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The Coleman–Noll inequality in thermodynamics

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Abstract. It is shown that the fundamental inequality used to define a local state of thermal equilibrium by Coleman and Noll in their theory of thermostatics of continua, is wrong. The variation of states employed in it does not exclude states connected by symmetry transformations to the postulated state of thermal equilibrium. For such states the inequality must be an equality. This error is especially important for a material whose symmetry (isotropy) group is continuous, such as a simple fluid and an isotropic material. The proofs of three theorems given by Coleman and Noll are, as a result, invalid. These theorems essentially state that the pressure of a fluid must be positive, and that for isotropic materials 'the greater stretch will occur in the direction of the greater force' (the ordered force inequality of Truesdell and Toupin).

1. Introduction

Coleman and Noll (1959) proposed an inequality which has been named the CN inequality (Truesdell and Toupin 1963, Truesdell and Noll 1965). It was introduced to define a state of thermal equilibrium, ie it was part of a fundamental postulate in their theory of the thermostatics of continua. It has been further used to develop many results and other inequalities such as that described by Truesdell and Noll (1965) as the generalized Coleman–Noll inequality (GCN).

Coleman and Noll (1959) used this definition to prove three theorems (theorems 6, 8, 8*a* in their 1959 paper). Theorem 6 essentially stated that the pressure of a simple fluid must be positive, while theorems 8, and 8*a* essentially state that for an isotropic medium, if the principal stretch v_i is greater than the principal stretch v_k , then the principal stress measured per unit area of the undistorted reference state, in the direction of v_i is greater than that in the direction of v_k . Here v_i , $i = 1, 2, 3$ are the eigenvalues of the positive-definite symmetric matrix V which is a factor in the unique polar decomposition

$$F = QV \tag{1}$$

where F is the deformation gradient tensor, and where Q is an orthogonal matrix (the notation of Coleman and Noll 1959, is used throughout).

It is now shown in this paper that the proofs of these three theorems are invalid and that the postulate of thermal equilibrium must be modified. In fact the three theorems cannot be justified, even when the postulate is suitably altered. This alteration is required simply because the implications of the symmetry properties of the material considered were not taken fully into account.

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2. Coleman–Noll inequality

The CN inequality is expressed in terms of a state function

$$\hat{\lambda}(F, \eta) = \hat{\varepsilon}(F, \eta) - (1/\rho_r) \text{Tr}(FS_r) - \eta\theta \tag{2}$$

where $\eta, \hat{\varepsilon}$ are, respectively, the entropy and energy density (per unit mass); ρ_r is the mass density at the reference state. S_r is the Kirchhoff stress tensor; $\text{Tr}(A)$ denotes the trace of any tensor A . The local state in (2) is defined by (F, η) .

The definition of thermal equilibrium given by Coleman and Noll is as follows.

A local state (F, η) is called a state of thermal equilibrium under a given force temperature pair (S_r, θ) if: (a) The Cauchy stress tensor

$$S = (\rho/\rho_r)FS_r \tag{3}$$

is symmetric; (b) the inequality

$$\hat{\lambda}(F^*, \eta^*) > \hat{\lambda}(F, \eta) \tag{4}$$

holds for all states $(F^*, \eta^*) \neq (F, \eta)$, such that

$$F^* = GF \tag{5}$$

where G is symmetric and positive-definite. ρ is the mass density at the state (F, η) .

As stated in the introduction this definition was used to prove theorems 6, 8, 8a. For the purposes of this paper we should note that these proofs for both the simple fluid and isotropic material, depended in each case on transformations G of (5), which are unimodular and therefore such that $v^* = v$, where v^* and v are the specific volumes of the states (F^*, η^*) and (F, η) ; ie $v = 1/\rho$.

Theorems 8 and 8a are not consistent with results obtained theoretically by Rivlin (1948) and this was pointed out by Rivlin (1967). As to theorem 6, no known physical considerations of actual fluids require this to be true. In fact it has been shown experimentally that fluids can sustain negative pressures, which in the case of water can be surprisingly large (see eg Briggs 1950, Winnick and Cho 1971). Briggs, for example, showed for water that the limiting negative pressure had a maximum value at 10 °C of 280 atm! Near 0 °C the limiting negative pressure dropped rather sharply to about 10% of the maximum value. Above 10 °C it dropped more gradually to about 150 atm at 50 °C.

3. Simple demonstration of the invalidity of the CN theorems 6, 8, 8a

On using (3) to eliminate the tensor S_r from (2) in favour of the Cauchy stress tensor, it is easy to show that

$$\hat{\lambda}(F, \eta) = \hat{\varepsilon}(F, \eta) + 3\pi v - \eta\theta \tag{6}$$

where

$$\pi = -\frac{1}{3} \text{Tr}(S) \tag{7}$$

where this definition of π is such that it becomes the pressure p when hydrostatic conditions prevail, ie when $S = -pE$, where E is the unit matrix.

Now in the case of a simple fluid, it can be shown that

$$\hat{\epsilon}(F, \eta) = \bar{\epsilon}(v, \eta), \quad (8)$$

ie the energy density is a function of v and η , only.

To prove theorem 6, Coleman and Noll applied the inequality (4) to a case where $\eta^* = \eta$ and where G is unimodular, ie where $v^* = v$. However, we see from (8) that in this case $\bar{\epsilon} = \bar{\epsilon}^*$, and the result of applying inequality (4) is that

$$(\pi^* - \pi)v > 0, \quad (9)$$

thus the result of the inequality is that

$$\pi^* > \pi, \quad \text{ie} \quad p^* > p, \quad (10)$$

as would be expected in classical hydrostatic thermodynamics—although Gibbs used \geq rather than $>$ in the inequality corresponding to (4). There is no sign in the above procedure of the requirement that p be positive emerging as a result.

Similarly in the case of isotropic materials, η^* was taken equal to η , and a transformation G was chosen as a unimodular tensor which commuted with V , the positive-definite symmetric factor of F in (1). G was, in particular, chosen such that if v_1, v_2, v_3 are the eigenvalues (principal stretches) of V , then v_1^*, v_2^*, v_3^* those of $V^* = GV$, are respectively v_2, v_1, v_3 . Thus again $v^* = v$ and since $\hat{\epsilon}$ can be shown to be a symmetric function of v_1, v_2, v_3 , then again $\bar{\epsilon} = \bar{\epsilon}^*$ and the application of (4) leads again to (9) and (10), with no sign of the results of theorems 8, 8a emerging.

Thus we have demonstrated that the proofs of the CN theorems 6, 8, 8a are invalid.

4. Where is the error?

The reason for these invalid proofs is that the effects of the isotropy group of the material have not been fully considered in the postulate for thermal equilibrium, as can be directly demonstrated.

$\hat{\lambda}$ is a state function of the material, and so like $\hat{\epsilon}$ and η , its behaviour is affected by the isotropy group (symmetry group) of the material, ie $\hat{\lambda}$ must be invariant to symmetry transformations R such that

$$\hat{\lambda}(FR, \eta) = \hat{\lambda}(F, \eta). \quad (11)$$

Thus if we take a transformation G such that

$$G = FRF^{-1}, \quad \text{ie} \quad GF = FR \quad (12)$$

where R is a member of the symmetry group, then we see from (11) that the inequality (4) cannot apply in this case—we have equality.

For a simple fluid, we see that for any unimodular transformation G , as in (5), there is a corresponding transformation R which is unimodular and thus is a member of the symmetry group for a simple fluid—which is the group of unimodular transformations. Thus if we wish to use (4) as part of a definition of thermal equilibrium of a simple fluid, we must exclude positive-definite symmetric transformations G which are unimodular. It requires a glance only at the Coleman and Noll proof of theorem 6 to see that it is exactly such a transformation which is employed.

In their treatment of an isotropic material, it may be seen that for the transformation $F^* = \tilde{G}F$, they have taken

$$\tilde{G} = QGQ^T \quad (13)$$

where G commutes with the polar factor V . On using (1) we verify that, in this case

$$R = F^{-1}\tilde{G}F = G. \quad (14)$$

If R is a symmetry transformation as in (11), then we see that the inequality (4) again cannot hold. As described in § 3, the G chosen—and so R —is indeed a symmetry transformation.

5. The definition of thermal equilibrium

From the preceding discussion, it is clear that the CN definition should be modified by either substituting \geq for $>$, or by stating that G must not only be symmetric and positive-definite, but also must be such that $F^{-1}GF$ is not a symmetry transformation in the sense of (11). Since F^* is in the neighbourhood of F this restriction will be especially important for materials with continuous symmetry groups.

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