Proc. IX Intl. Congress on Rheology, Mexico, 1984.

FORTY YEARS OF NON-LINEAR CONTINUUM MECHANICS

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ABSTRACT

An account is given of the author's involvement with the development of non-linear continuum mechanics. The manner in which the formulation of a phenomenological theory for finite elastic deformations of rubber-like materials led naturally to the development of phenomenological theories for the deformation of viscoelastic solids and fluids is described. This in turn led to the development of a general theory for the formulation of non-linear constitutive equations.

KEYWORDS

Finite elasticity; viscoelastic fluids; materials with memory; non-simple materials; constitutive equations.

1. INTRODUCTION

It is almost exactly forty years since I first became interested in non-linear continuum mechanics - in October 1944. I came to the subject with almost complete ignorance of continuum mechanics of any kind. This resulted in a certain amount of re-discovery. On the other hand it meant that I was able to approach the subject without the prejudices of accepted wisdom.

In this talk I shall attempt to review that part of my own involvement in the field which has contributed to the evolution of my understanding of the principles governing the formulation of continuum-mechanical theories. The fact that I so restrict myself must not be taken as a lack of recognition of the importance of the contributions of others, even when they have not had a major impact on my own thinking.

The major objective of any theory in continuum mechanics is the development of a formalism which enables one, at any rate in principle and one hopes in practice, to solve problems of the following type. Given a body, whether solid or fluid, we wish to calculate the deformation or flow which results from the application to it of specified forces - the direct problem - or, conversely, the forces necessary to produce in the body a specified deformation - the inverse problem.

The solution to these problems for elastic materials which undergo infinitesimal deformations and for Newtonian viscous fluids were fully developed in the nineteenth century. In both cases the equations of the theory consist of field equations, which express the validity of Newton's laws of motion for elements of the material, and a constitutive equation, which expresses in an intrinsic fashion the response of the material to applied forces.

If we wish to extend these theories so that they are applicable to other materials, the constitutive equation must be changed. Provided that the deformation of the body can be completely described, as in the classical theories, by the time dependence of the first spatial derivatives of the displacement, the field equations need not be changed. However, the form in which it is most convenient to express them may depend on the class of materials considered and on the type of problem under discussion.

On the other hand, if in order to describe fully the deformation in the body other fields than the displacement gradient field must be specified, then the field equations must also be changed in an appropriate fashion. Most of this paper will be concerned with situations in which this is not the case.

2. NEO-HOOKEAN ELASTICITY

Shortly after I joined, in August 1944, an organization known as the British Rubber Producers' Research Association (BRPRA) which still exists under the name "Malaysian Rubber Producers' Research Association", I embarked on the task of constructing a theory which would play the same role for vulcanized rubber, which may undergo very large deformations, as does classical elasticity theory for metals and other materials in which the elastic deformations are necessarily small, i.e. which would enable one to calculate, at least in principle, the forces necessary to produce in a body specified deformations, and the deformations produced in it by specified applied forces. (I may say that many of the pundits assured me at the time that this was an impossible task. An exception was G.I. Taylor who was very encouraging of my efforts.)

In my initial attempt to construct such a theory I drew on the predictions of the molecular model for vulcanized rubber which had been developed in the preceding few years. In 1942 Guth and James and Flory had obtained, on the basis of a highly idealized model, the tensile force necessary to extend a rod of vulcanized rubber to λ, say, times its initial length, and the shearing force necessary to produce in a block of the rubber a shear of amount K, say. They did this by calculating from the model the change in the Helmholtz free-energy per unit volume when the rubber undergoes such isothermal deformations. In 1944 my colleague at the BRPRA, L. R. G. Treloar, extended their work by calculating the Helmholtz free-energy W associated with isothermal deformation of a unit cube of the rubber into a rectangular block with edge lengths $\lambda_1, \lambda_2, \lambda_3$. (Since rubber is substantially incompressible, we may take, as he did, $\lambda_1\lambda_2\lambda_3 = 1$, without significant error.) Treloar found (see, for example, [1])

$$W = \nu NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3), \tag{2.1}$$

where N is the number of polymeric chain segments per unit volume, T is the absolute temperature, k is Boltzmann's constant, and ν is a constant which depends on the details of the assumed molecular model. In view of the incompressibility of the material, the forces which must be applied to the faces of the block in order to maintain the deformation considered by Treloar are undetermined to the extent of an arbitrary hydrostatic pressure, here denoted p. If these forces are denoted by f_1, f_2, f_3, then

$$f_i = \frac{\partial W}{\partial \lambda_i} - \frac{p}{\lambda_i} \qquad (i = 1,2,3). \tag{2.2}$$

Denoting the corresponding forces, measured per unit deformed area, by $\sigma_i = f_i\lambda_i$, we have

$$\sigma_i = \lambda_i \frac{\partial W}{\partial \lambda_i} - p \qquad (i = 1,2,3). \tag{2.3}$$

From (2.1) and (2.2), or (2.1) and (2.3), it is easy to recover the result of Guth and James and Flory for the tensile force f necessary to extend a rod of unit cross-section to λ times its initial length:

$$f = 2\nu NkT(\lambda - \lambda^{-2}). \tag{2.4}$$

Since a shearing deformation may be considered to be a pure homogeneous deformation (i.e. a deformation of the type considered by Treloar) followed by a rotation, it is also easy to obtain the expression for the shearing force per unit area, σ say, necessary to maintain a simple shear of amount K:

$$\sigma = 2\nu NkTK. \tag{2.5}$$

The shapes of typical experimentally determined f vs. λ and σ vs. K curves show reasonably good agreement with (2.4) and (2.5) over fairly large ranges of values of λ and K. Moreover, the departures which occur at large values of λ and K can be readily understood, at any rate qualitatively, in terms of the mathematical simplifications which were introduced in exploiting the molecular model. Furthermore, measurements of the manner in which f changes with temperature in tensile measurements at fixed values of λ showed good agreement with (2.4). These facts led to a good deal of confidence in the model. However, it will be seen later that this agreement is to some extent illusory.

The deformations considered by Guth and James, by Flory, and by Treloar were all homogeneous deformations. If more general deformations of vulcanized rubbers are to be considered the result of Treloar has to be extended. That it contains sufficient physical information for our purpose follows from a theorem concerning deformations, which is essentially a theorem in matrix algebra - the Polar Decomposition Theorem.

We describe the deformation of a body in the following manner. Let $\mathbf{X}$ be the vector position of a particle of the body in some reference configuration. Let $\mathbf{x}$ be its vector position at time t. Then, if the dependence of $\mathbf{x}$ on $\mathbf{X}$ and t is known the deformation is completely described. (For static deformations, we need consider only the dependence of $\mathbf{x}$ on $\mathbf{X}$.) The Polar Decomposition Theorem tells us that if we look at an infinitesimal volume element of the body each particle in it could be taken from its initial position to its position at time t by subjecting the element to a translation followed by a pure homogeneous deformation and a rigid rotation. Of course the values of the λ's, i.e. the principal extension ratios, have to be appropriately chosen, as do the three perpendicular directions for these, and both will, in general, vary from infinitesimal element to infinitesimal element of the body. The expression $\lambda_1^2 + \lambda_2^2 + \lambda_3^2$ which occurs in Treloar's formula can be expressed in terms of the so-called deformation gradient matrix $\mathbf{g}$ defined by

$$\mathbf{g} = \partial \mathbf{x}/\partial \mathbf{X}. \tag{2.6}$$

Thus

$$\lambda_1^2 + \lambda_2^2 + \lambda_3^2 = \mathrm{tr}\mathbf{g}^{\dagger}\mathbf{g}, \tag{2.7}$$

where the dagger denotes the transpose. This leads to a specific free-energy of deformation (or strain-energy function as we call it in mechanics) of the form

$$W = C(\mathrm{tr}g^{\dagger}g - 3), \tag{2.8}$$

where C is a constant. I called [2] this form for the strain-energy function the neo-Hookean form.

Now it can be shown quite easily that for any dependence of W on g in an incompressible material,

$$W = W(g), \tag{2.9}$$

the Piola-Kirchhoff stress matrix Π (or engineering stress) and the Cauchy stress matrix σ (or true stress) are given by

$$\Pi = \frac{\partial W}{\partial g} - p(g^{-1}) \tag{2.10}$$

and

$$\sigma = \frac{\partial W}{\partial g}g^{\dagger} - p\delta, \tag{2.11}$$

where δ is the unit matrix. p is an arbitrary hydrostatic pressure. Its presence results from the fact, already noted, that the application to an incompressible material of a hydrostatic pressure leaves the deformation unaltered. The physical content of the passage from (2.8) to (2.10) or (2.11) is the following: the work done by the forces exerted on an infinitesimal material element of the body by the surrounding material in an infinitesimal virtual deformation is equal to the resulting change in W. (The contribution of the change in kinetic energy to this balance is of a higher degree in the dimensions of the element and can, accordingly, be omitted in the limiting case as the dimensions of the element tend to zero.)

The difference in the expressions for Π and σ merely reflects the different choices of the area elements used in defining them.

For a compressible material the corresponding expressions are

$$\Pi = \frac{\partial W}{\partial g}, \qquad \sigma = \frac{1}{\det g}\frac{\partial W}{\partial g}g^{\dagger}. \tag{2.12}$$

(Note that detg is the ratio between the volume of a material element in its deformed and undeformed configurations.)

For example, for the strain-energy function (2.8) we obtain, from (2.11),

$$\sigma = 2Cc - p\delta, \tag{2.13}$$

where c, known as the Finger strain matrix, is defined by

$$c = gg^{\dagger}. \tag{2.14}$$

Equation (2.13) is the constitutive equation for the Cauchy stress matrix in a neo-Hookean elastic material.

From equation (2.13) the results previously given for simple extension and for shear were easily recovered. However, two interesting new results emerged.

I found that the Cauchy stress associated with a simple shear of amount K, say, had a shear component 2CK and three unequal normal components acting in mutually perpendicular directions determined by the direction of shear and the normal to the plane of shear. Each of these components was, apart from the arbitrary hydrostatic pressure, proportional to K^2. I then showed [3] that this implied that if we wish to produce in a cylinder of radius a a torsion of amount ψ per unit length, it is not sufficient to exert over its ends tangential tractions in the circumferential direction of amount $2C\psi r$ per unit area, at a radial distance r from the cylinder axis. It is also necessary to exert normal forces of amount

$$-C\psi^2(a^2 - r^2) \tag{2.15}$$

per unit area. This is a thrust which takes its maximum value at $r = 0$ and the value zero at the edge. The arbitrary hydrostatic pressure disappears here because the curved surface of the cylinder is assumed to be free of traction.

The tangential forces have as their resultant a couple M given by

$$M = \pi C\psi a^4 \tag{2.16}$$

and the normal forces have resultant thrust N given by

$$N = -\tfrac{1}{2}\pi C\psi^2 a^4. \tag{2.17}$$

Evidently if the force N is not applied the cylinder will elongate.

If a tube, rather than a cylinder, is subjected to the torsion, we find that if the outer curved surface is force-free tangential and normal force distributions must be applied to the ends, but in addition a thrust P per unit area, given by

$$P = \tfrac{1}{2}C\psi^2(a^2 - b^2) \tag{2.18}$$

must be applied to the inner surface of the tube. In this formula a and b denote the outer and inner radii of the tube. We see that even if the ends of the tube are maintained at a constant separation, the tube will contract in radius unless the thrust P is applied to its inner surface.

After I had obtained these results it was drawn to my attention that the association of normal stresses with shear of an elastic material had been conjectured much earlier, in 1909, by Poynting on the basis of the existence of a radiation pressure when light is propagated in space, which he regarded as a luminiferous aether endowed with elastic properties. He verified this conjecture by torsion experiments on a steel wire and on a rubber rod. Accordingly, effects which arise from this normal stress are called Poynting effects.

3. THE GENERAL PHENOMENOLOGICAL THEORY OF RUBBER-LIKE ELASTICITY

At this point it occured to me that instead of drawing on the conclusions of the admittedly highly-idealized molecular model for vulcanized rubber in order to derive an appropriate strain-energy function, it should be possible to proceed in a much more general manner and one which is more in keeping with the spirit of the classical field theories. I argued [4] that for an elastic

material which is isotropic in its undeformed state, W must depend symmetrically on the three extension ratios $\lambda_1,\lambda_2,\lambda_3$. Since these are positive, it must equally depend symmetrically on $\lambda_1^2,\lambda_2^2,\lambda_3^2$ and accordingly be expressible in terms of the three quantities I_1,I_2,I_3 defined by

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2, \quad I_2 = \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 + \lambda_1^2\lambda_2^2, \quad I_3 = \lambda_1^2\lambda_2^2\lambda_3^2. \tag{3.1}$$

These can, in turn, be expressed in terms of the deformation gradient matrix g by

$$I_1 = \mathrm{tr}C, \quad I_2 = \tfrac{1}{2}[(\mathrm{tr}C)^2 - \mathrm{tr}C^2], \quad I_3 = \det C, \tag{3.2}$$

where C is the Cauchy strain matrix defined by

$$C = g^{\dagger}g. \tag{3.3}$$

We thus have

$$W = W(I_1,I_2,I_3). \tag{3.4}$$

Since, as has already been noted, detg = 1 if the material is incompressible, it follows from $(3.2)_3$ and (3.3) that

$$I_3 = 1 \tag{3.5}$$

and accordingly

$$W = W(I_1,I_2). \tag{3.6}$$

By introducing (3.4) or (3.6) into the appropriate expressions for the Piola-Kirchhoff stress and Cauchy stress matrices, and using the chain rule, we can obtain canonical expressions for them. For example, in the case when the material is compressible we obtain from $(2.12)_2$ the following expression for the Cauchy stress matrix:

$$\sigma = 2I_3^{-\frac{1}{2}}\{(W_1 + I_1W_2)c - W_2c^2 + I_3W_3\delta\}, \tag{3.7}$$

where W_1 and W_2 are given by

$$W_1 = \frac{\partial W}{\partial I_1}, \quad W_2 = \frac{\partial W}{\partial I_2}, \quad W_3 = \frac{\partial W}{\partial I_3}. \tag{3.8}$$

For an incompressible material we obtain from (2.11)

$$\sigma = 2\{(W_1 + I_1W_2)c - W_2c^2\} - p\delta. \tag{3.9}$$

The neo-Hookean material for which W is given by (2.8) is, of course, the special case of (3.6):

$$W = C(I_1 - 3). \tag{3.10}$$

On the basis of the constitutive equation (3.9) it is easy to calculate the edge forces T_1,T_2 required to deform a thin square sheet of vulcanized rubber, which initially has unit edge and thickness h, into a rectangle with edges λ_1,λ_2. These are given by

$$T_1 = 2h(\lambda_1 - \frac{1}{\lambda_1^3\lambda_2})(W_1 + \lambda_2^2 W_2),$$
$$T_2 = 2h(\lambda_2 - \frac{1}{\lambda_2^3\lambda_1})(W_1 + \lambda_1^2 W_2). \qquad (3.11)$$

Of course, so far W remains an unknown function of I_1, I_2, which are given in terms of λ_1, λ_2 by

$$I_1 = \lambda_1^2 + \lambda_2^2 + \frac{1}{\lambda_1^2\lambda_2^2}, \quad I_2 = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \lambda_1^2\lambda_2^2, \qquad (3.12)$$

If T_1 and T_2 are measured for some specified values of λ_1 and λ_2, we can use equations (3.11) to calculate W_1 and W_2 for the values of I_1 and I_2 which, through (3.12), correspond to these specified values. In this way Saunders and I [5] were able to determine experimentally the dependence of W_1 and W_2, and hence of W, on I_1 and I_2 over some range of values of the latter. Unfortunately the values so determined become rather inaccurate for low values of $I_1 - 3$ and $I_2 - 3$, i.e. when the deformation is small. For vulcanized rubbers which show little hysteresis (and consequently satisfy the assumption that they are elastic) we found a dependence of W on I_1 and I_2 of the form

$$W = C(I_1 - 3) + f(I_2 - 3), \qquad (3.13)$$

where C is a constant and f is a monotonically decreasing function of I_2-3 over the range considered.

These results showed a significant departure from the neo-Hookean form for W (i.e. from the predictions of the molecular theory as it then existed). Moreover, it is seen that this departure is associated with the dependence of W on I_2-3. This fact was confirmed by further experiments, involving other types of deformation, which were carried out with Saunders [5] and with Gent [6,7].

The technique which Saunders and I used in the experiments on biaxial deformation of a sheet was essentially the same as that which had been used earlier by Treloar. Since our experiments many attempts have been made to refine this technique in order to obtain values for W_1 and W_2 from equations (3.11) which are accurate for smaller deformations. However, the results obtained by different workers for small deformations do not agree.

Experiments of this type have also been used, notably by Fung and co-workers (see, for example [8]) to obtain expressions for $W(I_1, I_2)$ which characterize various biological tissues that behave substantially elastically.

An important special case of the relations (3.11) is that in which one of the forces T_1 and T_2 is zero. This gives us the result for simple extension of the material. Applied to a rod, or strip, of the material of initial cross-sectional area A, we obtain

$$T = 2A(\lambda - \frac{1}{\lambda^2})(W_1 + \frac{1}{\lambda}W_2), \qquad (3.14)$$

where I_1 and I_2 are given by

$$I_1 = \lambda^2 + \frac{2}{\lambda}, \quad I_2 = \frac{1}{\lambda^2} + 2\lambda \qquad (3.15)$$

and λ is the extension ratio in the direction of extension.

On the basis of the expression (3.9) for the stress, I was able to solve [4,9,10] a number of simple problems in which the deformation is inhomogeneous, without making further assumptions about W beyond those which result in the conclusion, expressed in (3.6), that W is a function of I_1 and I_2. For example, if a cylinder of radius a is subjected to a torsion of amount ψ per unit length and the curved surface of the cylinder is force-free, then the force system which must be applied to its plane ends consists of a distribution of tangential forces in the circumferential direction and a distribution of normal forces. These have as their resultant a couple M and a tensile force N given by

$$M = 4\pi\psi\int_0^a r^3(W_1 + W_2)dr,$$
$$N = -2\pi\psi^2\int_0^a r^3(W_1 + 2W_2)dr, \tag{3.16}$$

where W_1 and W_2 are functions of I_1 and I_2, which are given by

$$I_1 = I_2 = 3 + \psi^2 r^2. \tag{3.17}$$

The problem is an inverse problem and can be solved with this degree of generality because the deformation throughout the cylinder is determined kinematically.

About the same time I solved a number of further problems of this kind. Deformations, such as these, which can be produced by surface forces only and for which explicit expressions for these surface forces can be obtained for arbitrary dependence of W on I_1 and I_2 are known as controllable deformations. Subsequently further controllable deformations were presented by other workers.

In 1940 Mooney [11] had published a paper in which he considered a unit cube of vulcanized rubber to be deformed homogeneously into a rectangular block with edges $\lambda_1,\lambda_2,\lambda_3$. He then assumed, approximately in accord with experimental observation, that when the block is subjected to a shear the shearing force is proportional to the amount of shear. He deduced from this that W must be given by

$$W = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2 - 3), \tag{3.18}$$

where C_1 and C_2 are constants. He also stated that if the shearing force is not proportional to the amount of shear, then W must be expressible in the form

$$W = \sum_{i=1}^{n} [\alpha_{1i}(\lambda_1^{2i} + \lambda_2^{2i} + \lambda_3^{2i} - 3) + \alpha_{2i}(\lambda_1^{-2i} + \lambda_2^{-2i} + \lambda_3^{-2i} - 3)] \tag{3.19}$$

where the α's are constants. This is not, in fact, correct.

With the notation (3.1), the expression (3.18) for W can be rewritten as

$$W = C_1(I_1 - 3) + C_2(I_2 - 3), \tag{3.20}$$

and can then be applied to arbitrary deformations by using the expressions (3.2) for I_1 and I_2. It has become known as the Mooney-Rivlin form for the strain-energy function.

With this form for the strain-energy function, the theory I have outlined has been widely used in the stress analysis of rubber components. In such problems one is faced with the necessity for solving non-linear partial differential equations. It was this fact which, when I originally formulated the theory, led some people to comment that it was quite useless, because only very simple problems could be solved. However, with the advent of high-speed digital computers this criticism, whatever merit it may have had, ceased to be valid, and there now exist packaged computer programs for the solution of such stress analysis problems. For example, the widely used MARC General Purpose Finite Element Program provides for the solution of static, three-dimensional, large deformation problems. The input capability of the program includes not only the Mooney-Rivlin strain-energy function, but also a more general one which is a five term polynomial in I_1 and I_2. The latter is particularly useful when very large strains are involved.

In the MARC program the non-linear partial differential equations are solved by an iterative procedure based essentially on equations, equivalent to those mentioned in the next section, for the calculation of an infinitesimal unknown deformation superposed on a finite known deformation. With similar equations as a basis the program also allows for the analysis of small vibrations of statically-loaded rubber components.

4. APPROXIMATE ELASTICITY THEORIES

Once the form of the strain-energy function - and therefore of the constitutive equation for the stress - is known, whether for an isotropic or an anisotropic material, it is an easy matter to make a wide variety of approximations which are appropriate to various types of problem.

For example, one may suppose that the displacement gradients are small and systematically neglect in the strain-energy function terms of third degree and in the constitutive equation for the stress terms of second degree. One then arrives at the constitutive equation of classical linear elasticity theory. Again, one may retain in the strain-energy function and the stress terms of third and second degree respectively. Higher order theories, valid for increasingly large values of the displacement gradients, may be similarly obtained. I have called such theories incomplete theories. From a physical standpoint they express the fact that the extensions undergone in the deformation by line elements of the body are small and, in addition, the rotations undergone by volume elements are also small. One can also obtain constitutive equations which express the first of these assumptions, while allowing the rotations to be arbitrarily large. I have called such theories complete theories. An example of such a theory is the second-order theory for a compressible isotropic material published by Murnaghan [12] in 1937. The neo-Hookean and Mooney-Rivlin strain-energy functions are appropriate to first and second order complete theories respectively in the incompressible case. In deriving such theories for an incompressible material one has to bear in mind that, as a result of the constant volume condition $\det g = 1$, $\mathrm{tr}(g - \delta)$ is of second order in the displacement gradient matrix $g - \delta$, rather than of first order as might at first sight appear [13].

Another type of approximation which leads to linear boundary-value problems and has wide applicability arises in situations in which there is superposed on a known large deformation an infinitesimal deformation in terms of which the various relations of finite elasticity theory can be linearized. A formal theory for such initial-value problems was published by Green, Shield, and myself in 1950 [14].

Theories of this type have a wide range of applicability. They are particularly useful in discussing bifurcation problems, such as those which arise in connection with the buckling of rods and plates under thrust (see, for example, [15]). They have been used extensively in the last few years in the discussion of the so-called material stability conditions for compressible and incompressible materials (see, for example, [16,17,18,19]). The problem here is to derive conditions on the strain-energy function analogous to the well-known necessary and sufficient restrictions in classical elasticity theory that the shear modulus and Young's modulus be positive. It is made very much more difficult than the corresponding problem in classical elasticity theory due to the fact that most of the physical requirements which are necessary for material stability - such as the requirement that the stored-energy be positive when the body is deformed, or that if we increase the load the deformation increases - coalesce in the case of classical elasticity theory, while they do not in the case of the finite theory.

5. THE MOONEY-RIVLIN PLOT

Apart from its use in stress analysis the Mooney-Rivlin strain-energy function has also had wide use in the characterization of elastomers. The reason for this probably lies in its simplicity and that the constants C_1 and C_2 in it can be readily measured by simple extension experiments. By introducing the expression (3.20) into (3.14) we see that, for the Mooney-Rivlin strain-energy function, the force T vs. extension ratio λ relation for simple extension of a test-piece with initial cross-sectional area A becomes

$$T = 2A(\lambda - \frac{1}{\lambda^2})(C_1 + \frac{1}{\lambda}C_2). \tag{5.1}$$

If $T/[2A(\lambda - \lambda^{-2}]$ is plotted against $1/\lambda$ for a material for which the Mooney-Rivlin strain-energy function is valid, we obtain a straight line. $C_1 + C_2$ is given by its intercept on the line $\lambda=1$ and C_2 by its slope. This type of plot, which has become known as the Mooney-Rivlin plot, appears to have been used for the first time in my paper with Saunders [5]. We found that in practice it takes the form shown in Fig. 1.

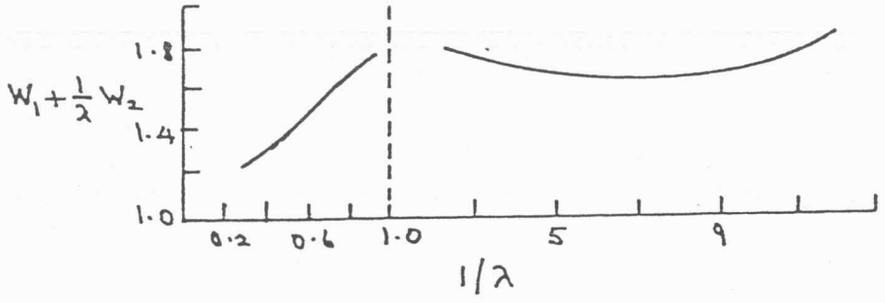

Fig. 1. Typical Mooney-Rivlin plot.

The portion of the curve on the left-hand side of the ordinate corresponds to extension and that on the right-hand side to compression. (The latter portion of the curve was, in fact, obtained from measurements on the equibiaxial extension of a thin sheet, which, since the material is substantially incompressible, is equivalent to compression in the thickness direction.) It is seen that for a substantial range of extensions the linearity required by the Mooney-Rivlin strain-energy function is obtained. However, it was shown in [5] that within experimental error this linearity is also predicted by a strain-energy function of the form (3.13), which we had found from experiments on the biaxial deformation of a thin sheet, with the additional merit that the observed behavior for $\lambda>1$, i.e. for compression, is also predicted and agreement is obtained with experimental results for other types of deformation.

It appears that the form of Mooney-Rivlin plot shown in Fig. 1 is typical. This is evidenced in the experiments of Saunders and myself [20] in which such plots were obtained for various natural rubber vulcanizates covering a wide range of hardnesses and in those of Gumbrell, Mullins and myself [21] in which plots were obtained for various natural and synthetic rubber vulcanizates swollen to various degrees with a variety of organic solvents. In the latter experiments it was found that the apparent values of C_2 obtained from the linear parts of the Mooney-Rivlin plots decreased as the volume fraction of solvent increased becoming approximately zero at high degrees of swelling.

6. ANISOTROPIC ELASTICITY

In 1952-53 I spent about sixteen months at the Naval Research Laboratory in Washington. I was asked to head a small group which consisted of three people - Ericksen, Toupin, and one other who was working on general relativity theory and with whom I had very little interaction. Ericksen had very recently received a Ph.D. degree from Indiana University where his thesis adviser was T. Y. Thomas. However, he had attended a course by Truesdell on non-linear continuum mechanics. Toupin was writing a thesis on a problem in solid-state physics under the direction of M. Lax of Syracuse University.

In the case when an elastic material is isotropic the strain-energy function depends on the Cauchy strain matrix C through the three strain invariants I_1, I_2, I_3, defined in (3.2). When the material is incompressible the dependence on I_3 can be omitted. Ericksen and I considered the case when the elastic material is not isotropic, but rather has fiber symmetry. We found [22] that in this case, with the 3-direction as the fiber direction, the strain-energy must be a function of I_1, I_2, I_3, C_{33} and $C_{31}^2 + C_{23}^2$. If the material is incompressible I_3 can again be omitted. When I moved to Brown University in 1953, I embarked on a broad program of work on the effect of material symmetry in determining the canonical form for non-linear constitutive equations. As part of this program I worked out with G. F. Smith, in explicit terms, the manner in which the dependence of the strain-energy function on the Cauchy strain matrix is restricted by the symmetry appropriate to each of the 32 crystal classes. This work was published [23] in 1956.

Ericksen and I realized that the problem we had solved was essentially the following. Given that W is a function of a second-order symmetric tensor (the Cauchy strain tensor C) and a unit vector (in the fiber direction), how is this function restricted by the consideration that it is invariant with respect to the full orthogonal group. We therefore suggested to Toupin that he develop a continuum-mechanical theory for electrostriction in isotropic materials on the basis of a strain-energy function which depends on C and the electric polarization vector P. His development of this idea, together with

his injection of many other ideas, resulted in an important paper [24] which has been much quoted.
At the time Adkins was writing his thesis with me, mainly on the deformation of elastic membranes [25], we also did some calculations on some simple systems consisting of vulcanized rubber reinforced by inextensible cords [26]. In my paper with Ericksen [22] we discussed in general terms the manner in which kinematic constraints could be introduced into the constitutive equations of elasticity theory. The mechanics of materials with one or more directions of inextensibility has been extensively studied since that time, the main contributors being Adkins, Pipkin, Rogers and Spencer (see, for example, the book by Spencer [21]). Apart from its evident interest in connection with the mechanics of fiber-reinforced materials, it has a number of interesting features from a mathematical point-of-view. Unlike the usual situation in elasticity theory, the governing equations are no longer elliptic, the directions of inextensibility forming characteristics [28]. Accordingly, the passage from a material with a direction of inextensibility to one with a direction of near inextensibility involves singular perturbations.

7. THE NORMAL STRESS EFFECT IN FLUIDS AND THE REINER-RIVLIN THEORY

At the time when I was developing the continuum-mechanical theory for rubber-like materials and had already realized that non-hydrostatic normal stresses, in addition to shearing stresses, are associated with finite shear of a rubber block, we were visited at the BRPRA by Weissenberg. He told us about some experiments he had carried out at Imperial College on flame-thrower fuels.

If a rod is rotated in such a fluid, the fluid is observed to climb up the rod to a considerable extent even at quite low rates of shear. Again, if the fluid is contained between two coaxial cups with flat disc-like bases, and the outer cup is rotated with constant angular velocity while the inner one is held stationary, forces are exerted normally to the plane bases of the cups. These are observed by introducing into the base of the inner cup, at various radial positions, vertical tubes which communicate with the fluid through small holes in the base. On rotating the outer cup, the fluid is seen to rise in the tubes by an amount which depends on the angular velocity and on the radial position of the tube, being a maximum at the center. Similar effects were observed to varying degrees in many liquids. Such effects are often called Weissenberg effects. Their recognition was in fact due to Garner and Nissan. However, Weissenberg was I believe the first person to attribute them to the association of non-hydrostatic normal stresses with steady shear flow.

Shortly afterwards I published a theory of these effects which was based on the evidently valid assumptions that the fluid is substantially incompressible and isotropic. I assumed further that for steady viscometric flows, the stress matrix σ depends on the flow field v only through its spatial gradient matrix ∇v. From these assumptions, together with the consideration that the superposition on the assumed flow field of an arbitrary time-dependent rotation causes the stress to be rotated by the amount of this rotation at the time t, say, at which the stress is measured, I was able to show that σ must be expressible in the form:

$$\sigma = \beta_1 A_1 + \beta_2 A_1^2 - p\delta, \tag{7.1}$$

where A_1 is the usual strain-velocity of classical hydrodynamics defined by

$$A_1 = \tfrac{1}{2}\{\nabla v + (\nabla v)^{\dagger}\} \tag{7.2}$$

and β_1 and β_2 are functions of trA_1^2 and trA_1^3. p is an arbitrary hydrostatic pressure which, as in the elasticity theory discussed earlier, reflects the fact that the material is incompressible. The constitutive equation (7.1) has become known, for reasons which will shortly appear, as the Reiner-Rivlin equation.

When the paper containing these calculations was nearly ready for publication, my attention was drawn to a paper by Reiner [29] which had appeared a few years earlier. In it he proposed a theory for dilatancy - the increase in volume, and consequent apparent drying, of water-logged sand when one walks on it. He developed an equation for the stress which is the analog for a compressible material of (7.1):

$$\sigma = \beta_0\delta + \beta_1 A_1 + \beta_2 A_1^2, \tag{7.3}$$

where the β's are functions of trA_1, trA_1^2, trA_1^3 and ρ, the density of the material. ($trA_1 = 0$ if the material is incompressible so that its volume cannot change.)

In deriving this equation Reiner started with the assumption that σ is a symmetric matrix polynomial in A_1, thus:

$$\sigma = \sum_{i=1}^{n} \beta_i A_1^i. \tag{7.4}$$

where the β's are functions of the density ρ. The Hamilton-Cayley theorem then allows us to express σ in the form (7.3).

8. NORMAL STRESS MEASUREMENTS

Having arrived at the constitutive equation (7.1) it was natural, following the path I had followed in finite elasticity theory, to solve a number of simple flow problems [30,31]: torsional flow between parallel plates (with the neglect of inertial forces), Couette flow, Poiseuille flow.

Early in 1947 I embarked on experiments to measure the normal stress effects. At the time I was spending a year at the Bureau of Standards in Washington. I became involved in a program of research at the Mellon Institute in Pittsburgh, which was funded by the Office of the Rubber Reserve. I set up a torsional flow arrangement of the type mentioned earlier, with the normal stresses measured by means of pressure taps. Such measurements had been carried out earlier by Russell [32], but they were obviously only of qualitative significance I quickly discovered that it was no easy matter to obtain good reproducible results and recognized that a much more carefully engineered apparatus would be necessary to do so. Accordingly, shortly after my return to England in the Fall of 1947, I constructed with Greensmith [33] an apparatus which was, in principle, similar to that which I had left behind at the Mellon Institute, but was capable of yielding much more reproducible results. This involved careful control of the parallelism of the discs between which the torsional flow took place, of the speed of rotation, and of the temperature. It also involved careful choice of the working fluid to ensure its stability and freedom from bubbles. Care was also taken to correct for the (small) effect of inertial forces and to ensure that the pressure taps did not interfere with each other. Their diameter was made small enough so that no appreciable change in the measurements would result by decreasing it further.

Just prior to my return to England from the United States I was offered a permanent appointment at the Mellon Institute. When I did not accept it, they appointed DeWitt (in 1948) and Markowitz (in 1949) to continue the work I had started there. At his request I sent the latter blueprints of the apparatus we were constructing in England. DeWitt and Markowitz carried out an extensive experimental program using a torsional flow configuration, a Couette configuration, and a configuration in which the fluid was contained between a stationary cone and a coaxial rotating disc. (A cone-and-plate arrangement was also used by Roberts [34] in England.) In all of these arrangements pressure taps were used to measure the normal forces.

Starting in 1953, Lodge and his co-workers also carried out, first in England and later at the University of Wisconsin in Madison, an extensive program of normal stress measurements, which has extended over many years to the present time. In attempting to correlate results obtained from different flow configurations they found [35] discrepancies which led them to question whether pressure taps could, even in principle, provide reasonably accurate measurements of the normal stresses. They argued that the mere presence of the pressure tap entry, no matter how small its diameter, introduced a systematic error in the pressure measurements. Calculations by Pipkin and Tanner [36] provided a sound mathematical basis for this insight. However, Lodge has been able to salvage the use of pressure taps as a means of finding the normal stresses associated with shear flows in viscoelastic fluids by applying empirical corrections to the measured pressures. Nevertheless, the difficulties associated with the pressure tap method and the absence of a more convenient alternative remain a great handicap in experimental non-Newtonian fluid mechanics. The development of a simple procedure for making normal stress measurements would be an extremely important contribution to the subject.

9. KINETIC THEORY OF NORMAL STRESS EFFECTS

At the time when the normal stress effects in fluids were discovered, it was. I think generally realized that the effects arose from the fact that the fluids in which they are observed possess elasticity. The prototypical fluid is accordingly a polymer solution. I therefore attempted to obtain an estimate of the magnitude of the effects on the basis of a molecular model for such a solution. The dissolved polymer molecules were modeled as chains of weightless, ideally thin, rigid links at the junctions of which there are massive "beads". The links were assumed to be capable of free rotation relative to their neighbors. This is the "pearl necklace" model which had been previously used by Kramers in 1944 to calculate the intrinsic viscosity of a polymer solution.

When the fluid undergoes an irrotational flow, the distributions of link orientations and of polymer chain end-to-end distances ceases to be isotropic and the tensions in the chains cutting unit areas normal to the principal flow directions result in a non-hydrostatic normal stress.

If the irrotational flow has velocity gradients $\kappa_1, \kappa_2, \kappa_3$ in the principal flow directions, the Reiner-Rivlin equation yields the following expression for the normal components σ_i (i=1,2,3) of the stress:

$$\sigma_i = \beta_1 \kappa_i + \beta_2 \kappa_i^2 - p. \tag{9.1}$$

The shear components of the stress are, of course, zero. For flows which are sufficiently slow so that terms of third degree in the κ's can be neglected, β_1 and β_2 in (9.1) are constants.

In 1949 I obtained [37] expressions for β_1 and β_2 on the basis of a very simple model of the type which I have just described, with the assumption that the solution is sufficiently dilute so that no tension is transmitted from one polymer molecule to another. β_1 and β_2 are then proportional to the number n of polymer molecules per unit volume. I obtained the result

$$\beta_1 = \frac{\zeta L^2 N^2 n}{18}, \quad \beta_2 = \frac{\zeta^2 L^4 N^4 n}{810kT}, \tag{9.2}$$

where N is the (large) number of links per polymer molecule, $-\zeta \mathbf{v}$ is the drag on a bead moving with velocity $\mathbf{v}$ relative to the fluid and L is the length of a link. T is the absolute temperature and k is Boltzmann's constant. From (9.2) we obtain

$$\beta_2 = \frac{2\beta_1^2}{5kTn}. \tag{9.3}$$

From about 1955 onwards Giesekus and from about 1968 Bird and his co-workers have made extensive calculations of various rheological constants for the pearl necklace model and a wide number of variants of it - dumbbells, branched configurations of massive beads connected by rigid links or elastic springs. It is interesting to note that Bird's co-worker Hassager [39] obtained in 1974 an extension of the result (9.1) to the case when N is not necessarily large. His results agree with (9.2) for large N. Their results up to about 1977 are collected in [38]. The methods used by Giesekus and by Bird are substantially different from that which I used and are not limited to irrotational flows.

From the expression for β_1 in (9.2) and the experimentally determined intrinsic viscosity for a dilute polymer solution, I calculated the value of $\zeta L^2 N^2$. This enabled me to obtain a numerical value for β_2, using the value of n appropriate to a solution sufficiently concentrated to exhibit, in experiments, a measurable normal stress effect. The value of β_2 obtained was too low by several orders of magnitude.

As I have already noted, the formulae (9.2) involve the assumption that the dissolved polymer molecules are non-interacting. It can be deduced from the numerical calculation and, indeed, from the concentration of the polymer solution considered and from the molecular weight of the polymer that this assumption is invalid. In order to obtain a more realistic value for β_2 I therefore assumed that the network of interacting polymer molecules could be modeled by fewer non-interacting molecules of greater molecular weight. The measured value of the viscosity (which was, of course, also much greater than that predicted from the intrinsic viscosity with the assumption of non-interacting molecules) was used to calculate an effective number of non-interacting molecules. With this value for n and the measured value of the viscosity $\beta_1/2$, the relation (9.3) yielded measurable values of β_2.

In [37] I also obtained corresponding expressions for β_1 and β_2 when the links are colinear and incapable of rotation relative to their neighbors. These are

$$\beta_1 = \frac{\zeta L^2 N^2 n}{36}, \quad \beta_2 = \frac{\zeta^2 L^4 N^4 n}{2160kT}, \tag{9.4}$$

These calculations were done at a time when I thought, incorrectly, that for viscometric flows the Reiner-Rivlin equation would provide an appropriate basis for calculation. In terms of the second-order theory discussed in Sec. 14 below (see equation (14.4))

$$\beta_1 = \alpha_0, \quad \beta_2 = 2\alpha_1 + \alpha_2. \tag{9.5}$$

10. OLDROYD'S THEORY

IN 1950 Oldroyd published an important paper [40] in which he developed a theory of a more general character than any previously presented.. The ideas which he advanced applied to both viscoelastic solids and fluids. He imagined an infinitely fine three-dimensional rectangular cartesian net to be embedded in the material and to deform with it. As the material is deformed the net becomes curvilinear. The deformation at any instant is characterized by the extension ratios of linear elements of the net and by the angles between them - in the language of tensor analysis by the metric tensor. Oldroyd proposed that the stress is determined by an integro-differential (tensor) equation relating the stress and the history of the metric tensor. Against this general background he proposed to choose particular cases motivated largely by models of the spring-and-dashpot type. He solved the problem of Couette flow in the annular region between two infinite coaxial cylinders on the basis of two different relatively simple choices of the constitutive equations.

A wide variety of flow problems have been solved over the years on the basis of constitutive equations which lie within the framework proposed by Oldroyd, notably by Walters and his collaborators, but also by many others. The approximations which have to be made in order to obtain analytic solutions usually result in their being, in effect, solutions within the framework of the second-order approximation to the Rivlin-Ericksen constitutive equation, which will be discussed later. This has been pointed out by Pipkin [41] and by Walters [42]. In such cases it is altogether simpler and physically clearer to adopt the second-order equation as the basis for solving the problems.

Since constitutive equations of the Oldroyd type are integro-differential - or at least differential - equations for the stress, the existence of solutions to them is not, in general, evident.

Oldroyd pointed out the important conclusion from his theory that the assumption underlying the Reiner-Rivlin constitutive equation, that for viscometric flows the stress matrix is, apart from a hydrostatic pressure, a function of the velocity gradient matrix only, is not generally valid for viscoelastic fluids. It took me some time to appreciate this point.

11. RIVLIN-ERICKSEN THEORY

By this time I was beginning my stay at the Naval Research Laboratory and, with Ericksen, I constructed a theory which, while conceptually similar to the Reiner-Rivlin theory, was not open to Oldroyd's criticism. We took as our starting point the assumption that in a viscoelastic material, not distinguishing for the moment between solids and fluids, the stress matrix depends on the deformation gradient matrix, the velocity gradient matrix, the acceleration gradient matrix, etc.. This assumption was motivated by the heuristic consideration that if the stress depends on the history of the deformation gradient matrix, then, for sufficiently smooth deformations, Taylor's theorem enables us to express it in terms of the instantaneous values of the deformation gradient matrix and its time derivatives.

We introduced the consideration that the superposition on the assumed deformation of a time-dependent rigid rotation rotates the Cauchy stress at time t by the amount of this rotation at time t. (This assumption has become known, quite inappropriately, as the "principle of material indifference".) We also introduced the assumption that the materials with which we were concerned are isotropic. These assumptions led to the conclusion that the stress matrix σ

must depend on the deformation gradient matrix g and its time derivatives through the Finger strain matrix c and the matrices $A_1, A_2, \ldots$ defined by:

$$c = gg^{\dagger}, \quad A_1 = \tfrac{1}{2}[\nabla v + (\nabla v)^{\dagger}], \quad \dot{A}_{n+1} = \dot{A}_n + (\nabla v)A_n + A_n(\nabla v)^{\dagger}, \qquad (11.1)$$

where the dot denotes the material time derivative. The matrices $A_1, A_2, \ldots$ have become known as the Rivlin-Ericksen matrices. The dependence of σ on the matrices $c, A_1, A_2, \ldots$ is, of course, isotropic. In our paper, Ericksen and I gave an explicit representation for σ which expresses this isotropy in the case when σ depends on only two of the kinematic matrices. The corresponding representation in the more general case when an arbitrary number of kinematic matrices is taken was obtained much later by Spencer and myself and will be discussed shortly.

In the case when the material is an incompressible isotropic fluid, we assumed that σ is independent of the deformation gradient matrix g and hence of the Finger strain c. We then obtained

$$\sigma = f(A_1, A_2, \ldots) - p\delta, \qquad (11.2)$$

where f is an isotropic matrix-valued function of its arguments.

Having recognized the inadequacy of the Reiner-Rivlin equation, I naturally re-calculated [44] the forces associated with the viscometric flows on the basis of the constitutive equation (11.2).

12. A COMMENT ON TRUESDELL'S INFLUENCE

In 1952 there appeared a long article by Truesdell [45] which reviewed the progress made up to that time and placed it in the perspective of earlier work, much of which was of nineteenth century vintage, but little known. In connection with this project I had supplied Truesdell with typescripts of some of my papers which were pending publication. In the article Truesdell drew attention to the fact that the constitutive equation (3.7) had, in fact, already been derived in a paper by Finger, published in 1894 and since forgotten.

Truesdell's 1952 paper and his subsequent mammoth articles with Toupin and Noll in the Handbuch der Physik [46,47] have been very valuable in collecting together earlier work and earlier ideas, much of which would have otherwise been lost. However, his 1965 article with Noll - "The Non-Linear Field Theories of Mechanics" - and his voluminous later writings, impressive and admirable though they be in many respects, are seriously marred by his evident contempt for physical reasoning and insight and by a tendency to present the work of his protegés as paradigms, without regard to its originality or its physical or mathematical soundness.

In his writings Truesdell evidences a strong taste for the dramatic and so there has been created a fantasy world in which various savants produce a stream of principles, fundamental theorems, capital results, and work of unusual depth. No matter that, on examination and stripped of the, often irrelevant, mathematical verbiage with which they are surrounded, they frequently turn out to be known results in disguise, or trivial, or physically unacceptable, or mathematically unsound, or some combination of these. Nonetheless, they have been widely and uncritically reproduced in the extensive

secondary literature and have provided the starting point for many, correspondingly flawed, theses and papers.

13. MATERIALS WITH MEMORY

The next stage in the development of my ideas came in a paper written in collaboration with A. E. Green [48] and published in 1957. In it we made a different constitutive assumption from that on which the Rivlin-Ericksen theory was based. We assumed that the stress σ at time t depends on the history of the deformation gradient matrix for all times up to and including t, i.e. that σ is a functional of $g(\tau)$:

$$\sigma = \Phi\{g(\tau)\} \qquad -\infty < \tau \leq t. \tag{13.1}$$

We assumed that σ is a continuous functional of its argument function in the sense of the supremum norm; i.e. if σ_1 and σ_2 are the stress matrices corresponding to two histories $g_1(\tau)$ and $g_2(\tau)$, then $\mathrm{tr}(\sigma_1 - \sigma_2)^2 \to 0$ as $\sup\{\mathrm{tr}[g_1(\tau) - g_2(\tau)][g_1^\dagger - g_2^\dagger(\tau)]\} \to 0$. It is not generally realized that this continuity requirement is not, from a physical standpoint, an assumption. If it were not satisfied it would not be possible to perform any meaningful experiment on the material.

We used the "principle of material indifference" to show that σ must be expressible in the form

$$\sigma = g(t)\Phi\{C(\tau)\}g^\dagger(\tau) \qquad -\infty < \tau \leq t, \tag{13.2}$$

where $C(\tau)$ is the Cauchy strain at time τ defined by

$$C(\tau) = g^\dagger(\tau)g(\tau). \tag{13.3}$$

In deriving this result we assumed that in (13.1) the functional dependence is polynomial, but it is a trivial matter to remove this limitation. In later papers we extended this result to the case when σ is assumed to depend not only on the history $g(\tau)$, but also on the instantaneous values at time t of the deformation gradient matrix and its time derivatives. The motivation for this was to generate a theory in which the dependence of σ on past history is smooth while allowing for instantaneous elastic response, instantaneous viscous response, and so on.

In the case when the material is incompressible, the constitutive assumption (13.1) is replaced by

$$\sigma = \Phi\{g(\tau)\} - p\delta, \tag{13.4}$$

where p is an arbitrary hydrostatic pressure, and equation (13.2) is replaced by

$$\sigma = g(t)\Phi\{C(\tau)\}g^\dagger(t) - p\delta \qquad -\infty < \tau \leq t. \tag{13.5}$$

Some eighteen months after the publication of my paper with Green, Noll [49] published a paper in which, with proper acknowledgement, he re-derived equations (13.2) and (13.5) by a different procedure from ours, which, while apparently more elegant, is open to certain objections.

Noll also sought to make a clear distinction between solids and fluids in terms of an invariance condition. He called materials for which the constitutive assumption (13.1) is valid simple materials. He defined a simple material as a material for which the matrix functional Φ in (13.1) or (13.4) satisfies the relation

$$\Phi\{g(\tau)\} = \Phi\{g(\tau)\mathbf{U}\} \tag{13.6}$$

for all unimodular $\mathbf{U}$, i.e. for all matrices $\mathbf{U}$ for which $\det\mathbf{U} = 1$. It can, however, be shown that this assumption, and the conclusions he draws from it, are unacceptable on both mathematical and physical grounds.

In our 1957 paper, Green and I showed that the constitutive functional Φ may, in principle, be approximated by a series of multiple integrals. Apart from the first term which has multiplicity zero, i.e. is a function of $C(t)$, a typical term in the series is

$$\int_{-\infty}^{t}\cdots\int_{-\infty}^{t} f_{ijp_1q_1\cdots p_nq_n}(t,\tau_1,\ldots,\tau_n)C_{p_1q_1}(\tau_1)\ldots C_{p_nq_n}(\tau_n)d\tau_1\ldots d\tau_n. \tag{13.7}$$

Corresponding representations were given in later papers for the cases when the constitutive assumption allows for instantaneous elastic response, instantaneous viscous response, and so on.

With the definition

$$E(\tau) = C(\tau) - \delta, \tag{13.8}$$

we may rewrite the series of multiple integrals as a series in which a typical term has the form

$$\int_{-\infty}^{t}\cdots\int_{-\infty}^{t} f_{ijp_1q_1\cdots p_nq_n}(t,\tau_1,\ldots,\tau_n)E_{p_1q_1}(\tau_1)\ldots E_{p_nq_n}(\tau_n)d\tau_1\ldots d\tau_n. \tag{13.9}$$

Since $E(\tau) = 0$ when the material is undeformed, this representation has the merit that for small deformations the successive terms are of successively higher order of smallness in $E(\tau)$. Of course, if a polynomial assumption is made initially, i.e. we assume that Φ is a polynomial functional of $C(\tau)$, or equivalently of $E(\tau)$, then its expression as series of multiple integrals is exact.

It may be remarked here that the assumption that Φ is n times Frechet differentiable is by definition nothing more than a statement that it can be approximated by a polynomial functional of $E(\tau)$ with an error which is of order n in $E(\tau)$.

Hereditary materials are materials for which the result of an experiment is independent of the actual time (i.e. hour, or year) at which the experiment is carries out. This is, of course, the situation in which we are usually interested in rheology. In this case the multiple integral (13.9) takes the form

$$\int_{-\infty}^{t}\cdots\int_{-\infty}^{t} f_{ijp_1q_1\cdots p_nq_n}(t-\tau_1,\ldots,t-\tau_n)E_{p_1q_1}(\tau_1)\ldots E_{p_nq_n}(\tau_n)d\tau_1\ldots d\tau_n. \tag{13.10}$$

In [48] we also established the relation between the functional constitutive equation of the form (13.2) and the Rivlin-Ericksen constitutive equation (11.2). This was done by expanding $C(\tau)$ as a Taylor series about the time t at which the stress is measured, thus:

$$C(\tau) = \sum_{\alpha=0}^{\mu} \frac{1}{\alpha!} \frac{d^{\alpha}C(\tau)}{d\tau^{\alpha}}\bigg|_{\tau=t} (\tau - t)^{\alpha} + R_{\mu}, \tag{13.11}$$

where the remainder R_{μ} is $O(\tau - t)^{\mu+1}$, and noting that

$$\frac{d^{\alpha}C(\tau)}{d\tau^{\alpha}} = \tfrac{1}{2}[g^{\dagger}(\tau)A_{\alpha}(\tau)g(\tau)]. \tag{13.12}$$

Of course the passage from the functional constitutive equation (13.2) or (13.5) to the Rivlin-Ericksen constitutive equation is only valid for the class of deformations which is sufficiently smooth so that the expansion (13.11) is valid.

Although Green and I did not say this in our paper, we could render the multiple integral representation appropriate to an incompressible fluid by taking as our reference configuration in (13.10) the configuration at time t and insisting that the kernels do not introduce any other time than the time t in a preferred manner. Such a procedure would have paralleled that which Ericksen and I adopted in our 1955 paper [43] and would have been in accord with a distinction between a solid and a fluid proposed by Oldroyd [40] in 1950. (However, it is easy to show, by example, that there exist constitutive equations which clearly describe fluid-like behavior but do involve a preferred configuration other than that at time t. Accordingly, the proposed procedure does not define all incompressible isotropic fluids, but merely an interesting class of fluids.) A typical term in the representation for the stress σ at time t as the sum of a series of multiple integrals would then take the form, in the hereditary case,

$$\int_{-\infty}^{t} \cdots \int_{-\infty}^{t} f_{ijp_1q_1\cdots p_nq_n}(t-\tau_1,\ldots,t-\tau_n)E_{p_1q_1}(\tau_1)\cdots E_{p_nq_n}(\tau_n)d\tau_1\cdots d\tau_n, \tag{13.13}$$

where

$$E_t(\tau) = ||E^{(t)}_{pq}(\tau)|| = C_t(\tau) - \delta = g^{\dagger}_t(\tau)g_t(\tau) - \delta \tag{13.14}$$

and $g_t(\tau)$ is the history of the deformation gradient matrix referred to the configuration at time t, rather than to a fixed reference configuration. However, a better configuration which is nearly, but not quite, equivalent would have as its typical term

$$\int_{-\infty}^{t} \cdots \int_{-\infty}^{t} f_{ijp_1q_1\cdots p_nq_n}(t-\tau_1,\ldots,t-\tau_n)\dot{E}^{(t)}_{p_1q_1}(\tau_1)\cdots\dot{E}^{(t)}_{p_nq_n}(\tau_n)d\tau_1\cdots d\tau_n, \tag{13.15}$$

where the dot denotes differentiation with respect to τ.

Of course, if the configuration at time t is taken as the reference configuration, then, since $g_t(t) = \delta$, the expression (13.5) for the stress becomes

$$\sigma = \Phi[C_t(\tau)] - p\delta. \tag{13.16}$$

Also it follows from (13.12) that

$$\dot{E}_t(\tau) = \dot{C}_t(\tau) = \tfrac{1}{2}[g^{\dagger}_t(\tau)A_1(\tau)g_t(\tau)]. \tag{13.17}$$

Usually one would like the kernels in the multiple integral representations, whether for a solid or a fluid, to be smooth decaying functions of the lapsed time, the decay expressing the fading memory of the materials considered.

A virtually endless number of modifications of the integral representations presented can be easily developed to express particular features of the material behavior. An early example was given by Green, Spencer, and myself [50,51] in which we introduced explicitly the dependence of the stress at time t on the instantaneous value of the deformation gradient matrix and its time derivatives at time t. This allows us to maintain the smoothness of the dependence of the kernels on time, while allowing the material to have instantaneous elasticity or instantaneous viscosity. It should be noted that even if the material does not possess instantaneous elasticity, in the expression (13.2) or (13.5) for the stress the functional Φ must depend on the instantaneous value at time t of $C(\tau)$, and hence of $g(\tau)$, in order to properly account for the effect of a superposed rigid rotation on the stress σ.

In each of the multiple integral representations, the restrictions which result from material symmetry can be introduced by using the relevant result of the general theory discussed in Secs. 15 and 16 below.

14. CLASSES OF DEFORMATIONS AND APPROXIMATE THEORIES

Just as in finite elasticity theory we can, from the rather general results so far discussed, write down more tractable constitutive equations which reflect special assumptions regarding the deformation or flow. These are of two kinds: those which reflect its character [52] and those which reflect a limitation on its magnitude. It may, of course, be useful in certain situations to make both types of specialization simultaneously.

As examples of the first kind I mention the restriction of the deformation to two dimensions - in the case of solids to plane strain or plane stress and in the case of fluids to two-dimensional flow.

Again in the case of solids we may consider the restriction of the class of deformations to stress relaxation experiments, i.e. experiments in which the body is deformed at some time, $t = 0$ say, and then held in this state of deformation. I showed that in this case, with the assumption that the body is initially isotropic and incompressible, the constitutive equation for the stress σ at times $t > 0$ takes the form

$$\sigma = \alpha_0 c + \alpha_1 c^2 - p\delta, \tag{14.1}$$

where c is the Finger strain defined in (2.14) and the α's depend on $\mathrm{tr}c$, $\mathrm{tr}c^2$, and t. We note the similarity to the constitutive equation (3.9) for the stress in an incompressible isotropic elastic material.

I used the constitutive equation (14.1), with the additional assumption that the deformations are small, but the behavior of the material is nevertheless non-linear, as the basis for the interpretation of a series of experiments, carried out in collaboration with Bergen and Messersmith at the Armstrong Cork Research Laboratories, on stress relaxation in simultaneously extended and twisted tubes of filled and unfilled PVC - materials of the type used in flooring.

There are a number of approximations to the Rivlin-Ericksen and Green-Rivlin constitutive equations which are particularly useful.

For example, Langlois and Rivlin [54] considered constitutive equations for a non-Newtonian fluid of the Rivlin-Ericksen type in which the non-Newtonian terms are small. Solutions to a boundary-value problem can then be obtained

as a perturbation on the solution to the problem when the fluid is Newtonian. The first solutions to be obtained for flow problems which are not of the inverse of semi-inverse type were obtained in this manner in [54].

Another type of approximation to the Rivlin-Ericksen equations for a non-Newtonian fluid involves the case when the dependence of the stress on the Rivlin-Ericksen tensors is polynomial and assumes that the flow is slow in the following sense. We consider a velocity field $\mathbf{v}$ given by

$$\mathbf{v} = \mathbf{v}(\mathbf{x}, t/\varepsilon), \tag{14.2}$$

where ε is a constant. It is evident from the definition of the Rivlin-Ericksen tensors in (11.1) that

$$\mathbf{A}_n = O(\varepsilon^n). \tag{14.3}$$

It then becomes possible to set up a hierarchy of approximations to the polynomial Rivlin-Ericksen constitutive equations valid for smaller and smaller values of ε. The first-order equation is then that for an incompressible Newtonian fluid. The second-order equation is

$$\boldsymbol{\sigma} = \alpha_0 \mathbf{A}_1 + \alpha_1 \mathbf{A}_2 + \alpha_2 \mathbf{A}_1^2 - p\boldsymbol{\delta}, \tag{14.4}$$

where the α's are constants. Higher order constitutive equations can be easily written down by using the results discussed in Secs. 15 and 16 for the canonical representation of a symmetric second-order tensor polynomial in an arbitrary number of symmetric second-order tensors. These approximations which are called retardation approximations were first suggested by Coleman and Noll [55] and have been much used. I emphasize the fact that they are merely truncations of the polynomial Rivlin-Ericksen constitutive equation, since this fact is obscured by Coleman and Noll.

In the case of steady flows, the time derivatives $\partial \mathbf{A}_n/\partial t$ in the defining expressions (11.1) for the Rivlin-Ericksen tensors are zero. Accordingly, if we replace $\mathbf{v}$ by $\varepsilon\mathbf{v}$, where ε is a small constant, in the expressions for $\mathbf{A}_n$ we see that (14.3) is again valid [56]. By retaining in the Rivlin-Ericksen relations terms of first, second, etc. degrees in ε we again obtain a hierarchy of approximations, valid for faster and faster flows, which are formally similar to those given by the retardation approximation. If the same procedure is used in the case when the flow is not steady, the first approximation, obtained by neglecting terms of higher degree than the first in ε, yields a constitutive equation for a linear viscoelastic fluid.

It is evident that analogous approximations may be introduced into the representations for the stress in a non-Newtonian fluid as the sum of a series of multiple integrals of the form (13.5).

Approximations may also be made to the Rivlin-Ericksen and Green-Rivlin constitutive equations for a solid, to express the assumption that the deformation is small in some sense, or that the rate of deformation is small in some sense.

For viscoelastic solids and non-Newtonian fluids we can also obtain constitutive equations which parallel the constitutive equations for initial stress problems in finite elasticity, by considering a small deformation or slow flow to be superposed on a basic deformation or flow and linearizing in the superposed field. This can be done in a variety of ways (see, for example [57,58]). Lockett and I used such a procedure to calculate the effect of

small non-Newtonian terms on the critical Reynolds number and cell aspect ratio of Taylor cells in Couette flow [59,60].

In view of the great variety of approximations which can be written down under various assumptions regarding the deformation or flow, and the fact that the procedures to be adopted in making such approximations are now well understood, it is, I feel, preferable that they be written down in connection with the solution of particular problems or groups of problems. This would avoid burdening the literature with a plethora of unattached constitutive equations.

15. THE GENERAL THEORY OF CONSTITUTIVE EQUATIONS

Contemporaneously with the development of the Green-Rivlin theory, I embarked on the problem of constructing a general theory for the formulation of constitutive equations, particularly in relation to the manner in which the restrictions due to material symmetry could be given explicit expression. This development commenced late in 1953, immediately after Ericksen and I had written our joint paper, and involved the collaboration of Spencer, G. F. Smith, and Pipkin. It occupied my attention to a varying extent until about 1965 (see, for example, the review articles by Spencer [61] and Rivlin [62]).

Suppose that in some phenomenological theory, a tensor $\mathbf{T}$ depends on n tensors $\mathbf{V}_1,\ldots,\mathbf{V}_n$. These tensors may, for the moment, be tensors of any order; a vector is regarded as a tensor of order unity and a scalar as a tensor of order zero. (In the Rivlin-Ericksen theory all of the tensors are symmetric second-order tensors.) Any symmetry which the material may have may be described by a group of transformations. For an isotropic material this is the full orthogonal group (i.e. the group of rotations and reflections) or the proper orthogonal group (i.e. the group of reflections) depending on whether the material does or does not have a center of symmetry. Again, for a crystal the appropriate group is one or other of the 32 finite sub-groups of the full orthogonal group.

For economy of notation, let us now denote by $\mathbf{T},\mathbf{V}_1,\ldots,\mathbf{V}_n$ the sets of components of the tensors in some rectangular cartesian reference system. Let $\mathbf{S}$ be a generic transformation of the symmetry group and let $\bar{\mathbf{T}},\bar{\mathbf{V}}_1,\ldots,\bar{\mathbf{V}}_n$ be the sets of components into which $\mathbf{T},\mathbf{V}_1,\ldots,\mathbf{V}_n$ are transformed by $\mathbf{S}$. Then material symmetry requires that

$$\bar{\mathbf{T}}(\bar{\mathbf{V}}_1,\ldots,\bar{\mathbf{V}}_n) = \mathbf{T}(\mathbf{V}_1,\ldots,\mathbf{V}_n) \tag{15.1}$$

for all choices of $\mathbf{S}$. Our task is to make explicit this implicit restriction on the manner in which $\mathbf{T}$ can depend on $\mathbf{V}_1,\ldots,\mathbf{V}_n$. Results for some simple cases have already been given.

In the case of finite elasticity, we have already seen in Sec. 3 how isotropy restricts the dependence of a scalar W on the second-order symmetric tensor C (the Cauchy strain), and in Sec. 6 we have seen the corresponding restriction for fiber symmetry. Again, in (7.3), we have seen how isotropy restricts the dependence of a second-order symmetric tensor (the Cauchy stress) on a single second-order symmetric tensor (the strain-velocity).

Two different problems are posed by a relation of the form (15.1) accordingly as we assume that $\mathbf{T}$ is a single-valued or a polynomial function of the argument tensors. Most of the work makes the assumption of polynomial dependence.

It can be easily seen from heuristic reasoning that the canonical representations for $\mathbf{T}$ so obtained will also provide representations in the case of single-valued function dependence. A formal proof of this was given by Pipkin and Wineman [63] in 1964.

For example, in the representation (7.3) for a second-order symmetric tensor function σ of a single second-order symmetric tensor $\mathbf{A}_1$, the α's are polynomial or single-valued functions of $\mathrm{tr}\mathbf{A}_1$, $\mathrm{tr}\mathbf{A}_1^2$, $\mathrm{tr}\mathbf{A}_1^3$ accordingly as the initially assumed dependence of σ on $\mathbf{A}_1$ is of the polynomial or single-valued function type. In some cases, although not in this one, it may be possible, when the dependence is of the function type, to omit without loss of generality some of the terms in the canonical expression which cannot be so omitted in the polynomial formulation. Such a case is that discussed in 1955 by Ericksen and myself [43] in which a canonical representation was given for an isotropic second-order symmetric single-valued tensor function of two second-order symmetric tensors. The corresponding result for polynomial dependence which I gave in [64] includes additional terms.

The canonical form which is obtained for $\mathbf{T}$ as a result of the relation (15.1) depends, of course, on the orders of the tensors $\mathbf{T},\mathbf{V}_1,\ldots,\mathbf{V}_n$ and on the symmetry of the group for which the relation (15.1) is valid. If $\mathbf{T}$ is a scalar we shall denote it by T to emphasize the fact. If T is a polynomial in the argument tensors, it may be expressed as a polynomial in a finite number of scalar polynomials, each of which is also invariant with respect to the symmetry group. Such a set of polynomials is called an integrity basis and if none of its elements is expressible as a polynomial in the remaining ones, it is called an irreducible integrity basis. As we have already noted, any invariant scalar function may be expressed as a function of the elements of the irreducible integrity basis. We may express this fact by saying that an integrity basis is also a function basis. However, while none of the elements of an irreducible integrity basis is expressible as a polynomial in the remaining ones, it may be expressible as a function of them, i.e. an irreducible integrity basis is not necessarily an irreducible function basis.

I showed that even if $\mathbf{T}$ in the relation (15.1) is not a scalar, the problem of finding in explicit form the restrictions on the way in which it depends on the argument tensors can be reduced to the problem of finding an integrity basis for the argument tensors and an additional arbitrary tensor having the same properties, i.e. the same order and the same symmetry, as $\mathbf{T}$. For example, suppose $\mathbf{T}$ and $\mathbf{V}_1,\ldots,\mathbf{V}_n$ are all second-order tensors. Let $\boldsymbol{\phi}$ be an arbitrary second-order tensor. Then from (15.1) we obtain the scalar equation

$$\mathrm{tr}\bar{\boldsymbol{\phi}}\bar{\mathbf{T}}(\bar{\mathbf{V}}_1,\ldots,\bar{\mathbf{V}}_n) = \mathrm{tr}\boldsymbol{\phi}\mathbf{T}(\mathbf{V}_1,\ldots,\mathbf{V}_n) = \Psi, \text{ say,} \tag{15.2}$$

where $\bar{\boldsymbol{\phi}},\bar{\mathbf{T}},\bar{\mathbf{V}}_1,\ldots,\bar{\mathbf{V}}_n$ are the matrices into which $\boldsymbol{\phi},\mathbf{T},\mathbf{V}_1,\ldots,\mathbf{V}_n$ are transformed by a generic transformation $\mathbf{S}$ of the material symmetry group. This relation says that Ψ is a scalar invariant function of $\boldsymbol{\phi},\mathbf{V}_1,\ldots,\mathbf{V}_n$, linear in $\boldsymbol{\phi}$. Accordingly, if $K_1,\ldots,K_\mu$ are the elements of an irreducible integrity basis for $\boldsymbol{\phi},\mathbf{V}_1,\ldots,\mathbf{V}_n$ which are linear in $\boldsymbol{\phi}$ and $I_1,\ldots,I_\nu$ are the elements of an irreducible integrity basis for $\mathbf{V}_1,\ldots,\mathbf{V}_n$, then Ψ must be expressible in the form

$$\Psi = \sum_{\alpha=1}^{\mu} A_\alpha K_\alpha \tag{15.3}$$

and therefore

$$\mathbf{T} = \frac{\partial \Psi}{\partial \boldsymbol{\phi}} = \sum_{\alpha=1}^{\mu} A_\alpha \frac{\partial K_\alpha}{\partial \boldsymbol{\phi}} \tag{15.4}$$

In (15.3) and (15.4) the A's are functions of $I_1,\ldots I_\nu$. They are polynomial functions if the initially assumed dependence of $\mathbf{T}$ on $\mathbf{V}_1,\ldots,\mathbf{V}_n$ is polynomial.

The problem of determining the canonical form for a tensor function of any number of tensors is thus reduced to the problem of determining an integrity basis for an appropriately augmented set of tensors. It might, at first sight, be thought that the difficulty of doing this would increase as the number of tensors increases. However, it follows from a theorem in the theory of invariants, known as Peano's theorem, which is discussed in the next section, that this is not the case. As an outcome of our program, tables of typical invariants exist for integrity bases of arbitrary numbers of vectors, for arbitrary numbers of second-order tensors, and for arbitrary numbers of second-order tensors and vectors, appropriate to centrosymmetric or non-centrosymmetric isotropic materials, materials with fiber symmetry, and for each of the crystal classes (see, for example, the review article by Spencer [61]).

16. PEANO'S THEOREM AND CONSTITUTIVE EQUATIONS OF THE FUNCTIONAL TYPE

It follows from Peano's theorem that when the tensors are all of the same kind, we can obtain the integrity basis for an arbitrary large number, N say, from that for a specific number, M say, by substituting in the latter all combinations of the N tensors taken M at time. The number M, which is provided by Peano's theorem, depends on the order and symmetry of the tensors and on the symmetry group involved.

For example, an irreducible integrity basis for N vectors, $\mathbf{V}_1,\ldots,\mathbf{V}_n$ say, with respect to the full orthogonal group, is obtained from

$$\mathbf{U}.\mathbf{U},\ \mathbf{U}.\mathbf{V} \tag{16.1}$$

by substituting each of the vectors $\mathbf{V}_1,\ldots,\mathbf{V}_n$, in turn, in $\mathbf{U}.\mathbf{U}$ and each selection of two vectors from the set in $\mathbf{U}.\mathbf{V}$. The list (16.1) is called a table of typical invariants.

If $\mathbf{V}_1,\ldots,\mathbf{V}_n$ are symmetric second-order tensors and the symmetry group is the full orthogonal group, then the table of typical invariants is much more extensive and consists of traces of products of the V's. None of the terms involves more than six of the tensors, nor is of total degree greater than six in them.

These examples apply to three-dimensional tensors. For two-dimensional vectors the table of typical invariants remains unchanged, i.e. it is that given in (16.1). However, for two-dimensional symmetric second-order tensors a much simpler result than that for three-dimensional tensors is obtained.

Somewhat similar considerations apply to integrity bases for sets of tensors of two or more kinds where the number of tensors of each kind is large, e.g. N_1 symmetric second-order tensors and N_2 vectors, where N_1 and N_2 are large. It is still possible to construct a table of typical invariants involving a

limited number of these, from which the desired integrity basis can be obtained by appropriate substitutions.

In many of the cases the table of typical invariants consists of many terms and appears rather complicated. Where this is the case it is doubtful that the integrity basis will find much use in its entirety in physical or engineering applications. It may, however, be treated as a reference table, from which desired parts can be read off. For example, although the table of typical invariants for an arbitrary number of symmetric second-order tensors, with respect to the proper or full orthogonal group, involves six tensors, it contains the integrity bases for one, two, three, etc. tensors.

The tables of typical invariants can be used [65,66] to write the multiple integral representations for constitutive equations of the functional type in canonical forms which express the material symmetry. Wineman and Pipkin [67] have proven a theorem which enables us to obtain canonical forms for functional constitutive equations without first expressing them in multiple integral form.

17. THEORIES OF THE COSSERAT TYPE

I have already mentioned in Sec. 6 Toupin's theory of the elastic dielectric published in 1956. This differs from any of the other theories I have so far discussed in that the field equations have to be modified. This stems from the fact that in Toupin's theory the independent variables in the constitutive equations are not only the first spatial derivatives of the displacement field, but additionally the electric polarization field.

Probably the earliest theory of this type was that published by the brothers E. and F. Cosserat in 1907, in which it was supposed that there is associated with each particle of the body a rigid orthonormal triad of unit vectors (called directors) which move with the particle. This imbues each particle of the body with an orientation in space which can be changed independently of its position. However, the Cosserats' work stimulated little interest until recently. Physicists have, of course, had a continuing interest in systems which lie within the scope of variations on the Cosserat theme, but they have generally tended to discuss them on an ad hoc basis, rather than as derivations from a general continuum theory. It is only since Toupin's 1956 paper that applied mathematicians and others interested in continuum mechanics have displayed an interest in theories of the Cosserat type.

However, since Toupin's paper, there has been a veritable efflorescence of such theories. Apart from Toupin's own development the earliest of these, and one of particular significance, is Ericksen's [68,69] theory of nematic liquid crystals, published in 1960 and 1961 and significantly extended by Leslie. In this theory the independent constitutive variables are taken to be the velocity gradients and a single director of variable length defining the crystallite orientations and lengths.

A great number of theories of the Cosserat type have been formulated which have as their objective to include within a continuum framework some description of the microstructure of the material.

For example, in an isotropic polycrystalline material one could, in principle, use the classical elasticity theory for anisotropic media to determine the displacement field within each crystallite, which results from the application to a body of the material of specified applied forces. This would require a

detailed description of the orientations, shapes, and sizes of the crystallites within the body. One would then have to solve a boundary-value problem in which account is taken of the boundary conditions at all the interfaces between adjacent crystallites. This would, however, be prohibitively difficult.

An alternative approach, which has been attempted by a number of people, is to supplement the usual displacement field, which may be interpreted physically as the average displacement in a domain which contains many crystallites but is small compared with the dimensions of the body and with the scale on which the average displacement field varies, by further vector or tensor fields which together describe in some approximation the departure of the displacement field in the domain from the average displacement. To each of these additional fields there correspond conjugate forces and conjugate stress fields. A complete theory of this type involves equations of motion and boundary conditions, as well as constitutive equations, for all of the stress fields involved. A systematic procedure for obtaining these additional equations of motion and boundary conditions was given by Green and myself [70] in 1964.

18. SOME COMMENTS ON CONTINUUM THERMODYNAMICS

In the past twenty years a great deal of attention has been devoted to thermomechanical continuum theories based on the application by Coleman [71] of the Clausius-Duhem inequality to materials with memory. While extravagant claims are made for the success of the theory, it appears on examination that the results obtained are either incorrect or are based on the use of the Clausius-Duhem inequality in the degenerate case when the thermodynamic process involved is reversible, this fact being disguised by a morass of definitions and mathematics which is irrelevant to the result.

The unsatisfactory nature of the theory can be easily demonstrated. The Clausius-Duhem inequality states that, for a thermomechanical process,

$$\frac{dS}{dt} \geq \frac{Q}{T}, \tag{18.1}$$

where S is the entropy of the system considered, Q is the rate of heat supply and T is the absolute temperature. In Coleman's theory S is a functional of the history of the deformation gradient matrix and of the temperature. However, no prescription is given for determining this functional by thought experiments or otherwise. Indeed, we are told [72] "temperature and entropy join mass place and time as primitive undefined variables ...". One enquires in vain for the location of the standard of entropy and for a procedure by which the entropy of an arbitrary system can be compared with it.

An even more serious difficulty, if this be possible, has been pointed out by Meixner, who showed by concrete example that the assumption of an entropy function or functional, defined at each instant of an irreversible process, leads within the framework of phenomenological theory to a reductio ad absurdum.

Of course, for reversible processes the equality sign applies in (18.1) and the Clausius-Duhem inequality is equivalent, as has been recognized for a long time, to the Clausius integral expressing the entropy change in passing reversibly from one equilibrium state to another.

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