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ON DIATOMIC CRYSTALS

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Abstract—Strain energy functions which will appear in phenomenological theories of the mechanical behaviour of diatomic crystals are constructed in accordance with the constraints imposed by the crystal symmetry.

1. INTRODUCTION

The object of this work is the construction of single-valued scalar functions which exhibit the full geometrical symmetry of diatomic crystals. It is assumed that the stored energy per unit mass of the crystal, expressed as a function of the geometrical parameters that determine the current configuration of the crystal, is such a function. The problem is that set by Ericksen[1]. The theory allows phenomena such as the multivalued dependence of the strain energy on the (macroscopic) deformation gradient, so that, generally, the material is not elastic.

We are content here to divine the general forms of such functions and to exhibit just one concrete example of such a function. The extraction of detailed predictions from the model (by which the theory must stand or fall) is deferred for the time being, for it is not required, here, that the strain energy function entails mechanical behaviour which is, in any sense, physically reasonable. The construction of strain energy functions possessing the full symmetry of monatomic crystals has been performed by Parry[2], and the present work is a natural generalization of this construction. The further generalization to polyatomic lattices is evident, and so will not be discussed in detail.

The notion of the Brillouin zone, usually associated with the solid state physics of crystals, is fundamental to the argument. As noted by Ericksen[1], the most interesting predictions of the theory lie in its most general application, to wit, the representation of inelastic phenomena.

To begin with, existing work is reviewed briefly. Thus, the geometry of the crystal is specified and equations expressing the symmetry of the stored energy are written down explicitly (following Ericksen). Notions introduced by Parry[2] allow the most general stored energy function possessing this symmetry to be constructed. It will be evident that the formalism places no constraints at all on that configuration of the crystal to which the stored energy is referred. This covariance was emphasized in[2] (and applies equally to diatomic crystals). Finally, we make a few remarks about the appropriate continuity conditions and give an example of a simple function with the requisite symmetry.

2. THE SYMMETRY

The arguments in this section were first given by Ericksen[1]. The stored energy is supposed to exhibit the full geometrical symmetry of the crystal. Thus, any transformation which maps the crystal onto itself must leave the stored energy unchanged. The crystal may not be regarded as solid in the sense of Noll[3], for the isotropy group contains non-orthogonal transformations.

We shall suppose that diatomic crystals are composed of two monatomic lattices, one differing from the other by a uniform translation, $\mathbf{p}$ say, and we shall suppose that the atoms of one lattice may be distinguished from those of the other. Evidently, $\mathbf{p}$ may represent the vector difference between any two generically distinct atoms. Thus $\mathbf{p}$ is determined only to within transformations of the form

$$\mathbf{q} = \mathbf{p} + \mathbf{x}, \tag{2.1}$$

where

$$\mathbf{x} = \alpha_i \mathbf{a}_i, \tag{2.2}$$

where the α_i are integers, the $\mathbf{a}_i$ are three linearly independent vectors, and the Einstein summation convention is employed.

The set of all points $\mathbf{x}$, given by (2.2), is called the monatomic lattice L with basis $\mathbf{a}_i$. The basis is not uniquely determined by the lattice, for if

$$\mathbf{b}_i = \gamma_{ij}\mathbf{a}_j, \tag{2.3}$$

where the γ_{ij} are integers, and where

$$\det(\gamma_{ij}) = \pm 1, \tag{2.4}$$

then the set of vectors $\mathbf{b}_i$ is a basis of the same lattice. Moreover, every basis of the lattice may be obtained in this way.

We shall consider only materials which are such that the stored energy may be written in the form

$$w(\mathbf{p}, \mathbf{a}_i). \tag{2.5}$$

Since the vectors $\mathbf{p}, \mathbf{a}_i$ are determined by the diatomic lattice only to within transformations of the form (2.1) and (2.3), it is natural to require that

$$w(\mathbf{p}, \mathbf{a}_i) = w(\mathbf{q}, \mathbf{b}_i), \tag{2.6}$$

where $\mathbf{q}$ is as given by (2.1), and $\mathbf{b}_i$ as given by (2.3). This is a statement that the stored energy sees the lattice as a whole, having no regard for the individual atoms that are the constituents of the two monatomic lattices. We shall say that (2.1) and (2.3) express the full geometrical symmetry of the lattice.

Note that the function

$$w(\mathbf{p}, \mathbf{a}_i) = \Sigma\lambda(|\mathbf{p} + \mathbf{x}|) + \Sigma\mu(|\mathbf{x}|) + \Sigma\nu(|\mathbf{x}|), \tag{2.7}$$

where $\mathbf{x} \in L$ and the summation extends over bonds on the atoms in a given unit cell, corresponds to the classical prescription of the stored energy per unit mass under central force interaction between pairs of atoms (there being three generically distinct pair potentials) and that this function exhibits this full geometrical symmetry.

In order to construct a strain energy per unit mass as a function of the macroscopic deformation gradient, we have firstly to relate the lattice vectors to the deformation gradient. It seems natural to assume that the lattice vectors are embedded in the (macroscopic) deformation. Secondly, we have to invoke an equilibrium equation

$$\mathbf{p} = \mathbf{p}(\mathbf{a}_i). \tag{2.8}$$

A possibility is suggested in Section 4 (following Ericksen). Therefore, with this apparatus, the construction of the stored energy per unit mass as a function of $\mathbf{p}, \mathbf{a}_i$ leads to the construction of the requisite strain energy as a function of the deformation gradient.

3. THE CONSTRUCTION OF STORED ENERGY FUNCTION

It is required to construct scalar, single-valued objective functions which satisfy (2.6). Objectivity demands that

$$w(\mathbf{p}, \mathbf{a}_i) = w(R\mathbf{p}, R\mathbf{a}_i), \tag{3.1}$$

where R is a proper or improper orthogonal transformation, that is

$$RR' = R'R = I.$$

Therefore,

$$w(\mathbf{p}, \mathbf{a}_i) = \bar{\alpha}(\mathbf{p}^2, \mathbf{p} \cdot \mathbf{a}_i, \mathbf{a}_i \cdot \mathbf{a}_j) = \alpha(\mathbf{p} \cdot \mathbf{a}_i, \mathbf{a}_i \cdot \mathbf{a}_j), \tag{3.2}$$

since $\mathbf{p} \cdot \mathbf{a}_i$ and $\mathbf{a}_i \cdot \mathbf{a}_j$ determine $\mathbf{p}^2$, and where α is arbitrary over its domain of definition. Thus, objectivity is assured by associating the components of $\mathbf{p}$ with the Lagrangian triad of the deformation.

It remains to satisfy (2.6). This is done by defining uniquely just one set of scalar products $\mathbf{p}^r \cdot \mathbf{a}_i^r$, $\mathbf{a}_i^r \cdot \mathbf{a}_j^r$, say, corresponding to geometrical parameters $\mathbf{p}^r, \mathbf{a}_i^r$, that generate the lattice. Thus, one and only one set of scalar products $\mathbf{a}_i^r \cdot \mathbf{a}_j^r$ corresponding to basis vectors $\mathbf{a}_i^r$ is chosen from the set of all sets of scalar products $\mathbf{b}_i \cdot \mathbf{b}_j$ corresponding to basis vectors $\mathbf{b}_i$, given

by (2.3); likewise, one and only one set of scalar products $\mathbf{a}_i^r \cdot \mathbf{p}^r$ is chosen from the set of all sets of scalar products $\mathbf{b}_i \cdot \mathbf{q}$, given by (2.3) and (2.1). Then, the general solution of (2.6) and (3.1) may be written as

$$w(\mathbf{p}, \mathbf{a}_i) = \bar{\theta}(\mathbf{p}^r \cdot \mathbf{a}_i, \mathbf{a}_i^r \cdot \mathbf{a}_j^r) = \theta(\mathbf{p}^r, \mathbf{a}_i^r), \tag{3.3}$$

where $\bar{\theta}$ is *arbitrary* over its domain of definition. The function θ is introduced for later convenience.

The interpretation of w as a stored energy function and the implicit introduction of some reference configuration of the lattice has no effect on the analysis. Therefore, as stated in the introduction, we are able to construct stored energy functions appropriate to arbitrary reference configurations of the crystal.

The detailed calculations that follow are restricted to two dimensions, solely for the sake of manipulative ease. There is no difficulty in extending all the calculations to the full three dimensional case, but it does not seem worthwhile to set down the algebra, which is disproportionately more cumbersome.

To proceed we must define uniquely just one set of scalar products corresponding to the geometrical parameters which specify the diatomic lattice. Firstly, choose as basis vectors,

$$(\mathbf{a}_1^r, \mathbf{a}_2^r) \equiv (\boldsymbol{\alpha}, \boldsymbol{\beta}),$$

"the" two shortest linearly independent vectors (unique to within sign and order) in one of the monatomic lattices. It is easy to show, geometrically, that these (eight sets of) two vectors generate the lattice (Parry[2]). Thus

$$\max(\boldsymbol{\alpha}^2, \boldsymbol{\beta}^2) \leq (l\boldsymbol{\alpha} + m\boldsymbol{\beta})^2, \tag{3.4}$$

l and m being any non-zero integers. It is necessary and sufficient for (3.4) that

$$\min(\boldsymbol{\alpha}^2, \boldsymbol{\beta}^2) \geq 2|\boldsymbol{\alpha} \cdot \boldsymbol{\beta}|. \tag{3.5}$$

Adjoin the inequalities

$$\boldsymbol{\alpha}^2 \leq \boldsymbol{\beta}^2; \quad \boldsymbol{\alpha} \cdot \boldsymbol{\beta} \geq 0 \tag{3.6}$$

to (3.5), so that the scalar products $\mathbf{a}_i^r \cdot \mathbf{a}_j^r$ are *uniquely* determined. The domain of the scalar products $\mathbf{a}_i^r \cdot \mathbf{a}_j^r$ is henceforward called the "least domain", and denoted $\mathscr{D}$.

Likewise, from the set of all vectors $\mathbf{q}$ which separate the two monatomic lattices, select that one vector of shortest length. (There are degenerate case with which we do not concern ourselves at the moment). Let this vector be denoted $\mathbf{p}^r$, so that

$$|\mathbf{p}^r| \leq |\mathbf{p}^r + \mathbf{x}|, \tag{3.7}$$

for all $\mathbf{x} \in L$, as given by (2.2). We shall say that $\mathbf{p}^r$ lies in a Brillouin zone of the lattice, $\mathbf{p}^r \in \mathscr{B}$, say. (I believe this is a more strict definition than is given in the literature.) Thus, the $\mathbf{a}_i^r \cdot \mathbf{p}^r$ are uniquely specified.

So the general solution to (2.6) and (3.1) is written as

$$w(\mathbf{p}, \mathbf{a}_i) = \bar{\theta}(\mathbf{p}^r \cdot \mathbf{a}_i^r, \mathbf{a}_i^r \cdot \mathbf{a}_j^r) = \theta(\mathbf{p}^r, \mathbf{a}_i^r), \tag{3.3 bis}$$

where $\mathbf{p}_i^r \in \mathscr{B}$, $\mathbf{a}_i^r \in \mathscr{D}$, and $\bar{\theta}$ is arbitrary over its domain of definition.

4. CONTINUITY CONDITIONS

The infinite set of inequalities (3.7) may be simplified somewhat. Let l and m be integers. Then (3.7) reads that

$$|\mathbf{p}^r| \leq |\mathbf{p}^r + l\boldsymbol{\alpha} + m\boldsymbol{\beta}|, \tag{4.1}$$

for all l and m. Denote by $P(k)$ the proposition that (4.1) is true for all l and m in the range

$$\max(|l|, |m|) \leq k. \tag{4.2}$$

Then it is easy to show that $P(1)$ is necessary and sufficient for the validity of (4.1). This routine calculation is presented in the appendix to this paper.

Thus, the inequalities (3.7) reduce to six, which may be visualized as in the following diagram.

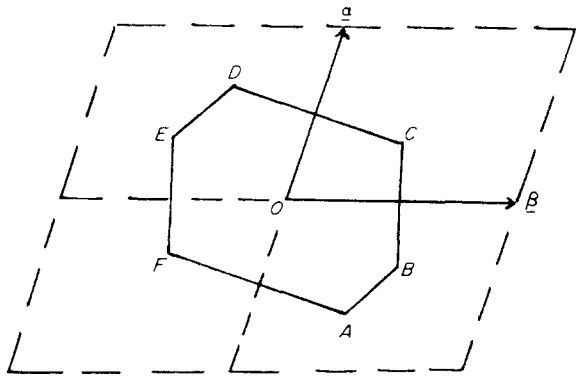

Fig. 1.

$\mathbf{p}^r$ must lie in the Brillouin zone ABCDEF, which is the inner envelope of the eight straight lines which are the perpendicular bisectors of the lines joining O to its "nearest neighbours". $\mathscr{B}$ is an irregular hexagon.

Suppose, following Ericksen, that there are no generalized forces which do work in changing $\mathbf{p}$ i.e. there are no body forces which differentiate between the atoms in the two lattices. Then, using (3.3),

$$\frac{\partial w}{\partial \mathbf{p}} = \frac{\partial \theta}{\partial \mathbf{p}^r} = 0. \tag{4.3}$$

Suppose that this equation may be inverted to give

$$\mathbf{p}^r = \mathbf{p}^r(\mathbf{a}_i^r). \tag{4.4}$$

This is the required equilibrium equation (see 2.8). Generally, there will be more than one branch to $\mathbf{p}^r$. Substituting in (3.3), one obtains

$$w(\mathbf{p}, \mathbf{a}_i) = \theta(\mathbf{p}^r(\mathbf{a}_i^r), \mathbf{a}_i^r) = \pi(\mathbf{a}_i^r), \text{ say.} \tag{4.5}$$

The associated symmetry is monatomic in character, as noted, differently, by Ericksen. If $\mathbf{p}^r(\mathbf{a}_i^r)$ is single-valued, (4.5) represents elastic behaviour. Differentiating (4.5), and using (4.3),

$$\frac{\partial w}{\partial \mathbf{a}_i} = \frac{\partial \theta}{\partial \mathbf{a}_i^r} = \frac{\partial \pi}{\partial \mathbf{a}_i^r}. \tag{4.6}$$

It seems reasonable to require that w depends continuously on $\mathbf{p}$ and $\mathbf{a}_i$, for the domains $\mathscr{B}$ and $\mathscr{D}$ are merely mathematical constructions, and discontinuities precisely on the somewhat arbitrary boundaries of these domains are unlikely.

According to Parry [2], the continuity of w with respect to $\mathbf{a}_i$ is automatic provided that θ, as given by (3.3), is a continuous function of $\mathbf{a}_i^r$. To ensure that w is continuous with respect to $\mathbf{p}$, we demand, for example, that

$$\theta(\mathbf{p}^r, \mathbf{a}_i^r) = \theta(\mathbf{p}^r \mp \boldsymbol{\alpha}, \mathbf{a}_i^r), \quad \text{on } \boldsymbol{\alpha}^2 = \pm 2\boldsymbol{\alpha} \cdot \mathbf{p}^r.$$

(This equation is most easily obtained from the figure. The formulation is just as simple in three dimensions.)

It also seems reasonable to require that the first and second derivatives of w (or π) with respect to $\mathbf{a}_i$ be continuous. Equations necessary and sufficient for this are given in (2).

However, it is likely that the range of the function $\mathbf{p}^r(\mathbf{a}_i^r)$ is not the whole of $\mathscr{B}$, or at least that there are singularities at various points (notably the origin), for otherwise the two monatomic lattices may coincide for some values of the (common) lattice vectors. (The question of continuity with respect to $\mathbf{p}$ does not arise if this range is strictly contained in $\mathscr{B}$.)

With these remarks, it is easy to construct a stored energy function with the required

properties. For example, suppose that $\mathbf{p}^r$ enters only through its length. Then continuity is automatic, and we may write

$$w(\mathbf{p}, \mathbf{a}_i) = \theta(\mathbf{p}^r, \mathbf{a}_i^r) = f(|\mathbf{p}^r|, |\det(\mathbf{a}_i^r)|),$$

where $\det(\mathbf{a}_i^r)$ is the determinant of the matrix with columns $\mathbf{a}_i^r$, and where f is arbitrary over its domain of definition, except perhaps than it is singular at $|\mathbf{p}^r| = 0$. Of course, this will imply the existence of singularities of w at the corresponding lattice points.

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APPENDIX

Lemma. P(1) is necessary and sufficient for (4.1).

Proof. By induction. We assume $P(1)$, $P(q)$ and deduce $P(q+1)$. Denote $|\mathbf{p}^r + l\boldsymbol{\alpha} + m\boldsymbol{\beta}|$ by $d(l, m)$.

It is required to prove that

$$|\mathbf{p}^r| \leq \min\{d(\pm(q+1), m), d(l, \pm(q+1)), d(q+1, \pm(q+1)), d(\pm(q+1), q+1)\}$$

where

$$\max(|l|, |m|) \leq k. \tag{A1}$$

It is elementary to show that

$$d^2(\pm(q+1), m) = d^2(\pm q, m) + (\boldsymbol{\alpha}^2 \pm 2\boldsymbol{\alpha} \cdot \mathbf{p}^r) + 2(q\boldsymbol{\alpha}^2 \pm m\boldsymbol{\alpha} \cdot \boldsymbol{\beta}),$$

$$d^2(l, \pm(q+1)) = d^2(l, \pm q) + (\boldsymbol{\beta}^2 \pm 2\boldsymbol{\beta} \cdot \mathbf{p}^r) + 2(q\boldsymbol{\beta}^2 \pm l\boldsymbol{\alpha} \cdot \boldsymbol{\beta}),$$

$$d^2(\pm(q+1), \pm(q+1)) = d^2(\pm q, \pm q) + (\boldsymbol{\alpha}^2 \pm 2\boldsymbol{\alpha} \cdot \mathbf{p}^r) + (\boldsymbol{\beta}^2 \pm 2\boldsymbol{\beta} \cdot \mathbf{p}^r) + 2\boldsymbol{\alpha} \cdot \boldsymbol{\beta} + 2q(\boldsymbol{\alpha}^2 + \boldsymbol{\beta}^2 + 2\boldsymbol{\alpha} \cdot \boldsymbol{\beta}),$$

$$d^2(\pm(q+1), \mp(q+1)) = d^2(\pm q, \mp q) + (\boldsymbol{\alpha}^2 + \boldsymbol{\beta}^2 \pm 2\mathbf{p}^r \cdot \boldsymbol{\alpha} \mp 2\mathbf{p}^r \cdot \boldsymbol{\beta} - 2\boldsymbol{\alpha} \cdot \boldsymbol{\beta}) + 2q(\boldsymbol{\alpha}^2 + \boldsymbol{\beta}^2 - 2\boldsymbol{\alpha} \cdot \boldsymbol{\beta}).$$

But, by $P(1)$,

$$\boldsymbol{\alpha}^2 \pm 2\boldsymbol{\alpha} \cdot \mathbf{p}^r \geq 0,$$

$$\boldsymbol{\beta}^2 \pm 2\boldsymbol{\beta} \cdot \mathbf{p}^r \geq 0,$$

$$\boldsymbol{\alpha}^2 + \boldsymbol{\beta}^2 \pm 2\mathbf{p}^r \cdot \boldsymbol{\alpha} \mp 2\boldsymbol{\beta} \cdot \mathbf{p}^r - 2\boldsymbol{\alpha} \cdot \boldsymbol{\beta} \geq 0.$$

Therefore, by $P(1)$, $P(q)$, (3.5) and (3.6), (A1) is proven.

QED.

The three dimensional case may be treated similarly. The corresponding Brillouin zone is found to possess at most twenty-six distinct faces (fewer in cases of greater symmetry).