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MULTI-VALUED STRAIN ENERGY FUNCTIONS FOR CRYSTALS

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Abstract—Various studies in crystal elasticity suggest that the strain energy should, in some cases, be regarded as multi-valued, with branches related in a rather definite way. My purpose is to elaborate this.

1. INTRODUCTION

Although expositions of elasticity theory ignore the matter, the strain energy function for some crystals is multi-valued. For example, a quartz crystal can contain Dauphiné twins. The strain energy functions for the twins differ from each other by a simple symmetry transformation. Application of a shear stress to the crystal generally produces different deformations and energies in the two twins and, if the shear stress is large enough, one type of twin will convert to the other. After removal of the load, the crystal is no longer twinned and there need be no net deformation of the parts. Elementary theory for this, based on linear elasticity theory is presented by Thomas and Wooster[1] and Wooster[2]. Practically, this has been used to convert defective (twinned) quartz crystals to good ones. Similar tricks have been employed on other kinds of crystals. Using ideas deriving from molecular theory, Parry[3] analyzed some kinds of phase transitions which again involve multi-valued strain energy functions. At least some of the known examples fit a common pattern. My purpose is to explain what this is. To some degree, motivations for considering it are also included in discussions like those of Cohen *et al.*[4].

2. THE PATTERN

As usual, we consider, as a reference configuration, an homogeneous configuration of minimum energy of a crystal, what is commonly called a natural state. Associated with this is a set of lattice vectors E_a $(a = 1, 2, 3)$ describing the periodicity which is characteristic of crystals. Given these, we can calculate a maximal point group P. It contains every orthogonal transformation Q which satisfies an equation of the form

$$QE_a = \sum_{b=1}^{3} m_a{}^b E_b, \tag{1}$$

where the $m_a{}^b$ are integers such that

$$\det. \|m_a{}^b\| = \pm 1. \tag{2}$$

In particular, P will always contain $Q = 1$ and $Q = -1$ and, from the classical theory of crystallographic groups, it is known that P is always a finite group. We think of applying, as point transformations, all such transformations to the atoms in the crystal. If, to within a trivial translation, all map the atoms to positions previously occupied by identical atoms, we use P as the basic invariance group for linear theories, including linear elasticity theory. Commonly, the same group is used for nonlinear theories of finite deformation. Current thinking is that this is only appropriate for relatively small deformations, and that, for larger deformations, the invariance group should be enlarged to include non-orthogonal transformations. Studies such as that of Parry[5] give some idea of how large deformation can be before we need to consider the latter complication. We ignore this kind of complication, which means that we restrict our attention to theory appropriate for small but finite deformations. With the provisos indicated, present experience indicates that it is reasonable to consider the strain energy as single valued, with P adequately describing material symmetry.

Another kind of situation arises if not every $Q \in P$ maps atoms into positions previously occupied by identical atoms, apart from a trivial translation. Generally, a subset will and it is easy to show that these will form a (proper) subgroup P_1. The standard practice is then to take P_1 as the basic invariance group, in considering constitutive equations. As I see it, this is better interpreted as referring to one branch of the constitutive equation, giving the strain energy per unit reference volume W as a function of the deformation gradient F or after accounting for Galilean invariance, as a function of $C = F^TF$. Standard practice is then summarized in the equation

$$W = W_1(C) = W_1(Q^TCQ), \qquad Q \in P_1. \tag{3}$$

As is obvious, and well known, any such constitutive equation is invariant under the central inversion $Q = -1$. Thus, if P_1 is obtained from P just by deletion of this transformation, W_1 will be invariant under P and, effectively, we are back to the previous situation, insofar as elasticity theory is concerned.

Now consider any $Q = \hat{Q}$ which is in P, but not in P_1. Conceptually, it will map atoms in the reference configuration to positions which an observer will see as distinguishable from what they were previously. Generally, if $\hat{Q} \neq -1$, we expect the two configurations to exhibit slightly different elastic response to a given deformation. In trying to give objective rules for identifying particular elastic moduli, we commonly rely on specifications of lattice vectors, their lengths, angles between them, etc. Particularly if we interpret "objective" as mirror imaging, lattice vectors related by P should be regarded as equivalent, from this objective point of view. Observers might agree that our different configurations are different from each other, but be hard pressed, at least, to give any objective rule to tell which is which. In itself, this gives a reason for considering the set as a unit rather than the individual configurations. Elementary symmetry considerations, such as are used in the analysis presented by Thomas and Wooster[1], then lead to the conclusion† that we can get the second strain energy function W_2 from the first, as indicated by

$$W_2(C) = W_1(\hat{Q}^TC\hat{Q}). \tag{4}$$

Generally, W_2 and W_1 are different functions. However, in the original reference configuration, where $C = 1$, we have, since $\hat{Q}^T\hat{Q} = 1$,

$$W_2(1) = W_1(1). \tag{5}$$

If it were otherwise, one of these configurations would be less stable than the other, contradicting the spirit of objectivity, at least. Tacitly, we have assumed that the relevant domain of W_1 is invariant under P, so (4) makes sense. In turn, this means that (4) can be inverted to read

$$W_1(C) = W_2(\hat{Q}C\hat{Q}^T). \tag{6}$$

Also, we can define a group P_2 conjugate to P_1, consisting of the orthogonal transformations Q_2 given by

$$Q_2 = \hat{Q}Q_1\hat{Q}^T, \qquad Q_1 \in P_1. \tag{7}$$

From (3) and (4), we then have

$$\begin{aligned} W_2(Q_2{}^TCQ) &= W_1(\hat{Q}^TQ_2{}^TCQ_2\hat{Q}) \\ &= W_1(Q_1{}^TQC\hat{Q}Q_1) \\ &= W_1(\hat{Q}^TC\hat{Q}) \\ &= W_2(C), \end{aligned} \tag{8}$$

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†Actually, this represents an assumption. If, say, one crystal is a minor image of another then, reasonably, applying a deformation to one and the mirror imaged deformation to the other will give rise to the same value of the energy stored.

so P_2 serves as the invariance group for W_2. In brief, the two are on equal footing, it makes no difference which we regard as the first. By similar reasoning, we could also write (4) as

$$W_2(C) = W_1(\breve{Q}^T C \breve{Q}), \tag{9}$$

provided $\breve{Q}$ and $\hat{Q}$ are related as indicated by

$$\breve{Q} = \pm \hat{Q} Q_1, \qquad Q_1 \in P_1. \tag{10}$$

It may happen, and does in the case of the Dauphiné twinning in quartz, that every $Q \in P$ is either in P_1 or included in the set described by (10). Then, we get just the two branches indicated. The physical experience is that we can induce a crystal to shift from one branch to the other, by applying suitable loadings. For the obvious reason, the two kinds of configurations are called twins by experts on crystal behavior. In passing from one twin to another, some atoms must jump to new locations, a process called "shuffling". Differences between shuffle transformations and martensitic transformations, which do not involve shuffling, are discussed in some detail by Cohen *et al.*[4], for example.

If P contains some element $\hat{\hat{Q}}$ not in P_1 and not accounted for in (10), we can use it to define a third branch, viz.

$$W_3(C) = W_1(\hat{\hat{Q}} C \hat{\hat{Q}}), \quad \text{etc.} \tag{11}$$

Proceeding in this way until we use up all transformations in P, we must get a finite number of branches, since P is a finite group. Subgroups of point groups, like our P_1, are also counted as point groups and all possible point groups are characterized, in the theory of crystallographic groups. Considered as abstract groups, there are 32 point groups. For elasticity theory, we can restrict our attention to those which contain $Q = -1$, there being 11 of these. Information on these groups, on possible sets of lattice vectors associated with them, etc. is given by Seitz[6, 7], for example. Clearly, one could use such information to classify all of the possible kinds of branching, but I will not pursue this.

In the above analysis, it is not really necessary that the reference configuration be taken as a natural state. The assumption is made more to enable us to draw upon experience with classical linear theory, familiar considerations of crystal symmetry, etc. What is important is that the different atomic configurations be related as indicated to the one taken as reference. I am not sure that I fully understand the implications of this, so will ignore such possibilities, here.

3. REMARKS

We again consider the configuration which originally served as a reference. Suppose that we were to pick another reference configuration, obtained by applying a finite rotation R to this. Employing standard reasoning in the theory of change of reference configurations, introduced by Gibbs[8], we get a different strain energy function $\bar{W}_1(C)$, related to the former by

$$\bar{W}_1(C) = W_1(R^T C R). \tag{11}$$

From (4), it is clear that, if we take

$$R = \hat{Q} \text{ or } R = -\hat{Q}, \tag{12}$$

whichever has the positive determinant, we will have

$$\bar{W}_1(C) = W_2(C). \tag{13}$$

Thus, the configurations associated with $\bar{W}_1$ and W_2 are elastically equivalent, although other types of experiments might discern the difference. In this sense, the difference between having a single-valued or multi-valued energy function is somewhat minor. For example, it is a very familiar fact that if we subject a crystal to an hydrostatic pressure, we will get a change of volume which is independent of the choice of R. Thus W_1 and W_2 will yield the same pressure-volume curve, in such circumstances. For this reason, a thermodynamicist is likely to conclude that our different configurations are in the same thermodynamic phase. A transition shifting us from one branch to another could be regarded as a phase transformation, by one interpretation of the terminology used by Cohen *et al.*[4], and it does have some of the earmarks of a phase transition, at least. I don't wish to make an issue of this matter of jargon.

Of particular interest is the response to loadings or changes in temperature of bodies containing two or more of our configurations, variations on the theme in the work reported by Thomas and Wooster[1]. Such experience suggests that elasticity theory can have only limited success in predicting when we will have a shift from one branch to another. This is not surprising since such theory is too crude to enable any description of the shuffling motions involved. We tolerate the yield conditions which are tacked on to predict the onset of plasticity and, it seems, something like this must be done for these phenomena. In this respect, a more refined theory, accounting for these subtler motions seems to be more promising, as is discussed by Rivlin[9]. Such alternatives seem to be worth exploring. Here, one is getting closer to molecular theory and, perhaps, one should go all the way.

In at least some cases, there are indications that nature seems to prefer that these composite bodies be put together so that a change in temperature or hydrostatic pressure will not produce shear stresses in the parts. With (13), this is elastically equivalent to forming a body from a material with a single-valued energy function by joining parts, rotated relative to each other, in such a way as to avoid shear stresses. Some elementary theory of this is given by Ericksen[10], and some of James'[11] theory of twinning, trilling, etc. can be adapted, rather easily. James encounters some difficulty with the theory of loaded bodies, when he tries to use reasoning analogous to that used for unloaded crystals. For the latter, his assumptions are in good accord with those which have been used by crystallographers, etc. From the treatment of shear loading of quartz presented by Thomas and Wooster[1], it is pretty clear that no such analogy applies. Thus, as is made rather clear by James, one has to adopt less restrictive assumptions to treat loaded bodies, in general. I am not so sure that there are not similar problems with unloaded bodies, in general. At least some of those knowledgeable about shuffle transformations think it can be important to account for interfacial energy associated with surfaces where two parts meet, as is mentioned by Cohen *et al.*[4], for example, and the aforementioned authors don't allow for this. If so, this would modify the usual jump conditions assumed for the stress tensor, among other things. Thus, the elasticity theory which seems pertinent for these composite bodies is roughed out, but hardly finished, and it seems to me worthwhile to put it in better order. Of course, there are similarities between these problems and those encountered in other composite bodies, for example those considered in sandwich construction so, basically, it is the transition theory which needs improvement.

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