the light of the discussion in Section 1 it is reasonable to suppose that at $\theta = \theta_c$ both the cubic and tetragonal phases minimize W, so that in particular $\mathbf{1}$ minimizes W. By (4.1) we thus have that all matrices $Q \in SO(3)$ minimize W. The linear transformations describing the distortion of the cubic lattice to the tetragonal lattice in each of the three cubic directions correspond to the matrices.

$$\begin{aligned} U_1 &= \operatorname{diag}(\eta_2, \eta_1, \eta_1), \\ U_2 &= \operatorname{diag}(\eta_1, \eta_2, \eta_1), \\ U_3 &= \operatorname{diag}(\eta_1, \eta_1, \eta_2). \end{aligned} \tag{4.2}$$

We thus suppose that each of the matrices U_i also minimizes W, which by (4.1) implies that all matrices in the sets $SO(3)U_i$ minimize W. Assuming without loss of generality that $W \geq 0$, we are thus led to the hypothesis that at $\theta = \theta_c$ the minimizers of W are given by

$$M := \{A : W(A) = 0\} = SO(3) \cup SO(3)U_1 \cup SO(3)U_2 \cup SO(3)U_3. \tag{4.3}$$

It is easily verified that the four 'wells' on the right-hand side of (4.3) are disjoint.

To see what zero-energy microstructures are possible, the first step is to calculate the possible interfaces, i.e. to find those pairs A, $B \in M$ with rank $(A - B) = 1$. The result of this calculation is as follows.

(i) If A, B are distinct and belong to the same well then rank $(A - B) > 1$.

(ii) If $A \in SO(3)$, $B \in SO(3)U_i$ for some i then rank $(A - B) > 1$.

(iii) If $i \neq j$ and $A \in SO(3)U_i$ then there exist precisely two matrices $B \in SO(3)U_j$ with rank $(A - B) = 1$.

The pairs A, B in (iii) are called *twins*, and the orientations of the corresponding interfaces agree with experiment.

By (ii) we cannot have a standard interface between austenite and martensite. However, it is possible to have an 'approximate interface' $x \cdot m = \alpha$, say, corresponding to a zero-energy microstructure with Young measure

$$\nu_x = \begin{cases} \delta_Q & \text{for } x \cdot m > \alpha \\ \lambda\delta_A + (1-\lambda)\delta_B & \text{for } x \cdot m < \alpha \end{cases} \tag{4.4}$$

where $Q \in SO(3)$, $0 < \lambda < 1$, and A, B are twins. This corresponds to finding $Q \in SO(3)$, $A \in SO(3)U_i$, $B \in SO(3)U_j$, λ, a, n, b and m such that

$$A - B = a \otimes n,\ Q - (\lambda A + (1-\lambda)B) = b \otimes m. \tag{4.5}$$

This is possible, and the results correspond to the formulae of the classical *crystallographic theory of martensite* (see Wechsler, Lieberman & Read [45]). The phase fraction λ and approximate interface normal m are in good agreement with observation. For details of the calculation see [9].

The theory we have described applies to other changes of symmetry than cubic to tetragonal in the obvious way. We are typically led to a zero-energy set M of matrices of the form

$$M = \bigcup_{i=1}^{N} SO(3)U_i, \tag{4.6}$$

with $U_i = U_i^T > 0$. The simplest nontrivial case, that of $N = 2$, is called the *two-well problem*. In [10] a detailed study of zero-energy microstructures for the two-well problem is made for the case when $\det U_1 = \det U_2$. In particular it is shown rigorously that for some linear boundary conditions the minimum of I is not attained. To produce minimizing sequences constructions involving 'layers within layers' are used; such microstructures are commonly observed (see e.g. Arlt [2]). Other results for the N-well case, $N \geq 2$, are due to Bhattacharya *et al* [13], Kinderlehrer & Pedregal [23], Kohn [25], Matos [28], Pipkin [33] and Šverák [43].

An interesting feature of the theory is its prediction of special zero-energy microstructures that are possible only for special values of the lattice parameters defining the change of shape at the phase transformation. For example, Bhattacharya [12] has studied the 'wedge' microstructure observed in certain alloys. In the special case of a cubic to tetragonal transformation he shows that the wedge is a possible zero-energy microstructure if and only if the relation

$$\eta_1^2 = \frac{(1-\eta_2^2)^2 + 4\eta_2^2(1+\eta_2^2)}{(1-\eta_2^2)^2 + 8\eta_2^4} \tag{4.7}$$

holds. Materials for which the wedge microstructure is observed do seem to approximately satisfy (4.7).

A 'linearized', but still nonlinear, theory containing several of the ingredients of the theory in [9, 10], was earlier proposed by Khatachuryan, Roitburd and Shatalov [20, 21, 22, 35, 36]. To avoid inconsistent results this theory has to be used with great care. For example it predicts that for cubic to tetragonal transformations the wedge angle of the wedge microstructure is zero. The difficulties with the linearized theory arise to a large extent from its failure to satisfy frame-indifference. Discussions of the relationship between the linearized and nonlinear theories can be found in Kohn [24], Bhattacharya [11] and [10, Section 9].

5 Current developments and concluding remarks

Some areas of current activity in connection with the theory are:

(a) understanding the effects of incorporating interfacial energy in the model (see, for example, [18, 26, 27, 29, 30]),

(b) the numerical computation of microstructure (see [15, 16]),

(c) the study of dynamical models, including attempts to understand whether appropriate dynamical equations have solutions exhibiting the creation of microstructure (see [1, 6, 7, 31, 38, 37]),

An interesting analogy to the theory is with the problem of paper-folding (see Kohn & James [19]). A folded configuration of paper can be regarded as a map $y : \Omega \to \mathbf{R}^2$, $\Omega \subset \mathbf{R}^2$, with $Dy(x) \in O(2)$ a.e.. Since $O(2) = SO(2) \cup SO(2) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ it follows that we have a (somewhat pathological) version of the two-well problem. The theory holds some surprises; for example in [19] can be found an example of a deformation y with$Dy(x) \in O(2)$ a.e. and $y|_{\partial\Omega} = 0$. Similar considerations arise in the deformation of membranes and fabrics (*cf.* Pipkin [32]).

Microstructure arises naturally in many optimization problems, for example in the construction of composite materials with optimal properties and the reproduction of images of varying colour and intensity using a limited number of fixed colours. Perhaps there are other important areas of application that have yet to be identified.

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References

[1] G Andrews and J M Ball. Asymptotic behaviour and changes of phase in one-dimensional nonlinear viscoelasticity. *J. Differential Eqns*, 44:306–341, 1982.

[2] G Arlt. Twinning in ferroelectric and ferroelastic ceramics: stress relief. *J. Materials Science*, 22:2655–2666, 1990.

[3] J M Ball. Convexity conditions and existence theorems in nonlinear elasticity. *Arch. Rat. Mech. Anal.*, 63:337–403, 1977.

[4] J M Ball. Strict convexity, strong ellipticity, and regularity in the calculus of variations. *Proc. Camb. Phil. Soc.*, 87:501–513, 1980.

[5] J M Ball. A version of the fundamental theorem for Young measures. In M. Rascle, D. Serre, and M.Slemrod, editors, *Proceedings of conference on 'Partial differential equations and continuum models of phase transitions'*, pages 3–16. Springer Lecture Notes in Physics. No. 359, 1989.

[6] J M Ball. Dynamic energy minimization and phase transformations in solids. In *Proceedings of ICIAM 91*. SIAM, 1992.

[7] J M Ball, P J Holmes, R D James, R L Pego, and P J Swart. On the dynamics of fine structure. *J. Nonlinear Sci.*, 1:17–90, 1991.

[8] J M Ball and R D James. To appear.

[9] J M Ball and R D James. Fine phase mixtures as minimizers of energy. *Arch. Rat. Mech. Anal.*, 100:13–52, 1987.

[10] J M Ball and R D James. Proposed experimental tests of a theory of fine microstructure, and the two-well problem. *Phil. Trans. Roy. Soc. London A*, 338:389–450, 1992.

[11] K Bhattacharya. Linear and nonlinear thermoelasticity theory for crystalline solids. In preparation.

[12] K Bhattacharya. Wedge-like microstructure in martensites. *Acta Metallurgica et Materialia*, 39:2431–2444, 1991.

[13] K Bhattacharya, N Firoozye, R D James, and R V Kohn. Restrictions on microstructure. To appear.

[14] M Chipot and D Kinderlehrer. Equilibrium configurations of crystals. *Arch. Rat. Mech. Anal.*, 103:237–277, 1988.

[15] C Collins and M Luskin. The computation of the austenitic-martensitic phase transition. In M Rascle, D Serre, and M Slemrod, editors, *Partial Differential Equations and Continuum Models of Phase Transitions*, pages 34–50. Lecture Notes in Physics 344, Springer-Verlag, 1990.

[16] C Collins and M Luskin. Numerical modeling of the microstructure of crystals with symmetry-related variants. In I Ahmad, A Crowson, C Rogers, and M Aizawa, editors, *US-Japan Workshop on Smart/intelligent materials and systems*, pages 309–318, Lancaster, PA, 1990. Technomic Publishing Company.

[17] J L Ericksen. Special topics in elastostatics. In C.-S. Yih, editor, *Advances in Applied Mechanics*, volume 17, pages 189–244. Academic Press, 1977.

[18] I Fonseca. Interfacial energy and the Maxwell rule. *Arch. Rat. Mech. Anal.*, 106:63–95, 1989.

[19] R D James and R V Kohn. Paper folding and the microstructure of crystals. In preparation.

[20] A G Khachaturyan. Some questions concerning the theory of phase transformations in solids. *Soviet Physics - Solid State*, 8:2163–2168, 1967.

[21] A G Khachaturyan. *Theory of Structural Transformations in Solids.* John Wiley, 1983.

[22] A G Khachaturyan and G A Shatalov. Theory of macroscopic periodicity for a phase transition in the solid state. *Soviet Physics JETP*, 29:557–561, 1969.

[23] D Kinderlehrer and P Pedregal. Remarks about Young measures supported on two wells. In preparation.

[24] R V Kohn. The relationship between linear and nonlinear variational models of coherent phase transformations. In F Dressel, editor, *Trans. 7th Army Conf. on Applied Mathematics and Computing*, 1989.

[25] R V Kohn. The relaxation of a double-well energy. *Continuum Mechanics and Thermodynamics*, 3:193–236, 1991.

[26] R V Kohn and S Müller. Branching of twins near an austenite/twinned-martensite interface. Preprint.

[27] R V Kohn and S Müller. Surface energy and microstructure in coherent phase transformations. 1992.

[28] J P Matos. Young measures and the absence of fine microstructure in a class of phase transitions. *European J. Applied Maths*, 3:31–54, 1992.

[29] S Müller. Singular perturbations as a selection criterion for periodic minimizing sequences. To appear.

[30] G P Parry. On shear bands in unloaded crystals. *J. Mech. Phys. Solids*, 35:367–382, 1987.

[31] R L Pego. Phase transitions in one-dimensional nonlinear viscoelasticity: admissibility and stability. *Arch. Rat. Mech. Anal.*, 97:353–394, 1987.

[32] A C Pipkin. Some examples of crinkles. In J L Ericksen, D Kinderlehrer, R V Kohn, and J-L Lions, editors, *Homogenization and effective moduli of materials and media, IMA*. Springer-Verlag, 1986.

[33] A C Pipkin. Elastic materials with two preferred states. *Quarterly J. Mech. Appl. Math.*, 44:1–15, 1991.

[34] Y G Reshetnyak. Liouville's theorem on conformal mappings under minimal regularity assumptions. *Siberian Math. J.*, 8:631–653, 1967.

[35] A L Roitburd. *Kristallografiya*, page 567 ff., 1967. in Russian.

[36] A L Roitburd. Martensitic transformation as a typical phase transformation in solids. *Solid State Physics*, 33:317–390, 1978.

[37] P Rybka. Dynamical modelling of phase transitions by means of viscoelasticity in many dimensions. *Proc. Royal Soc. Edinburgh*, 121A:101–138, 1992.

[38] P J Swart and P J Holmes. Energy minimization and the formation of microstructure in dynamic anti-plane shear. *Arch. Rat. Mech. Anal.*, to appear.

[39] L Tartar. Some remarks on separately convex functions. In *Proceedings of conference on Microstructures and phase transitions, IMA, Minneapolis, 1990.*

[40] L Tartar. Compensated compactness and applications to partial differential equations. In R J Knops, editor, *Nonlinear analysis and mechanics; Heriot-Watt Symposium, Vol. IV*, pages 136–192. Pitman Research Notes in Mathematics, 1979.

[41] L Tartar. The compensated compactness method applied to systems of conservation laws. In J M Ball, editor, *Systems of Nonlinear Partial Differential Equations*, pages 263–285. NATO ASI Series, Vol. C111, Reidel, 1982.

[42] V Šverák. On regularity for the Monge-Ampère equation without convexity assumptions. To appear.

[43] V Šverák. On the problem of two wells. In *Proceedings of conference on Microstructures and phase transitions, IMA, Minneapolis, 1990.*

[44] V Šverák. Rank-one convexity does not imply quasiconvexity. *Proc. Royal Soc. Edinburgh*, 120A:185–189, 1992.

[45] M S Wechsler, D S Lieberman, and T A Read. On the theory of the formation of martensite. *Trans. AIME J. Metals*, 197:1503–1515, 1953.