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CHANGES OF INVARIANCE IN INTERNAL VARIABLE THEORIES

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Abstract—We show how to construct internal energy functions which have arbitrarily specified symmetries on the two sides of a phase transition.

INTRODUCTION

In thermoelasticity, the symmetry of the internal energy function is usually presumed to be independent of any state variables. Thus the internal energy function corresponding to an isotropic solid generally depends explicitly on the three principal invariants of strain and the temperature, say, and the material remains solid and isotropic in the entire range of temperature where the internal energy is defined. Of course some solids, and there are isotropic solids among them, melt and sublimate under certain conditions, and the internal energies of the ensuing fluids are commonly written as functions of density and temperature only. So it seems that if thermoelasticity is to model such changes of phase, then different internal energies must be assigned to the same material in different ranges of temperature, and it is characteristic of these different energies that they have distinct symmetries. There are various arguments against this procedure, some more substantial than others. Naively, the patching together of different functions using constraints like continuity of energy or stress seems somehow less satisfactory than an unified theory using smooth functions. More concretely, the existence and nature of the phase changes should be explained, rather than hypothesized. Raveché and Stuart[8] have gone some way towards this in their study of melting by a route coming directly from statistical mechanics, where the partition function plays the role of the smooth unifying function. Similarly, Bhatt and Macmillan[1] and Parry[3, 4] have analysed phase transitions in crystal mechanics using internal variable theories based on geometrial ideas to unify the description of separate phases.

It is surely *necessary* that functions which describe different phases of one material derive from a unified theory, since those functions are just coarse representations of the behaviour of all the particles in the material. Said differently, the functions must derive from an internal variable theory by elimination of the internal variables. It is clear that the symmetry of a phase is important in considerations of this type. Thus, in the context of continuous transitions using no internal variables, Landau[2] remarks that "on one side of the transition point the crystal has the higher symmetry $G_0, \ldots$ and on the other side the symmetry G is lower, so that the group G is a subgroup of the group G_0". Various questions arise regarding the *practice* of using different free energies in different domains. Firstly, how is the nature of transition correlated with the change in symmetry? Landau addressed this question. Also, in[3, 6], the evidence is (loosely) that some lack of smoothness results when phases with different symmetries derive from an internal variable theory. Secondly, and this is the question we address here, is the practice of patching together different functions *consistent* with the necessary condition that these functions derive from an internal variable theory? We provide a limited answer by constructing prototype internal energies which model transitions between phases of *arbitrary* symmetry.

The merit of the construction lies not in the possible use of the functions for modelling, since the internal variables are not obviously physically significant, but in the fact that its existence is a limited validation of practice.

CONSTRUCTION OF INTERNAL ENERGY FUNCTIONS

Let C denote the Cauchy–Green tensor and θ the temperature, so that a thermoelastic internal energy function may be written as $W(C, \theta)$. The symmetries of the material at this level are described by the *isotropy group* G which consists of all those unimodular transformations g which solve

$$W(C, \theta) = W(g'Cg, \theta), \tag{1}$$

for all C, θ, and with g' the transpose of g. For brevity, write

$$g'Cg = g.C, \tag{2}$$

henceforth.

We try to construct internal energy functions $\phi(\boldsymbol{\alpha}, C, \theta)$, depending on an internal variable $\boldsymbol{\alpha}$, such that the elimination of $\boldsymbol{\alpha}$ via the equilibrium equations

$$\frac{\partial \phi}{\partial \boldsymbol{\alpha}}(\boldsymbol{\alpha}, C, \theta) = 0 \tag{3}$$

gives thermoelastic internal energies with *arbitrary* isotropy groups G_1 and G_2 in different temperature ranges. To arrive at the general construction we consider a succession of simpler cases.

CASE 1

Suppose that $G_1 \subset G_2$, that both groups are either finite or compact (so that functions of C invariant under either of the groups are expressible in terms of a finite list of invariants) and that the invariants of G_1 contain the invariants of G_2. So denote the invariants of G_1 by $i_1, i_2, \ldots, i_l$, and those of G_2 by $i_{k+1}, i_{k+2}, \ldots, i_l$.

Consider internal energies of the form

$$\phi(f(\alpha, i_1, i_2, \ldots, i_k), i_{k+1}, i_{k+2}, \ldots, i_l, \theta), \tag{4}$$

where f is an arbitrary scalar function of its arguments and α is a scalar. Eliminating α via (3), one obtains

$$\frac{\partial \phi}{\partial f}\frac{\partial f}{\partial \alpha} = 0, \tag{5}$$

so that either $\partial\phi/\partial f = 0$ or $\partial f/\partial\alpha = 0$. If $\partial\phi/\partial f = 0$, then one generally obtains f as a function of $i_{k+1}, i_{k+2}, \ldots, i_l$ (assuming that $\partial^2\phi/\partial f^2 \neq 0$), and if $\partial f/\partial\alpha = 0$, then one obtains α as a function of $i_1, i_2, \ldots, i_k$ (assuming that $\partial^2 f/\partial\alpha^2 \neq 0$). Thus there are two branches of solutions of (3) with corresponding thermoelastic internal energies

$$\phi_1 \triangleq \phi(f(i_{k+1}, i_{k+2}, \ldots, i_l), i_{k+1}, i_{k+2}, \ldots, i_l, \theta) \tag{6}$$

and

$$\phi_2 \triangleq \phi(f(\alpha(i_1, i_2, \ldots, i_k), i_1, i_2, \ldots, i_k), i_{k+1}, i_{k+2}, \ldots, i_l, \theta),$$

in a loose notation. It is clear that ϕ_1 has the isotropy group G_2 and that ϕ_2 has the isotropy group G_1. One naturally thinks of the two branches of α as corresponding to different phases of the material, and the material presumably selects the equilibrium phase according to the energy criterion of stability. Thus the thermoelastic potential will be taken as

$$\bar{\phi} = \min(\phi_1, \phi_2), \tag{7}$$

so that the phase boundary in the space of (C, θ) is given by $\phi_1 = \phi_2$. In an experiment where stress is prescribed (so that $\partial\bar{\phi}/\partial c = \sigma$, say), the equilibrium path $c = c(\theta)$ is generally discontinuous at this phase boundary. Likewise, if the transition is supposed to be continuous, then there is generally a discontinuity of stress. Generally, the phase boundary divides the equilibrium path into two connected components, so that the phases are associated with different ranges of temperature in a given experimental set-up, see Parry[6] for a detailed analysis.

The simplest example of this kind of phase transition is the isotropic solid to fluid transition. The invariants of the orthogonal group corresponding to the isotropic solid may be chosen as

$$(\lambda_1+\lambda_2+\lambda_3),\ (\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1),\ \lambda_1\lambda_2\lambda_3 \triangleq i_1,\ i_2,\ \rho$$

say, where the λ_i are the principal stretches of the deformation from the natural state, and the single invariant of the unimodular group corresponding to the fluid phase is ρ. Thus any internal energy of the form

$$\phi(f(\alpha, i_1, i_2), \rho, \theta)$$

has solid and fluid branches, loosely speaking. The interpretation of the internal variable α is problematic in the absence of any clear cut and accepted continuum model of a liquid.

CASE 2

It is easy to remove the restriction $G_1 \subset G_2$ by introducing another internal variable, β. Consider the internal energy

$$\phi(f(\alpha^2, u_1, u_2, \ldots, u_k), g(\beta^2, v_1, v_2, \ldots, v_l), \theta), \tag{8}$$

with f and g arbitrary functions, and the u_i, v_j as yet unspecified lists of invariants. Since

$$\frac{\partial\phi}{\partial\alpha} = \frac{\partial\phi}{\partial f}\frac{\partial f}{\partial\alpha^2}.2\alpha,\ \frac{\partial\phi}{\partial\beta} = \frac{\partial\phi}{\partial g}\frac{\partial g}{\partial\beta^2}.2\beta, \tag{9}$$

there are generally at least nine branches of solutions to (3). We restrict attention to two of these branches, namely those such that

$$\left(\alpha = 0 \text{ and } \frac{\partial g}{\partial\beta^2} = 0\right) \text{and} \left(\beta = 0 \text{ and } \frac{\partial f}{\partial\alpha^2} = 0\right). \tag{10}$$

When $\partial g/\partial\beta^2 = 0$, then β^2 may be found as a function of $v_1, v_2, \ldots, v_l$, if $\partial^2 g/\partial(\beta^2)^2 \neq 0$, and there is a corresponding result for $\partial f/\partial\alpha^2 = 0$. If the functions f and g are constrained to vanish with their first arguments, then corresponding to the two equilibrium branches given in (10) we have the thermoelastic internal energies

$$\phi(0, g(\beta^2(v_1, v_2, \ldots, v_l), v_1, v_2, \ldots, v_l, \theta)$$

and

$$\phi(f(\alpha^2(u_1, u_2, \ldots, u_k), u_1, u_2, \ldots, u_k), 0, \theta). \tag{11}$$

Thus if $v_1, v_2, \ldots, v_l$ and $u_1, u_2, \ldots, u_k$ are chosen to be lists of invariants corresponding to G_1 and G_2 respectively, then the first branch in (11) has the isotropy group G_1 and the second has the isotropy group G_2. It is fairly clear that the branch ($\partial\phi/\partial f = 0$ and $\partial g/\partial\beta^2 = 0$), say, gives another thermoelastic internal energy with isotropy group G_1, so that the formalism can certainly describe phenomena like triple points, for example.

CASE 3

Finally, the form of (8) is suggestive enough to allow us to give a prototype internal energy appropriate when lists of invariants for G_1 and G_2 do not exist, or are not known.

Specifically, this allows treatment of solid crystals, where the isotropy group is infinite and discrete.

Notice that the arbitrary functions in (8) are invariant under G_1 and G_2 respectively. Consider first G_1. Suppose that each C may be written uniquely as

$$C = g_1 . C_1, g_1 \in G_1, \tag{12}$$

for C_1 in some fundamental domain D^1. (The fundamental domain is constructed so that there is *exactly* one $g_1 \in G_1$ such that (12) holds for all C.) Then by the invariance of f, viz,

$$f(\alpha^2, C) = f(\alpha^2, g_1 . C), \text{ for all } g_1 \in G_1, \tag{13}$$

it follows that

$$f(\alpha^2, C) = f(\alpha^2, C_1). \tag{14}$$

Conversely if f is defined by

$$f(\alpha^2, C) = \chi(\alpha^2, C_1), C_1 \in D^1,$$

together with (12), where χ is an arbitrary function, then (13) follows by the *uniqueness* of the decomposition (12). So it is natural to consider internal energies like

$$\phi(f(\alpha^2, C), g(\beta^2, C), \theta), \tag{15}$$

where f and g are defined by

$$\begin{aligned} f(\alpha^2, C) &= \sigma(\alpha^2, C_1), C_1 \in D^1, \\ g(\beta^2, C) &= \pi(\beta^2, C_2), C_2 \in D^2, \end{aligned} \tag{16}$$

where D^1 and D^2 are the fundamental domains appropriate to G_1 and G_2, and where σ and π are defined arbitrarily in these domains. With these representations, (3) translates to

$$\begin{aligned} \frac{\partial\phi}{\partial\alpha} &= \frac{\partial\phi}{\partial f}\frac{\partial\sigma}{\partial\alpha^2} . 2\alpha, \\ \frac{\partial\phi}{\partial\beta} &= \frac{\partial\phi}{\partial g}\frac{\partial\pi}{\partial\beta^2} . 2\beta, \end{aligned} \tag{17}$$

with the obvious arguments. Picking out two branches of interest, as before, consider

$$\left(\alpha = 0 \text{ and } \frac{\partial\pi}{\partial\beta^2}(\beta^2, C_2) = 0\right) \text{ and } \left(\beta = 0 \text{ and } \frac{\partial\sigma}{\partial\alpha^2}(\alpha^2, C_1) = 0\right).$$

If, again, π and σ vanish with their first arguments, then the corresponding thermoelastic internal energies are

$$\phi(0, \pi(\beta^2(C_2), C_2), \theta)$$

and

$$\phi(\sigma(\alpha^2(C_1), C_1), 0, \theta), \tag{18}$$

and the corresponding isotropy groups are G_2 and G_1 respectively.

Crystal to fluid transitions fall into this category. The fundamental domain appropriate to the crystal phase has been found in Parry[5] and that corresponding to the fluid phase consists, for example, of the set of all dilatations. The examples considered in[1, 3, 4] also belong here, but it is an open problem to determine the fundamental domain corresponding to the 1-lattice phase in the 2-lattice description (see Pitteri [7] for the terminology).

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