THE CHANGE OF SYMMETRY IN PHASE TRANSITIONS

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1. Introduction

One of the quantities which can be considered as describing some properties of a given material is its symmetry. Speaking about symmetry we can distinguish more aspects as for example the symmetries of a configuration of a crystal or invariance properties of constitutive relations (which must reflect some features of the physical properties of the material under consideration). About invariance properties of constitutive relations , used in the modern continuum mechanics , a first mathematical definition of the local symmetry group was given by W. Noll [1] .

From an experimental point of wiew it is clear that in a process in which the temperature increase some materials undergo changes of their symmetry properties. This symmetry changes are commonly associated with a "phase transition" . In fact, the general term "phase transition" is used in order to indicate suddenly changes of some physical properties (and the symmetry may be one of it), but in this paper we shall refer only to phase transitions in which the symmetry changes.

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A theoretical approach for phase transitions was made by Landau [2] . He distinguish between these the first order phase transitions and the second order phase transitions . According to Landau ;

> "... the second order phase transition is a continuous transition in sense that the state of the body vary continuous. We underline that the symmetry in the transition point is changed sudden and in every moment we can say to which phase the body belongs... at first order phase transitions, in the transition point, there are in equilibrium two different states of the body while at second order phase transitions the state of both phases is the same..."

The theory proposed by Landau excludes from the theoretical point of wiew some types of transitions - in which the symmetry is changed - which seems to be observed in experiments as being of second order (see [4],[5],[6],[7])

A critical constructive analysis to this approach is presented by Ericksen [4],[5] ; he constructed with the aid of the symmetries of the crystaline configuration (point groups ; latice groups) a possible description of the changes of symmetries in crystals, but his study deals only with the crystaline symmetries and not with invariance properties of the constitutive relations .

Motivating his point of wiew Ericksen [4] says:

" What we see in the phase transitions is a change in the symmetry of a configuration . "

At this point an observation must be made: if we use a macroscopic theory for describing the behaviour of a medium and if we want to take into account some realities from the microscopic level we need a hypothesis which must link quantities from a microscopic level (as might be the crystallographic symmetry group) by the quantities from the macroscopic level (constitutive equations , invariance properties) . One of the hypothesis of this type is the hypothesis about crystalline solids, was stated by Noll [8], and state that for a solid crystal in an undistorted configuration the material symmetry group is the group generated by the crystallographic symmetry group (point group) and the inversion -1 . This hypothesis will be used in this paper.

The fact that the symmetry is changed with modifications of the temperature and volume is sure but the aim of this paper is the mechanism of this change at a phase transition . The basic idea is to generalize what happens inside a phase.

Most of the authors which study phase transitions in the framework of continuum mechanics [9], [10], [11] associate this fact with a discontinuity of the deformation gradient at the transition point .

This kind of description might be suitable for a first order phase transition (in Landau's description), but since we are interested in the changes of symmetry in second order phase transitions we will suppose that at the transition point the deformation gradient is continuous.

The present paper treats only constitutive aspects of phase transitions and develops a mechanism for symmetry changes. The second section presents the basic definitions, and results in the framework of non-linear thermoelasticity when the symmetry is changed by temperature only. The third section includes general results about extensions of groups , the classification of the extensions from the isotropic phase and a comparision of the results obtained with some experimental results from the physics of liquid crystals . The fourth section includes a generalisation of the results from section 2 to non-simple materials and in this framework treats the transition cubic-tetragonal. It is shown that in the framework of materials of grade $r \geq 2$ the transition cubic-tetragonal is possible as a group extension . At the end of section 4 we present some modifications which could be made in order to treat the change of symmetry when the volume is varied.

2. The change of symmetry in the elastic case

Let K_1 be a fixed reference configuration of a thermoelastic body $\mathcal{B}$ and let us suppose that the temperature field in a fixed point has a value θ_1. A deformation whose gradient is F give rise to a Cauchy stress $T_{K_1}(F,\theta_1)$. Following Noll [1] the material symmetry group in the point X (which is fixed for the whole paper) at the temperature θ_1 with respect to K_1 is :

$$G^{K_1}_{\theta_1} = \left\{ H \in U(3) \,\middle|\, T_{K_1}(F,\theta_1) = T_{K_1}(FH,\theta_1), \text{ for all } F \in GL(3) \right\}$$

We shall denote by $U(3)$ - the unimodular group, by $O(3)$ - the orthogonal group , by $GL(3)$ - the linear group and by $M(3)$ the ring of linear transformations in the real three-dimensional space.

Let us observe that an analogous definition was given earlier by Gurtin and Williams [12] ; their definition make the group dependent on the local volume also, but their paper deals only with the classification of possible phases of elastic materials. We shall present in the last section the modifications which need to be made in order to obtain results of the present section in such a case; we choose this simplified version to make the hypothesis more accesible.

Definition 1 : The temperatures θ_1 and θ_2 are called equivalent in the configuration K_1 if the groups $G^{K_1}_{\theta_1}$ and $G^{K_1}_{\theta_2}$ are conjugate; this means that there exists a non-singular matrix $A_{K_1}(\theta_1;\theta_2)$ so that:

$$G^{K_1}_{\theta_1} = A^{-1}_{K_1}(\theta_1;\theta_2)\, G^{K_1}_{\theta_2}\, A_{K_1}(\theta_1;\theta_2) \tag{2.1}$$

From (2.1) it follows that the material response at θ_2 is the same as if the material is at temperature θ_1 but deformed by a deformation whose gradient is $A^{-1}_{K_1}(\theta_1;\theta_2)$ It follows easily the following proposition:

Proposition 1: If the temperatures θ_1 and θ_2 are equivalent in the configuration K_1 then they are also equivalent in any configuration.

Proof Let K_2 be a configuration obtained from K_1 by a deformation whose gradient is P ; then :

$$G^{K_2}_{\theta_1} = P\, G^{K_1}_{\theta_1}\, P^{-1} \quad , \quad G^{K_2}_{\theta_2} = P\, G^{K_2}_{\theta_2}\, P^{-1} \quad ,$$

so that :

$$G^{K_2}_{\theta_1} = A^{-1}_{K_2}(\theta_1;\theta_2)\, G^{K_2}_{\theta_2}\, A_{K_2}(\theta_1;\theta_2) \, ,$$

where : $A_{K_2}(\theta_1;\theta_2) = P A_{K_1}(\theta_1;\theta_2) P^{-1}$. $\square$

Let us observe that the equivalence from definition 1 is indeed an equivalence relation on $\mathbb{R}^*_+$ (which is choose as the range for the temperature field) and we have the following properties for the function A_k :

1. $A_k(\theta;\theta) = 1$

2. $A_k(\theta_1;\theta_2) = A_k^{-1}(\theta_2;\theta_1)$

3. $A_k(\theta_1;\theta_3) = A_k(\theta_2;\theta_3)\cdot A_k(\theta_1;\theta_2)$

(obviously relation 2 has sense only when $A_k(\theta_1;\theta_2)$ is invertible).

Definition 2 : An equivalence class obtained by factorization through the above equivalence relation is called a phase.

Definition 3 : a) A temperature θ_0 is called regular if there exist a neighbourhood U of θ_0 (in $\mathbb{R}_+^*$) so that θ_0 is equivalent with every θ in U .

b) A temperature θ_0 is called critical if it is not regular .

We shall suppose that there exists a finite number of critical temperatures (for a fixed material) so that there exist also a finite number of phases.

Let us observe that if θ_0 is a regular temperature then in a neighbourhood of it the symmetry group is changed by the conjugation rule (2.1) and so its structure is unchanged , and this fact **happens** in the interior of every phase. The basic problem is to link the symmetries of two neighbouring phases, and this link must generalize the conjugation rule. For this we shall give the following definition :

Definition 4 : Let $A \in M(3)$, G a group, $G \subset U(3)$. The set :

$$_A G = \{ h \in U(3) \mid \text{there exist } g \in G,\ hA = Ag \}$$

is called the left extension through A of G in $U(3)$. In a similar way, the set :

$$G_A = \{ h \in U(3) \mid \text{there exist } g \in G,\ Ah = gA \}$$

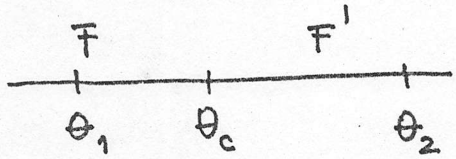
is called the right extension through A of G in $U(3)$.

Proposition 2 : If G is a group, $_A G$ and G_A are groups.

Proof : We consider the right extension only ; $1 \in G_A$ because $1 \in G$, let $h_1 \in G_A$ and $h_2 \in G_A$ thus exists $g_1, g_2 \in G$ so that $Ah_1 = g_1 A$, $Ah_2 = g_2 A$ and so $Ah_1 h_2 = g_1 g_2 A$; if $Ah = gA$ then $Ah^{-1} = g^{-1}A$ so $h \in G_A$ implies $h^{-1} \in G_A$. $\square$

We observe that the concept of left and right extensions generalize in a natural way the conjugation rule ; more exactly if A is invertible the left extension is the same thing with conjugation by A and the right extension is the same thing with conjugation by A^{-1} ; also we have in this case (A invertible) $_A(G_A) = ({_A G})_A = G$. About this "reversibility" relation we shall prove an important proposition in the next section.

Let Θ_c a critical point , F and F' open intervals at both parts of Θ_c coresponding at two different phases; let $\Theta_1 \in F$ and $\Theta_2 \in F'$ (see below) :



We shall suppose that for K and Θ_1 fixed the function $A_K(\theta_1;\theta)$ is continuous on F , $A_K(\theta;\theta_2)$ is continuous on F' for θ_2 fixed,and that :

a) $\lim\limits_{\substack{\theta \to \theta_c \\ \theta > \theta_c}} A_K(\theta;\theta_2)$ exists and is invertible ,

(and we denote this limit by $A_K(\theta_c,\theta_2)$)

b) at least one of the limits :

$$\lim_{\substack{\theta \to \theta_c \\ \theta < \theta_c}} A_K(\theta_1;\theta) \qquad \lim_{\substack{\theta \to \theta_c \\ \theta < \theta_c}} A_K^{-1}(\theta_1;\theta)$$

exists (we denote them by $A_K(\theta_1;\theta_c)$ and $A_K^{-1}(\theta_1;\theta_c)$)

Let us consider G_{θ_1} known and we shall indicate a mechanism for construct G_{θ_2} in the above hypothesis ; (from now on we omit the fixed configuration K)

Let $A(\theta_1;\theta_2) = A(\theta_c;\theta_2)\cdot A(\theta_1,\theta_c)$ (if $A(\theta_1;\theta_c)$ exists) and respectively $A^{-1}(\theta_1;\theta_2) = A^{-1}(\theta_1;\theta_c)\cdot A^{-1}(\theta_c;\theta_2)$ (if $A^{-1}(\theta_1;\theta_c)$ exists). In the above hypothesis we can construct either $A(\theta_1;\theta_2)$ or $A^{-1}(\theta_1;\theta_2)$; moreover any of them

is singular (because θ_1 and θ_2 are not equivalent)
Let us suppose that we can construct $A(\theta_1;\theta_2)$;
then we can define :

$$G_{\theta_2} = {}_{A(\theta_1;\theta_2)}(G_{\theta_1}) .$$

If $A^{-1}(\theta_1;\theta_2)$ exists we can define :

$$G_{\theta_2} = (G_{\theta_1})_{A^{-1}(\theta_1;\theta_2)} .$$

We shall postulate that symmetries in neighbouring phases are linked through this extensions. Thus we had construct the symmetry group G_{θ_2} (the symmetry group in the phase F') with the aid of G_{θ_1} (the symmetry group in the phase F) and the constitutive function A . But the same construction could be made starting from $\theta_1' \in F$ to a $\theta_2' \in F'$ and then through conjugation to θ_2 . We can prove the following result :

Theorem 1 : The construction of G_{θ_2} as above does not depend of $\theta_1 \in F$, of $\theta_2 \in F'$; it depends only of the phase F and of the constitutive function A .
Proof : Let $\theta_1 \in F$, θ_2 and $\theta_2' \in F'$. We can construct G_{θ_2} from G_{θ_1} through an extension or from $G_{\theta_2'}$ by conjugation after $G_{\theta_2'}$ was constructed from G_{θ_1} by extension . Let us suppose that $A(\theta_1;\theta_2)$ exists (so that $A(\theta_1;\theta_2')$ exists) so that :

$$G_{\theta_2} = {}_{A(\theta_1;\theta_2)}G_{\theta_1}$$

$$G_{\theta_2'} = {}_{A(\theta_1;\theta_2')}G_{\theta_1}$$

It is easy to see that if B is invertible we have :

$$B({}_{A}G)B^{-1} = {}_{AB}G \quad ,$$

so that the two possible ways to construct G_{θ_2} give the same result. The same thing is possible if we start with $\theta_1' \in F$, $\theta_1 \in F$ and $\theta_2 \in F'$, or if $A^{-1}(\theta_1;\theta_2)$ exists.

The above result shows that the constitutive function A (which is not neccesary invertible because does not represent a deformation gradient) and the symmetry in the phase F determine in a unique way the symmetry in the phase F' .

3. Group extensions ; the isotropic case.

For the whole section A will be a singular transformation in $M(3)$, G a group , $G \subset U(3)$. One of the problems that arise naturaly is the reversibility of such symmetry changes; we know that ${}_{A}(G_A) = ({}_{A}G)_A = G$ for an invertible A . What happens when A is not invertible?

Let $g \in G$ and define :

$$g_A = \{ h \in U(3) \mid Ah = gA \} \quad .$$

Then :

$$G_A = \bigcup_{g \in G} g_A = \bigcup_{\substack{g \in G \\ g_A \neq \emptyset}} g_A \quad . \qquad (3.1)$$

This result and the following observation permit us to give an answer to the "reversibility" problem . If $h \in g_A$ then $Ah = gA$ so that $g \in_A h$.

Proposition 3 : For A fixed there exists at least one group $\mathcal{H} \subset U(3)$ so that ${}_A(\mathcal{H}_A) = \mathcal{H}$.

Proof : The proof will be constructive. Let :

$$\mathcal{H} = \{ h \in U(3) \mid h_A \neq \emptyset \} \quad .$$

We shall prove that $\mathcal{H}$ is a group ; $1 \in \mathcal{H}$ because $1 \in 1_A$; if $h_1 \in \mathcal{H}$ and $h_2 \in \mathcal{H}$ we have $h_1 A = Ag_1$, $h_2 A = Ag_2$ for some $g_1, g_2 \in U(3)$ so that $h_1 h_2 A = Ag_1 g_2$. If $h \in \mathcal{H}$ then $hA = Ag$ so that $h^{-1}A = Ag^{-1}$ thus $h^{-1} \in \mathcal{H}$. We shall show that ${}_A(\mathcal{H}_A) = \mathcal{H}$; it is clear that $\mathcal{H}_A = \bigcup_{h \in \mathcal{H}} h_A$ and so if $h \in \mathcal{H}$, $h_A \neq \emptyset$ and from the above observation $k \in h_A$ implies $h \in_A k$ thus $h \in {}_A(h_A)$ and we obtain $\mathcal{H} \subset {}_A(\mathcal{H}_A)$. Now if $h \in {}_A(\mathcal{H}_A)$ there exist a $k \in \mathcal{H}_A$ so that $h \in_A k$ thus $k \in h_A$; so that $h_A \neq \emptyset$ and so $h \in \mathcal{H}$ and the proof is complete . $\square$

We can observe that $\mathcal{H}$ is maximal with this property but may have subgroups "stable" in this sense .

We can prove also the following :

Proposition 4 : Let G a group , $G \subset U(3)$, H a subgroup of G , A singular ; then :

1. H_A is a subgroup in G_A .
2. 1_A is a normal subgroup in G_A for every G .
3. $G_A = (G \cap \mathcal{H})_A$ (for the definition of $\mathcal{H}$ see the above proposition)
4. $G_A \subset \mathcal{H}_A$ for every G .
5. Denoting $\overset{1}{G} = {}_A(G_A)$, $\overset{2}{G} = {}_A(\overset{1}{G}_A)$ and so on we have an increasing sequence :

$$\overset{1}{G} \subset \overset{2}{G} \subset \ldots \subset \mathcal{H} .$$

Proof : For 1. we have $H_A = \bigcup_{h \in H} h_A \subset \bigcup_{g \in G} g_A = G_A$ and $\mathcal{H}_A$ is obviously a group ; for 2. let $g \in G_A$ and $h \in 1_A$; we show that $g h g^{-1} \in 1_A$; we have $Ag = kA$ with $k \in G$ and $Ah = A$ so that $Aghg^{-1} = A$.
3. is clear from the above proposition , 4. follows from (3.1) and the definition of $\mathcal{H}$; for 5. we shall prove that $\overset{i}{G} \subset \overset{i+1}{G}$ ($i \geq 1$) . Let us observe that $\overset{i}{G}_A = \bigcup_{g \in \overset{i}{G}} g_A$ and all $g_A \neq \emptyset$ (from the definition of $\overset{i}{G}$) ; then if $k \in \overset{i}{G}_A$ we have $k \in h_A$ with $h \in \overset{i}{G}$ thus $h \in {}_A k$ and so $\overset{i}{G} \subset {}_A(\overset{i}{G}_A)$. $\square$

The last assertion in the above proposition shows that the symmetry in a proccess which pass cyclic through a transition point tends to a "stable" symmetry.

The following proposition establishing a property of the extensions, in the elastic case, is very useful for computing the extensions from $O(3)$ (the isotropic phase)

Proposition 5 : Let G a group , $G \subset U(3)$, $A \in M(3)$ non-invertible . Then G_A is not compact .

Proof : Clear G_A contains 1_A . We shall prove a stronger result which state that 1_A is not compact . From the definition $1_A = \{ h \in U(3) \mid Ah = A \}$

If dim(ker A) = 3 then $A = 0$ so that $1_A = U(3)$ which is not compact . If dim (ker A) = 2 there exists $R \in O(3)$ so that if e_1 span (ker A)$^\perp$ we have $RAe_1 = \lambda e_1$, $\lambda \neq 0$ thus in an orthonormal basis (e_1 , e_2 , e_3) we have :

$$RA = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \lambda \neq 0 . \qquad (3.2)$$

But $1_A = 1_{RA}$ for R invertible , and :

$$1_{RA} = \left\{ \begin{pmatrix} 1 & 0 & 0 \\ a & b & c \\ d & e & f \end{pmatrix} , |bf - ec| = 1 \right\}$$

thus 1_A is not compact . If dim (ker A) =1 there exists $R \in O(3)$ so that :

$$RA = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \lambda_1 > 0, \lambda_2 > 0, \qquad (3.3)$$

(in a basis in which (e_1, e_2) span $(\ker A)^{\perp}$)

so that :

$$1_{RA} = \left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ a & b & \pm 1 \end{pmatrix}, a, b \in R \right\},$$

thus it is not compact so the proof is complete . $\square$

The formulas (3.2) and (3.3) are analogous with the polar decomposition theorem and are very useful in describing the extensions from the isotropic phase.

Proposition 6 : Let $A \in M(3)$ be non-invertible ; then :

(a) if dim (ker A) = 3 , $O(3)_A = U(3)$.

(b) if dim (ker A) = 2 , e_1 span $(\ker A)^{\perp}$ and (e_1, e_2, e_3) is an orthonormal basis we have :

$$O(3)_A = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ y_1 & y_2 & y_3 \\ z_1 & z_2 & z_3 \end{pmatrix} \right\} \cap U(3) . \qquad (3.4)$$

(c) if dim (ker A) = 1 , e_1 and e_2 span $(\ker A)^{\perp}$ and (e_1, e_2, e_3) is an orthonormal basis we have :

$$O(3)_A = \left\{ \begin{pmatrix} a_1 & \omega a_2 & 0 \\ b_1/\omega & b_2 & 0 \\ z_1 & z_2 & \pm 1 \end{pmatrix} \;\middle|\; \begin{pmatrix} a_1 & a_2 \\ b_1 & b_2 \end{pmatrix} \in O(2) \right\}, \qquad (3.5)$$

... $\lambda_2/$ ... and λ_1, λ_2 are those from (3.3)

Proof ; (a) is obviously and (b) and (c) can be easily obtained from the definition taking into account the fact that if we denote $B = RA$ and $R \in O(3)$ then $O(3)_A = O(3)_B$. □

Let us observe that all the propositions from this section were stated for right extensions but analogous results hold obviously for the left extensions . For the left extensions from $O(3)$ we can observe that :

$$_{A^T}O(3) = \left(O(3)_A\right)^T .$$

At this point we will compare this theoretical results with some experimental facts from the monography "The Physics of Liquid Crystals " [13] . We begin by recalling some definitions from Noll [8] , Gurtin and Williams [12] (see also Wang [14] , Coleman [15]) In a fixed point, a material is called solid if there exists a configuration K so that $G_K \subset O(3)$; if $G_K \supset O(3)$ the material is called isotropic ; if $G_K = U(3)$ the material is called fluid and if for every configuration K , $G_K \setminus O(3) \neq \emptyset$ and $G_K \neq U(3)$ the material is called liquid crystal (Wang [14] or Coleman [15]) or we say that the material is in a mesomorphic phase.

Let us analyse the result of the last proposition; in the case (a) we have a transition from a solid isotropic phase to a fluid phase , and in the other two cases we have transitions from an solid isotropic phase to a mesomorphic phase with symmetry group given by (3.4) and (3.5) . There exists a qualitative difference betwen the groups (3.4) and (3.5). In the case (3.4) the transformations from the mesomorphic phase leave the plane (e_2, e_3) invariant and preserve the areas from this plane unchanged and also preserve the distances in the direction of the e_1 axis . In the case (3.5) the transformations from the symmetry group preserve the distances in the direction of the e_3 axis and in the plane spanned by e_1 and e_2 act (modulo a change of the configuration of the plane) as orthogonal transformations.

Thus in the case (b) we have to deal with a symmetry group of a mesophase with properties of a fluid in the plane (e_2, e_3) and in the case (c) with a symmetry group which describes a mesophase with properties of a solid in the (e_1, e_2) plane.

A comparision with results from physics is now suitable. P.G. de Gennes [13] state (page 1) :

> "... mesophases can be obtained in two different ways :
>
> (1) Imposing positional order in one or two dimensions rather than in three dimensions. This does happen in nature. In the main practical case we have positional order in one direction only; the system can be wiewed as a set of two dimensional liquid

layers stacked on each other with a well-defined spacing ; the coresponding phases are called smectics ... "

and about smectics (page 273) :

" Inside the broad class of layered materials, we may distinguish two major subgroups [...] :

Group 1 : Each layer is a two-dimensional liquid...

Group 2 : Each layer has some features of a two-dimensional solid ... " .

Thus it seems probably that the groups obtained at (b) and (c) could describe some qualitative aspects observed in experiments , so that the mecnanism of symmetry changes previously presented appears to be quite well motivated.

4. The change of symmetry in non-simple bodies; the cubic - tetragonal transition

As we proved in a proposition of the preceding section if A is not invertible G_A is not compact because 1_A is not compact and so the orthogonal group $O(3)$ which is compact can not be obtained by an extension. We shall present in this section a mechanism for symmetry changes for non-simple bodies which represents the natural generalization of the ideas from the section 2 and which overleap the above mentioned difficulty.

Denoting by X the position of a particle in a reference configuration K, denoting the motion of the body by $x(X,t)$, for a fixed time t the i^{th} deformation gradient ($i \geq 1$) will be :

$$\overset{i}{F} = \nabla^i x(X)$$

Naturaly we shall impose $\det \overset{1}{F} \neq 0$. We shall suppose constitutive equations (for non-simple materials of grade r) of the form :

$$T_K(X,\theta) = T_K(\overset{1}{F}, \overset{2}{F}, \ldots, \overset{r}{F}, \theta)$$

(of course for $r \geq 2$, $\overset{r}{F}$ is symmetric in the last r indices) . If we change the reference configuration from K to K' (by a volume preserving deformation) through a map $\phi^{-1}(X)$, we can compute the i^{th} deformation gradient for $x(X)$ with respect to K' by :

$$\overset{i}{G} = \nabla^i (x \circ \phi) \tag{4.1}$$

using the chain rule , so that , for example , in components :

$$\overset{1}{G}_{ij} = \overset{1}{F}_{ik} \overset{1}{H}_{kj} \quad , \quad \overset{2}{G}_{ijk} = \overset{2}{F}_{ilm} \overset{1}{H}_{mj} \overset{1}{H}_{lk} + \overset{1}{F}_{il} \overset{2}{H}_{ljk} \tag{4.2-3}$$

In (4.2) and (4.3) :

$$\overset{1}{H}_{kj} = (\nabla \phi_k)_j \quad , \quad \overset{2}{H}_{ijk} = (\nabla^2 \phi_i)_{jk} \; ,$$

$$|\det \overset{1}{H}| = 1 ,$$

and we easy observe that the set of all r - tuples ($\overset{1}{H}$, $\overset{2}{H}$,..., $\overset{r}{H}$) for which :

$$T_{K'}(\overset{1}{F},\overset{2}{F},\dots,\overset{r}{F},\theta) = T_{K'}(\overset{1}{G},\overset{2}{G},\dots,\overset{r}{G},\theta)$$

do form a group which will be called the symmetry group with respect to K' at temperature θ .

At this point all ideas from section 2 are direct applicable (all definitions and theorems hold) but this time the constitutive function A will be a r - tuple ($\overset{1}{A}$, $\overset{2}{A}$,..., $\overset{r}{A}$). We are interested in extensions through a r - tuple in which $\overset{1}{A}$ is not invertible so that the application A is singular . Let us observe that such a framework in which we work with non-simple bodies offers more information about the singularity of the map A at the transition point , so that it gives a larger class of extensions. We shall adopt the classification of phases given in section 3 which uses only the linear of the symmetry group and we are mainly interested in extensions which have as a linear part the group $O(3)$.

We shall denote by $\mathcal{P}$ the projection of the first component of a r - tuple $(\overset{1}{G}, \overset{2}{G}, \dots, \overset{r}{G})$. thus $\mathcal{P}(\overset{1}{G}, \overset{2}{G}, \dots, \overset{r}{G}) = \overset{1}{G}$.
We easily see that if $\mathcal{G}$ is a symmetry group for a body of grade r then $\mathcal{P}(\mathcal{G})$ is also a group, and $\mathcal{P}(\mathcal{G}) \subset U(3)$. Let $\mathcal{G}$ be a symmetry group of a body of grade r; let $A = (\overset{1}{A}, \overset{2}{A}, \dots, \overset{r}{A})$ be a singular map (so that $\det \overset{1}{A} = 0$). The extension $\mathcal{G}_A$ is defined by :

$$\mathcal{G}_A = \Big\{ H = (\overset{1}{H}, \overset{2}{H}, \dots, \overset{r}{H}),\ |\det \overset{1}{H}| = 1,\ \overset{i}{H} \text{ is symmetric in the last } i \text{ indices and there exists } G \in \mathcal{G},\ G = (\overset{1}{G}, \overset{2}{G}, \dots, \overset{r}{G}) \text{ so that } A \circ H = G \circ A \Big\}$$

where the symbol $\circ$ denotes the composition rule described in (4.1).

We shall prove the following theorem which solves the problem raised at the begining of this section .

Theorem 2 : For any $r \geq 2$, there exists a symmetry group $\mathcal{G}$ and a non-invertible A so that $\mathcal{P}(\mathcal{G}_A) = O(3)$.
Proof : The proof will be constructive. First we shall reduce the problem to the case $r = 2$ by observing that if $\mathcal{G} = (\overset{1}{G}, \overset{2}{G})$ is a symmetry group for a body of grade 2 , the group $\tilde{\mathcal{G}} = (\overset{1}{G}, \overset{2}{G}, 0, \dots, 0)$ with $(\overset{1}{G}, \overset{2}{G})$ in $\mathcal{G}$ is also a symmetry group for a body of grade r .

So we restrict our attention to bodies of grade 2. Let $\mathcal{G}$ be such a group and $A = (\overset{1}{A}, \overset{2}{A})$ be a non-invertible map ; the group extension $\mathcal{G}_A$ consist of pairs $(\overset{1}{H}, \overset{2}{H})$ for which there exist $(\overset{1}{G}, \overset{2}{G}) \in \mathcal{G}$ so that :

$$\overset{1}{A}_{ij}\overset{1}{H}_{je} = \overset{1}{G}_{ij}\overset{1}{A}_{je} \tag{4.4}$$

$$\overset{2}{A}_{ijk}\overset{1}{H}_{je}\overset{1}{H}_{ks} + \overset{1}{A}_{ij}\overset{2}{H}_{jes} = \overset{2}{G}_{ijk}\overset{1}{A}_{je}\overset{1}{A}_{ks} + \overset{1}{G}_{ij}\overset{2}{A}_{jes} \tag{4.5}$$

We shall choose $\mathcal{G}$ to be the group consisting by the pair $(\overset{1}{G}, \overset{2}{G}) = (\delta_{ij}, 0)$ so that $P(\mathcal{G}_A) = 1_A$. Because we want $O(3) \subset P(\mathcal{G}_A)$ we must have $O(3) \subset 1_A$ so that from proposition 5 of the preceding section we must have $\overset{1}{A} = 0$. Thus relation (4.5) becomes :

$$\overset{2}{A}_{ijk}\overset{1}{H}_{je}\overset{1}{H}_{ks} = \overset{2}{A}_{ies} \tag{4.6}$$

so that choosing $A_{1ij} = A_{2ij} = A_{3ij} = \delta_{ij}$ the relation (4.6) shows that $\overset{1}{H}_{ij}$ belongs to $P(\mathcal{G}_A)$ if and only if :

$$(\overset{1}{H})^T\overset{1}{H} = 1$$

so that $P(\mathcal{G}_A) = O(3)$ and the proof is complete . $\square$

In what follows we shall treat the change of symmetry in the cubic - tetragonal transition in the above mentioned context . As we already observed in the introduction this was treat by Ericksen [4], [5] in order to overpass some difficulties which seems to appear in Landau's theory of phase transitions . We shall work in the framework of bodies of grade 2 because we have to deal with two compact groups.

The cubic and tetragonal symmetries are described in Noll ([8] , page 169, ref. 5 , 7) and are generated by : $\{R_i^{\pi/2}, R_j^{\pi/2}, -1\}$ - 48 elements - for the cubic symmetry , and by : $\{R_i^{\pi/2}, R_j^{\pi}, -1\}$ - 16 elements - for the tetragonal symmetry . We denoted by R_e^{α} the rotation around the axis e by an angle α . By an element of the cubic symmetry group (in the context of bodies of grade 2) we understand a pair (G , O) with G in the group above mentioned and O a third order tensor ; analogously for an element of the tetragonal symmetry group .

Theorem 3 : For materials of grade 2 the transition cubic-tetragonal is possible as an extension .

Proof : Let $\mathcal{G}$ be the group generated by the set $\{R_i^{\pi/2}, R_j^{\pi/2}, -1\}$ and $\mathcal{H}$ the group generated by $\{R_i^{\pi/2}, R_j^{\pi}, -1\}$; let $\tilde{\mathcal{G}} = \{(G,0), G \in \mathcal{G}\}$ and $\tilde{\mathcal{H}} = \{(H,0), H \in \mathcal{H}\}$. We want to show that there exists an $A = (\hat{A}, \hat{\hat{A}})$ so that $P(\tilde{\mathcal{G}}_A) = \mathcal{H}$; this means :

$$\overset{1}{A}_{ij}\, H_{jk} = G_{ij}\, \overset{1}{A}_{jk} \qquad (4.7)$$

$$\overset{2}{A}_{ijk}\, H_{jl}\, H_{km} = G_{ij}\, \overset{2}{A}_{jlm} \qquad (4.8)$$

We choose $\overset{1}{A} = e_2 \otimes e_2 + e_3 \otimes e_3$ (here (e_1, e_2, e_3) form an orthogonal basis) and $\overset{2}{A}_{2ij} = \overset{2}{A}_{3ij} = 0$, $\overset{2}{A}_{1ij} = \delta_{ij}$ so that :

$$P(R_i^{\pi/2})_{\overset{1}{A}} = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \right\} .$$

Moreover with this choice of $(\overset{1}{A}, \overset{2}{A})$ we have $G_A \neq \phi$ only if $G_{11} = 1$.

Straightforward computations show that :

$$P(1_A) = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\} ; \quad P(R_i^{\pi})_A = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \right\} ;$$

$$P(R_i^{3\pi/2})_A = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \right\} ; \quad P(-R_j^{\pi})_A = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\} ;$$

$$P(-R_j^{\pi} \cdot R_i^{\pi})_A = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \right\} ; \quad P(-R_j^{\pi} \cdot R_i^{\pi/2})_A = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \right\} ;$$

$$P(-R_j^{\pi} \cdot R_i^{\frac{3\pi}{2}})_A = \left\{ \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \right\} ,$$

and we obtain $P(\tilde{\mathcal{G}}_A) = \mathcal{H}$ so the proof is complete. $\square$

Before ending this section we mention some modifications which make possible changes in symmetry when the volume is varied also . First the definition of the symmetry group must be given in such a way to make the group dependent of the volume. As we already mention this was done earlier by Gurtin and Williams [12] , and following them :

$$G^{k}_{(\theta,V)} = \{ H \in U(3) \mid T_k(FH,\theta,V) = T_k(F,\theta,V) \text{ for all } F \in U(3) \}$$

Now two states $S_1 = (\theta_1, V_1)$ and $S_2 = (\theta_2, V_2)$ will be called equivalent if the coresponding groups are conjugate . Then we can define regular and critical states and we need some hypothesis about critical states and the constitutive function A . Such suitable hypothesis are :

1. The critical states are all the points of some continuous curves in the (θ, V) quadrant which does not intersect betwen them and which are in a finite number .
2. The constitutive function A has at any two

different points situated on the same critical curve the same type of singularity . This means that the two singularities are conjugated through an invertible transformation .

Under these hypothesis similar results with that of section 2 can be proved , and also a path independence of the symmetry group and symmetry group extension is now easy to prove.

We end this section with an important observation ; There exist a strong similarity betwen what we called here a group extension (the formal definition) and some definitions in singularity theory and bifurcation theory (see for example J. Damon [16] , formula (2.1)) Far from being only formal this similarity may play an important role in understanding the complex phenomena of phase transitions using strong tools from singularity theory and bifurcation theory .

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