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LETTERS TO THE EDITOR

Some thoughts on thermodynamics of internal variables

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THE THOUGHTS and ideas expressed here are meant to address the remarks and comments that were made by various speakers during the 31st Polish Solid Mechanics Conference. It was felt at the time that a complete picture of the theory on thermodynamics of internal variables appeared to be lacking in some issues that are of critical interest technically as well as historically. These comments are meant to address these issues.

The first point concerns the question of entropy. As is known, entropy is not a primitive quantity like energy. Its existence as a thermodynamic state function can be established only by integration of the First Law, if the First Law is integrable – as in the case of a perfect gas. The conditions of integrability of the 1st Law, which is basically a Pfaffian form, were established by Caratheodory, on the basis of inaccessibility of thermodynamic states. This, however, was done only for non-dissipative, i.e., reversible processes. The application of the Caratheodory principle to irreversible processes, associated with the deformation of materials with memory, leading to a proof of existence of entropy in the presence of such processes, was done by VALANIS [1, 2], using the concept of internal variables. These were used not so much as agents of dissipation, as is commonly done, but as additional variables necessary to render such quantities as energy and entropy as STATE FUNCTIONS, which they are not if the internal variables are missing.

One important aspect of the proof is that dissipative processes, associated with the deformation of materials with memory, do possess entropy at levels *far* removed from equilibrium – i.e., not just for processes near equlibrium as was the case with the traditional "thermodynamics of irreversible processes". Thus in the case of thermodynamics of internal variables, *equilibrium* does *not* enjoy a *special place* in the theory, so that the Kestin "paradox" in plasticity, that a succession of "equilibrium states" constitutes none-the-less a dissipative process, is resolved by means of the endochronic theory, where time is the length of the strain path.

The alternative is to begin with a functional form of a constitutive theory of materials with memory and to assume that such materials possess entropy as a primitive state function and further, to assume the existence of entropy inequalities. This is nothing short of a leap of faith since there is no fundamental mathematical or physical basis neither for the existence of entropy in this mathematical framework, nor for the associated inequalities.

The second point regards the contention that the thermodynamical theory of internal variables is not fully general since it cannot describe Markov processes. To the extent that such processes are a mathematical model for viscocity (and diffusion), it is much more satisfactory if one deals with viscosity *per se*. It was said, on one occasion of an invited address, that internal variables cannot describe viscous materials such as viscous liquids of the Navier-Stokes type. But on the contrary, internal variables do describe the constitutive behaviour of viscous liquids, albeit in an *asymptotic* sense!! In other words, viscous liquids are asymptotic ideals of "linear" viscoelastic solids!

To show that this is in fact the case, first for small deformation and then for large, we first consider the deviatoric response of a linear viscoelastic solid where the deviatoric stress is a linear memory integral of the history of the deviatoric strain as in Eq. (1). Its large deformation counterpart is given in Eq. (2).

$$s_{ij} = \int_0^t 2\mu(t-t')\, de_{ij}/dt'\, dt', \tag{1}$$

$$\tau_{\alpha\beta} = \int_0^t \mu(t-t')\, dC_{\alpha\beta}/dt'\, dt' + pC_{\alpha\beta}. \tag{2}$$

In Eq. (1) $\mathbf{s}$ is the deviatoric stress tensor, $\mathbf{e}$ the deviatoric strain tensor and μ the memory kernel. In Eq. (2) $\boldsymbol{\tau}$ is the (covariant) Piola stress and $\mathbf{C}$ the Right Cauchy-Green tensor, and again μ is the memory kernel. Also p is the (indeterminate) hydrostatic stress for incompressible materials.

In the linear theory of internal variables the memory kernel is a sum of positive decaying exponential terms. It is shown in the Appendix that when the relaxation times tend to zero, the memory kernel becomes a Dirac delta function so that the material becomes a viscous liquid. The theory is remarkable in this sense. No material can have, physically speaking, a zero relaxation time, simply because relaxation processes take a finite time to be completed. Thus a zero relaxation time is an idealization and the viscous liquid is a mathematical construction, true only in an asymptotic sense.

The same is true in plasticity where the constitutive behaviour is represented by an endochronic integral. In this case, a perfectly plastic solid is an "ideal" which results when the endochronic relaxation times tend to zero.

Appendix

We begin with Eq. (1). The interest is to show that the material, whose constructive behaviour is given by Eq. (1), degenerates into a viscous liquid, when its relaxation times tend to zero. Since, according to the theory of internal variables, the memory function $\mu(t)$ in Eq. (1) is the sum of decaying exponential terms, one such term suffices in the proof. Thus, let:

$$\mu(t) = \mu_0 e^{-\alpha t}, \tag{3}$$

where α is the inverse relaxation time λ and is equal to μ_0/η. We note that μ_0 is the (instantaneous) modulus of the material while η is the viscosity. Evidently λ is equal to η/μ_0 and tends to zero as μ_0 tends to infinity. In the light of Eq. (3), Eq. (1) becomes:

$$\alpha \mathbf{s} + d\mathbf{s}/dt = 2\mu_0 \, d\mathbf{e}/dt \tag{4}$$

or

$$\mathbf{s} + (\eta/\mu_0)\, d\mathbf{s}/dt = 2\eta \, d\mathbf{e}/dt. \tag{5}$$

Thus, as μ_0 tends to infinity:

$$\operatorname{Lim} \mathbf{s} = \eta \, d\mathbf{e}/dt. \tag{6}$$

Hence viscous behaviour is the mathematical ideal of zero relaxation time s.

In a similar manner Eq. (2) becomes:

$$\tau_{\alpha\beta} = pC_{\alpha\beta} + \eta \, dC_{\alpha\beta}/dt. \tag{7}$$

The Cauchy stress T_{ij} is related to $\tau_{\alpha\beta}$ by the transformation:

$$T_{ij} = x^{\alpha}{}_{,i}\, x^{\beta}{}_{,j}\, \tau_{\alpha\beta}\,, \tag{8}$$

where x^{α} and y_i are the material and spatial coordinates, respectively, and a comma denotes a derivative with respect to y_i. In view of Eqs. (7) and (8)

$$T_{ij} = p\,\delta_{ij} + 2\eta\, d_{ij} \tag{9}$$

since

$$x^{\alpha}{}_{,i}\, x^{\beta}{}_{,j}\, dC_{\alpha\beta}/dt = 2d_{ij}\,, \tag{10}$$

where d_{ij} is the deformation rate tensor. We remark that Eq. (9) is the Navier-Stokes equation for a linear incompressible viscous liquid.

References

1. K.C. VALANIS, *Irreversibility and existence of entropy*, Int. J. Non-Lin. Mech., **6**, 337–360, 1971.
2. K.C. VALANIS, *Partial integrability as the basis of existence of entropy in irreversible systems*, ZAMM, **63**, 73–80, 1983.

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