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## Thermo-Mechanics of Rubberlike Materials

P. Chadwick

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## THERMO-MECHANICS OF RUBBERLIKE MATERIALS

BY P. CHADWICK

*School of Mathematics and Physics, University of East Anglia, Norwich**(Communicated by R. Hill, F.R.S. – Received 6 August 1973 – Revised 24 October 1973)*

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A theoretical study is made in this paper of the formulation of constitutive equations describing the thermo-mechanical response of solid polymers in the temperature range in which they exhibit rubberlike behaviour. An expression for the Helmholtz free energy of such a material is first constructed on the basis of two assumptions which are motivated by physical arguments concerning the relation of the molecular structure of a cross-linked polymer to its bulk response. The constitutive equations for the stress

and the entropy generated by the proposed form of the free energy function are then employed in a detailed investigation of the extension of a cylindrical specimen under prescribed conditions of temperature and pressure, a situation which serves as a model of the experimental arrangement most frequently used in laboratory studies of the mechanical and thermo-mechanical properties of rubberlike solids. Qualitative consistency of the theoretical predictions with observed behaviour is shown to be assured, over the full range of circumstances for which measurements have been reported, by two simple inequalities affecting one of the three response functions appearing in the stress–deformation–temperature relations. The function concerned is closely related to the strain energy governing isothermal deformations of the material at a selected reference temperature and it is associated, by the physical considerations referred to above, with the contribution to the stress of the polymer network. This conclusion shows that a rational macroscopic theory of rubberlike thermoelasticity can be developed in rather general terms. In particular, the requirement that the constitutive equations shall reproduce the anomalous thermo-mechanical effects which are characteristic of solid elastomers imposes restrictions on the response functions no more severe than those which ensure that the purely mechanical behaviour of the material is physically realistic.

In the remainder of the paper the capability of the basic theory for furnishing results quantitatively agreeing with experiment is examined. Empirical forms of the three response functions are presented which accurately represent measurements made in tests involving compression at different fixed temperatures and stretching at the reference temperature. Numerical calculations relating to the analysis of the extension of a cylinder, given earlier, are then described and compared with the results of experiments in which thermoelastic inversion phenomena occur. Satisfactory agreement is secured, but it is noted that insufficiency of material data for the rubbers used in the tests precludes an exact correlation of theory and experiment.

The final section of the paper is concerned with isothermal deformations of rubberlike materials which are mechanically incompressible (in the sense that volume changes can be brought about by thermal expansion but not by loading at fixed temperature). This property closely approximates the typical behaviour of natural and synthetic rubbers, but its incorporation into a *general* treatment of rubberlike thermoelasticity presents difficulties and places an undesirable limitation on the scope of the theory. An analogue is shown to exist between the constitutive equations for deformations at the reference temperature and their counterparts in respect of isothermal deformations at other temperatures, and with its aid the problem of the combined extension, torsion and uniform heating of a circular cylinder is solved. Again, a numerical evaluation of the solution is compared with available experimental data.

## 1. INTRODUCTION

Experimental study of the thermo-mechanical behaviour of solid elastomers has a long history and has thrown much light on the physical nature of rubberlike elasticity (see Treloar 1958, chap. II and Flory 1953, chap. XI). The continuum approach to the thermo-mechanics of highly deformable elastic materials has also been pursued over a lengthy period and may now be said to have assumed a definitive form (see, for example, the presentations of Truesdell & Noll 1965, §96; Green & Adkins 1970, chap. VIII and Chadwick & Seet 1971). This paper is an attempt to unite the two lines of investigation. Specifically, our aim is to determine a form of the Helmholtz free energy function which accurately represents the observed thermo-mechanical properties of elastomeric solids and is faithful to accepted ideas on the manner in which the bulk response of such materials is influenced by their characteristic molecular structure. It should be emphasized at the outset that the present work is wholly phenomenological in spirit and that consideration is given here only to ‘perfectly’ elastic behaviour, effects associated with crystallization and stress relaxation lying outside the scope of our discussion.

At the macroscopic level the phenomenon of high elasticity consists first in an ability to sustain large deformations and secondly in the recovery of an initial configuration, without appreciable hysteresis, when applied forces are removed. These properties are exhibited predominantly by substances, of which vulcanized natural rubber is the prototype, composed of molecules which are polymerized into long chain-like structures and chemically cross-linked so as to form a three-dimensional network. A solid material of this kind, operating at temperatures above its glass transition zone, is referred to henceforth as a *rubberlike material*.

Next to high elasticity the anomalous thermoelastic properties of rubberlike materials represent perhaps their most distinctive form of material response, a well known example being the *increase* in temperature which accompanies the rapid elongation of a rubber strip. These effects have been the subject of increasingly refined experimentation, mainly through the medium of tests involving the extension of a cylindrical specimen under controlled environmental conditions. A theoretical model of the situation obtaining in such experiments, discussed in §§4 and 6, plays a leading part in our later considerations.

During the past 35 years much effort has been devoted to finding strain–energy functions which satisfactorily account for the stress–deformation behaviour of natural and synthetic rubbers under isothermal conditions, and success has been achieved in arriving at empirical functional forms which are at once suitable for use in practical problems of stress analysis and in close agreement with experimental data covering a wide range of strains.† Since the isothermal strain–energy function is obtained by evaluating the Helmholtz free energy at the fixed temperature at which deformation takes place, this work is directly relevant to the objectives stated above.

Our formulation of a theoretical model of rubberlike thermoelasticity accordingly starts, in §2, with the derivation of an expression for the Helmholtz free energy of an elastic material in which an isothermal strain–energy function appears explicitly (eq. (3)). We then introduce, in §3*a*, two assumptions which may be regarded as characterizing an idealized form of rubberlike response. One assumption specifies the degree of intrinsic symmetry possessed by the material and the other places restrictions on the dependence of the internal energy upon the deformation gradient and the temperature. The free energy function (eq. (7)) and the associated constitutive equations for the entropy, the internal energy and the stress (eq. (9)–(11)) which follow from the basic assumptions are the central results of the paper. The constitutive equations connecting the principal components of stress to the principal stretches and the temperature (eq. (11)) contain three scalar response functions which reflect in a natural way the influences of the polymer network and of inter-molecular forces on the thermo-mechanical behaviour of the material considered. It is shown in §4 that qualitative consistency of the theoretical model with observation is not crucially dependent on the form of these functions, but is ensured by merely subjecting the response function representing the action of the network to a pair of inequalities. This important result demonstrates that constitutive equations for rubberlike materials can be constructed by very simple means and their adequacy established, in general terms, at a stage preceding the detailed correlation of theoretical predictions with experimental results.

Empirical forms of the three response functions are proposed in §5 and shown to generate theoretical curves agreeing closely with readings taken in tests involving the realization of various homogeneous deformations at uniform temperature. The response function associated with the polymer network is intimately related to the strain–energy function governing deformations in which the temperature coincides with a selected reference point and the material is regarded as incompressible. In specifying this function appeal is therefore made to the extensive research on isothermal strain–energy functions which has been mentioned and, in particular, to results recently published by Ogden (1972*a, b*). In the last two sections of the paper the response functions introduced in §5 are employed in detailed calculations of thermo-mechanical effects for which experimental results are available. The physical properties of the rubbers used in these experiments are not known in sufficient detail to allow a complete determination of the constants appearing in the response functions and it is not possible, therefore, at the present time, to make

† Recent reviews have been given by Ogden (1972*a*, §2) and Treloar (1973, §6).

a rigorous comparison of theory and experiment of the kind described in §5. Nevertheless, it seems worthwhile to include a representative selection of the numerical results which have been obtained, not only for purposes of illustration but also because the computations agree sufficiently well with the experimental findings to sustain the confidence in the underlying theory which is argued on more general grounds in §§3*c* and 4*e*.

The only investigation known to the writer† with objectives similar to those of the present paper is due to Besseling & Voetman (1968). The method of approach of these authors is quite different, however, from that followed here, being based upon a conjectured form of the internal energy which is related to the well-known strain–energy function first propounded by Mooney (1940). Comments on the results obtained by Besseling & Voetman are made at appropriate places in the text of the paper, principally in §5. A non-linear theory of thermoelasticity for rubberlike materials has also been given by Blatz (1969, §IV), but with reference only to homogeneous deformations and under hypotheses considerably more restrictive than those stated in §3*a*. Blatz's analysis relates to *ideal elastomers*, that is to elastic materials for which the internal energy is independent of the deformation, and it is further supposed that volume changes are entirely due to thermal expansion. The assumption of mechanical incompressibility is both physically appropriate and mathematically convenient in a wide range of theoretical questions relating to elastomeric materials and its inclusion in the model of rubberlike thermoelasticity developed in §§3 to 5 is studied in some detail in §7.

## 2. PRELIMINARY ANALYSIS

When effects connected with the conduction of heat are absent, as they are taken to be throughout this paper, an elastic material is characterized by a single scalar function, the Helmholtz free energy  $A$  per unit mass. For homogeneous elastic materials, to which attention is confined,  $A$  is uniquely determined by the deformation gradient  $\mathbf{F}$  and the temperature  $T$ . The entropy  $S$  and the internal energy  $U$  (each measured per unit mass) are given in terms of  $A$  by the relations

$$S = -\partial A/\partial T, \quad U = A - T\partial A/\partial T, \quad (1)$$

and the specific heat at constant deformation  $c$  is defined by

$$c = \partial U/\partial T = -T\partial^2 A/\partial T^2 \quad (2)$$

(see, for example, Chadwick & Seet 1971, pp. 32–41). On integrating equation (2)<sub>2</sub> twice between a reference temperature  $T_0$  and  $T$  there results, with use of (1)<sub>2</sub>, the expression

$$A(\mathbf{F}, T) = A(\mathbf{F}, T_0) \frac{T}{T_0} - U(\mathbf{F}, T_0) \left( \frac{T}{T_0} - 1 \right) - \int_{T_0}^T \left( \frac{T}{T'} - 1 \right) c(\mathbf{F}, T') dT' \quad (3)$$

for the free energy.

In its elementary form the statistical theory of rubber elasticity predicts that the free energy is entirely entropic in origin and proportional to the temperature, no changes of internal energy occurring in response to deformation (see Treloar 1958, pp. 66–70). When  $U$  is equated to zero and the contribution to  $A$  of the specific heat is ignored equation (3) is seen to be consistent with this result. The simple analysis given above therefore provides, in equation (3), a structurally appropriate starting point for an enquiry into the form of the free energy function characterizing

† I am grateful to Professor S. Zahorski for drawing my attention to the work of Besseling & Voetman.



rubberlike materials. In the first term on the right side of (3),  $A(\mathbf{F}, T_0)$  is the strain-energy function per unit mass for isothermal deformations of the considered material at the reference temperature  $T_0$ . As mentioned in §1 this function is the subject of extensive investigations and its explicit appearance in equation (3) is of considerable advantage in the developments which follow.

### 3. THE FORM OF THE HELMHOLTZ FREE ENERGY FUNCTION FOR A RUBBERLIKE MATERIAL

#### (a) *Basic assumptions and their consequences*

Equation (3) is a representation of the free energy  $A$  which is valid for all elastic materials. In this section it is particularized to materials exhibiting rubberlike elasticity on the basis of two physically motivated assumptions.

- I. At every temperature in some interval  $\mathcal{T}$  the material under consideration has a stress-free configuration relative to which it is isotropic.
- II. Over the temperature interval  $\mathcal{T}$  the internal energy of the material is expressible as the sum of a function of the specific volume only and a function of the temperature only.

Before entering into the justification of these assumptions it is convenient to examine their mathematical implications. Let  $T_0$  be chosen arbitrarily from  $\mathcal{T}$  and let  $N_0$  denote the natural configuration (i.e. the stress-free undistorted state) of the material at temperature  $T_0$ . Then, on account of the first assumption, the free energy depends upon the deformation gradient  $\mathbf{F}$  through the principal stretches  $a_1, a_2, a_3$  measured from  $N_0$  as reference configuration and, moreover,  $A$  is a symmetric function of these variables (see Truesdell & Noll 1965, p. 317).

Assumption II implies that the internal energy at the reference temperature  $T_0$  is a function of the volume only and, via equation (2)<sub>1</sub>, that the specific heat  $c$  depends wholly on the temperature  $T$ . These properties allow the introduction of scalar response functions  $f, g$  and  $h$  defined as follows:

$$f(\mathbf{a}) = (\rho_0/\mu) \{A(\mathbf{F}, T_0) - A(J^{\frac{1}{3}}\mathbf{I}, T_0)\}, \quad (4)$$

$$g(J) = (\rho_0/\kappa) A(J^{\frac{1}{3}}\mathbf{I}, T_0), \quad (5)$$

$$h(J) = (\rho_0/\alpha T_0 \kappa) U(\mathbf{F}, T_0). \quad (6)$$

Here  $\mathbf{a}$  indicates symmetrical dependence on  $a_1, a_2$  and  $a_3$ ,  $\mathbf{I}$  is the identity tensor and the dimensionless specific volume  $J$  is defined by

$$J = \det \mathbf{F} = a_1 a_2 a_3 = \rho_0/\rho,$$

where  $\rho$  is the current density of the material and  $\rho_0$  the density in the natural state  $N_0$ . The remaining quantities in equations (4) to (6),  $\mu, \kappa$  and  $\alpha$ , are material constants relative to  $N_0$ ,  $\mu$  being the shear modulus,  $\kappa$  the isothermal bulk modulus and  $\alpha$  the volume coefficient of thermal expansion. It is assumed that these constants are positive. With use of the definitions (4) to (6) equation (3) takes on the simplified form

$$A(\mathbf{a}, T) = \frac{\mu}{\rho_0} f(\mathbf{a}) \frac{T}{T_0} + \frac{\kappa}{\rho_0} \left\{ g(J) \frac{T}{T_0} - \alpha h(J) (T - T_0) \right\} - \int_{T_0}^T \left( \frac{T}{T'} - 1 \right) c(T') dT'. \quad (7)$$

Comparison of equations (3) and (7) shows that definitions (4) and (5) effect a decomposition of the isothermal strain-energy function  $A(\mathbf{F}, T_0)$  into two parts, a dilatational component,

specified by the response function  $g$  and containing the bulk modulus  $\kappa$ , and a distortional part multiplied by the shear modulus  $\mu$  and involving the function  $f$  which vanishes when

$$a_1 = a_2 = a_3 (= J^{\frac{1}{3}}),$$

that is when the deformation is a dilatation. This decomposition, which has been discussed from rather different viewpoints by Spencer (1970, §10) and Ogden (1972*b*, §2), is of fundamental physical significance in rubber elasticity. Further comment is deferred to §3*c*, but we emphasize at this stage that the partitioning into dilatational and distortional parts carried out in equations (4) and (5) is a mathematical step entailing no assumption about the nature of the isothermal strain–energy function.

In an isotropic elastic material the principal axes of the Cauchy stress tensor coincide with the principal axes of stretch in the deformed configuration and the principal stresses  $\sigma_1, \sigma_2, \sigma_3$  are given by†

$$\sigma_i = \rho_0 J^{-1} a_i (\partial A / \partial a_i) \quad (8)$$

(see Truesdell & Noll 1965, p. 317). Substitution of the free energy function (7) into equations (1) and (8) leads to the expressions

$$S(\mathbf{a}, T) = -\frac{\mu}{\rho_0 T_0} f(\mathbf{a}) - \frac{\kappa}{\rho_0 T_0} \{g(J) - \alpha T_0 h(J)\} + \int_{T_0}^T c(T') \frac{dT'}{T'}, \quad (9)$$

$$U(J, T) = \frac{\alpha T_0 \kappa}{\rho_0} h(J) + \int_{T_0}^T c(T') dT', \quad (10)$$

$$\sigma_i(\mathbf{a}, T) = \mu J^{-1} a_i \frac{\partial f}{\partial a_i}(\mathbf{a}) \frac{T}{T_0} + \kappa \left\{ g'(J) \frac{T}{T_0} - \alpha h'(J) (T - T_0) \right\}, \quad (11)$$

for the entropy, the internal energy and the principal stresses, the primes in (11) denoting differentiation with respect to  $J$ .

#### (b) Normalization conditions

In the natural configuration  $N_0$ ,  $a_1 = a_2 = a_3 = J = 1$ ,  $T = T_0$  and  $\sigma_1 = \sigma_2 = \sigma_3 = 0$ . Further, the constants  $\mu$ ,  $\kappa$  and  $\alpha$  must have the meanings ascribed to them above and, without loss of generality, it can be supposed that  $S$  and  $U$  vanish in  $N_0$ . These requirements impose on the response functions  $f$ ,  $g$  and  $h$  *normalization conditions* which are now derived.

Since  $f$  is a symmetric function of  $a_1, a_2$  and  $a_3$  which vanishes when  $a_1 = a_2 = a_3$  its derivatives satisfy the relations

$$\left. \begin{aligned} \frac{\partial f}{\partial a_1} = \frac{\partial f}{\partial a_2} = \frac{\partial f}{\partial a_3} = 0 \\ \frac{\partial^2 f}{\partial a_1^2} = \frac{\partial^2 f}{\partial a_2^2} = \frac{\partial^2 f}{\partial a_3^2} = -2 \frac{\partial^2 f}{\partial a_2 \partial a_3} = -2 \frac{\partial^2 f}{\partial a_3 \partial a_1} = -2 \frac{\partial^2 f}{\partial a_1 \partial a_2} \end{aligned} \right\} \text{when } a_1 = a_2 = a_3. \quad (12)$$

In particular, equations (12)<sub>1–3</sub> hold in  $N_0$  and it is apparent from (9), (10) and (11) that  $S$ ,  $U$  and the  $\sigma_i$  are zero in this state if and only if  $g(1) = g'(1) = 0$  and  $h(1) = 0$ .

Results given by Chadwick & Ogden (1971, equations (3.17) and (3.19)<sub>1,2</sub>) show that the

† Here, and henceforth, the summation convention does *not* apply.

instantaneous shear and bulk moduli of an isotropic elastic material relative to a configuration which is conformal† to an undistorted state are respectively

$$\frac{1}{2}a \left( \frac{\partial \sigma_i}{\partial a_i} - \frac{\partial \sigma_i}{\partial a_j} \right) - \sigma \quad \text{and} \quad \frac{1}{3}a \left( \frac{\partial \sigma_i}{\partial a_i} + 2 \frac{\partial \sigma_i}{\partial a_j} \right) + \frac{1}{3}\sigma \quad (i \neq j), \quad (13)$$

where  $a$  is the all-round stretch and  $\sigma$  the all-round stress in the deformed configuration and the derivatives are evaluated at  $a_1 = a_2 = a_3 = a$ . Hence

$$\mu = \frac{1}{2} \left( \frac{\partial \sigma_i}{\partial a_i} - \frac{\partial \sigma_i}{\partial a_j} \right)_0, \quad \kappa = \frac{1}{3} \left( \frac{\partial \sigma_i}{\partial a_i} + 2 \frac{\partial \sigma_i}{\partial a_j} \right)_0 \quad (i \neq j),$$

the subscript 0 signifying evaluation in  $N_0$ . It now follows from equation (11), with use of (12), that

$$\left( \frac{\partial^2 f}{\partial a_i^2} \right)_0 = \frac{4}{3}, \quad \left( \frac{\partial^2 f}{\partial a_i \partial a_j} \right)_0 = -\frac{2}{3} \quad (i \neq j), \quad (14)$$

and  $g''(1) = 1$ .

By virtue of assumption I the rubberlike material under consideration has a natural configuration  $N$  at temperature  $T$  and since two undistorted states of an isotropic elastic material are necessarily conformal (see Truesdell & Noll 1965, p. 85), the principal stretches, measured from  $N_0$ , are all equal when the material occupies the configuration  $N$ .‡ The derivatives  $\partial f / \partial a_i$  therefore vanish in  $N$  (by (12)<sub>1-3</sub>), as do the principal stresses  $\sigma_i$ , and equation (11) reduces to the volume-temperature relation

$$g'(J) - \alpha T_0 h'(J) (1 - T_0/T) = 0. \quad (15)$$

This equation determines implicitly the volume change associated with the conformal deformation  $N_0 \rightarrow N$ , and the derivative  $J^{-1} \partial J / \partial T$ , calculated from (15), is the volume coefficient of thermal expansion of the material relative to  $N$ . On evaluating the expansion coefficient in  $N_0$  and equating the result to  $\alpha$  it is found that  $h'(1) = 1$ .

The complete set of normalization conditions satisfied by  $f$ ,  $g$  and  $h$  has now been obtained and for ease of reference the constraints on the volumetric response functions are collected together and restated as

$$g(1) = g'(1) = 0, \quad g''(1) = 1; \quad h(1) = 0, \quad h'(1) = 1. \quad (16)$$

### (c) Physical basis of assumptions I and II

In essence assumption I asserts that the mechanical response of a rubberlike material in a natural configuration exhibits no preferred direction and that anisotropic behaviour cannot be induced by merely imposing a uniform change of temperature. These properties, which are almost universally adopted in theoretical work on the mechanics and thermo-mechanics of unconstrained elastomeric materials, are due to the randomness of the arrangements taken up by the chain molecules in a stress-free state. In the absence of intrinsic directionality in the molecular network isotropy of response is assured and the situation is qualitatively unaffected by heating.

The physical conceptions underlying assumption II relate to the basic differences between the structural mechanisms controlling the ways in which rubberlike materials respond to changes of shape and volume. In being able to undergo large deformations at moderate levels of applied

† Two configurations are said to be *conformal* if the deformation carrying one into the other is a combination of a rotation and a dilatation.

‡ In physical terms, subjecting the material to a uniform temperature change  $T - T_0$  at zero stress simply dilates it by an amount specified by equation (15).



stress rubberlike solids resemble liquids. On the other hand they differ sharply from liquids in reverting to an initial configuration when the forces producing a deformation are removed. In structural terms the similarity with liquids extends to properties in which intermolecular forces are dominant; for example, rubberlike materials, like liquids, are nearly incompressible and have large thermal expansion coefficients. The structural feature which distinguishes rubberlike solids from liquids is the polymer network mentioned in § 1, and because of the pronounced extensibility of the chain molecules the deformation of a rubberlike solid in shear is characterized by a low elastic modulus (see Lodge 1964, pp. 80–86 for a more detailed discussion).

According to a postulate advanced by Flory (1961, § 1) the free energy of an amorphous cross-linked polymer is expressible as the sum of two terms, one, a function of deformation gradient and temperature, representing the elastic contribution attributable to the network, and the other, a function of volume and temperature, the liquid-like contribution arising from the interaction of the chain molecules. The expression for the free energy obtained from equation (3) by assuming that  $U$  (and hence  $c$ ) is a function of  $J$  and  $T$  is seen to conform with Flory's postulate. Furthermore, in the simplified free energy formula (7) associations, suggested by the foregoing considerations, between the first and second terms on the right (prefaced in turn by the shear and bulk moduli) and the respective contributions of the polymer network and intermolecular actions are corroborated. The corresponding separation of effects apparent in the isothermal strain–energy function  $A(\mathbf{a}, T_0)$  lends physical significance to the decomposition of this function which has been carried out in § 3*a*.

Inspection of equations (7), (9), (10) and (11) in the light of the interpretations just given shows first that the internal energy must be regarded as arising exclusively from the secondary intermolecular forces, and secondly that the parts of the free energy and the stress contributed by the network are entirely entropic. There is abundant support in the older literature for the proposition that the internal energy of a rubberlike solid is generally similar to that of a simple liquid and that, in particular, it depends upon the deformation through the volume. And the related conclusion that the contributions of the polymer network to the free energy and the stress are due wholly to entropy changes was likewise widely accepted in discussions of the physical basis of rubber elasticity published before 1960 (see Flory 1953, pp. 434–451 and Treloar 1958, pp. 20–38). More recently, however, important modifications of these ideas have been introduced and confirmed experimentally. Measurements by Allen *et al.* (1963, 1971) involving the extension of a rod at constant volume show that the internal energy of natural rubbers is weakly dependent upon distortion and that the proportion of the retractive force on the specimen due to internal energy changes is about 12%. Reported values of this fraction for other rubbery polymers vary between 3 and 42% (see Treloar 1973, p. 789). The possibility of the internal energy of an individual molecule varying with the conformation of the chain is excluded in the simpler statistical theories, but it has been pointed out by Flory *et al.* (1959) that the presence of energy barriers hindering free rotation about bonds will result in the chain having a configuration-dependent internal energy. In consequence the influence of the network on the free energy and the stress is no longer due entirely to entropy changes and the overall internal energy of the material contains a contribution from the network depending upon the distortion (see Treloar 1973, § 4 for further details).

It is evident from the preceding discussion that assumption II is to be viewed as a first approximation, consistent with the broad structural concepts which have been outlined, but not fully accurate in relation to current understanding of internal energy changes in rubberlike materials.

The over-simplification resulting from the neglect of the dependence of  $U$  upon distortion is compounded by the further assumption (tantamount to ignoring the variation of the specific heat  $c$  with deformation) that  $U$  depends additively upon the specific volume and the temperature. In a liquid possessing an internal energy of this form the pressure would be a linear function of the temperature with volume-dependent coefficients and it is known that equations of state of this type can provide a qualitatively satisfactory description of observed behaviour, the best-known example being the van der Waals equation. It might be expected that, despite the deficiencies in detailed modelling to which attention has been drawn, a continuum theory of rubberlike thermoelasticity embodying assumption II will be similarly capable of reproducing the essential features of a wide range of experimental findings, and it is confirmed in §§ 4–7 that such is indeed the case.

We note at this point that the internal energy function surmised by Besseling & Voetman (1968, eq. (3.3)) is the sum of a function of the specific volume, a function of the temperature and a function of the deformation gradient which vanishes in a state of dilatation. There would be no difficulty of principle in bringing into the present work, in a like manner, an additional response function representing the dependence of  $U$  upon distortion, but it appears to the writer to be highly desirable to explore first the potentialities of a constitutive theory with the simplest possible ingredients. The arguments developed in the present paper are uncomplicated and the roles of the essential components of the model, the network response function  $f$  and the volumetric response functions  $g$  and  $h$ , are plainly delineated. Elaboration of this basic structure, allowing the comparison of theory and experiment to be extended to the refined measurements of internal energy changes to which reference has been made, is set aside for later consideration.

(d) *Material data*

In order to have in mind typical magnitudes of the material constants introduced in § 3*a* we list in table 1 data for a peroxide-cured vulcanizate of natural rubber taken from a paper by Wood & Martin (1964). All the numerical results presented in the later sections are based upon these values. The isothermal bulk modulus of the chosen material is seen to exceed the shear modulus by a factor of  $4.6 \times 10^3$ , illustrating the disparity in the magnitudes of these moduli indicated in § 3*c*. Henceforth we make systematic use of the strong inequality  $\eta \ll 1$ , where

$$\eta = \mu/\kappa, \quad (17)$$

in deriving approximate results.

TABLE 1. MATERIAL CONSTANTS RELATIVE TO THE NATURAL CONFIGURATION AT 25 °C OF A PEROXIDE-CURED VULCANIZATE OF NATURAL RUBBER  
(From Wood & Martin 1964.)

density ( $\rho_0$ )	906.5 kg m <sup>-3</sup>
shear modulus ( $\mu$ )	$4.2 \times 10^3$ kPa
isothermal bulk modulus ( $\kappa$ )	$1.95 \times 10^6$ kPa
volume coefficient of thermal expansion ( $\alpha$ )	$6.36 \times 10^{-4}$ K <sup>-1</sup>
specific heat at constant deformation ( $c_0$ )	1662 J kg <sup>-1</sup> K <sup>-1</sup>

## 4. EXTENSION OF A CYLINDER: THEORETICAL CONSIDERATIONS

Experiments involving the elongation of a cylindrical specimen have been extensively applied to rubberlike materials and, in particular, the investigation of thermoelastic behaviour has been conducted almost exclusively on the basis of such tests. In this section a theoretical study is made of the situation shown in figure 1 which accurately represents the uniaxial experiment in question. The cylindrical test-piece, of arbitrary simply connected cross-section, is subjected to a uniform pressure  $\Pi$  over the whole of its boundary and maintained at uniform temperature  $T$ .

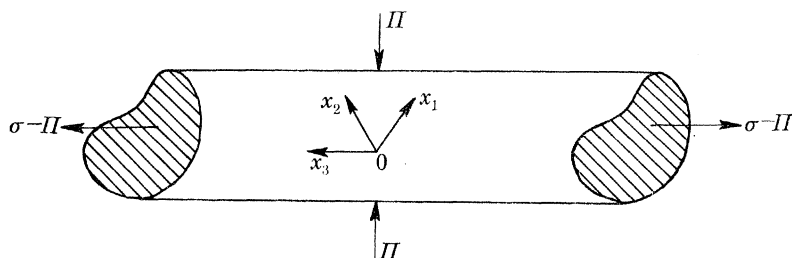


FIGURE 1. Illustration of the extension of a cylindrical specimen.

It is placed in a state of simple extension by the application to its plane end-faces of a uniform normal traction  $\sigma$  (measured per unit area in the deformed configuration). Taking the 3-direction of a rectangular Cartesian coordinate system to be aligned with the generators of the cylinder the principal stretches and the principal components of stress are thus given by

$$a_1 = a_2 = (JA^{-1})^{\frac{1}{2}}, \quad a_3 = A; \quad \sigma_1 = \sigma_2 = -\Pi, \quad \sigma_3 = \sigma - \Pi, \quad (18)$$

where  $A$  is the axial stretch and, as before,  $J = a_1 a_2 a_3$  is the dimensionless specific volume. No body forces act, the cylinder being held in equilibrium by the action of the prescribed surface tractions alone.

In order to make use of the principal stress–stretch–temperature relations (11) we appropriately redefine the network response function  $f$  by setting

$$F(J, A) \equiv f((JA^{-1})^{\frac{1}{2}}, (JA^{-1})^{\frac{1}{2}}, A). \quad (19)$$

Since  $f$  is invariant under interchange of its arguments  $a_1$  and  $a_2$ ,

$$\partial f / \partial a_1 = \partial f / \partial a_2 = (JA)^{\frac{1}{2}} F_J, \quad \partial f / \partial a_3 = JA^{-1} F_J + F_A, \quad (20)$$

where the derivatives of  $f$  are evaluated at  $a_1 = a_2 = (JA^{-1})^{\frac{1}{2}}$ ,  $a_3 = A$  and a suffix notation, typified by  $F_J = \partial F / \partial J$ , is used for the derivatives of  $F$ . On substituting for the principal stretches and stresses from equations (18) into (11) we obtain, with use of (17) and (20),

$$\eta F_J(J, A) + g'(J) - \alpha T_0 \left(1 - \frac{T_0}{T}\right) h'(J) = -\frac{\Pi T_0}{\kappa T}, \quad (21)$$

$$\sigma = \mu J^{-1} A F_A(J, A) \frac{T}{T_0}, \quad (22)$$

and equation (9) yields the expression

$$S = -\frac{\kappa}{\rho_0 T_0} \left\{ \eta F(J, A) + g(J) - \alpha T_0 h(J) \right\} + \int_{T_0}^T c(T') \frac{dT'}{T'} \quad (23)$$

for the uniform value of the entropy in the deformed cylinder. In experimental work it is customary to measure the applied stress per unit area in the reference configuration  $N_0$ . From equation (22) this traction,  $s$  (a component of the nominal stress tensor), is given by

$$s = J\Lambda^{-1}\sigma = \mu F_\Lambda(J, \Lambda) (T/T_0). \quad (24)$$

Equation (21), which we regard as determining  $J$  implicitly as a function of  $\Lambda$ ,  $T$  and  $\Pi$ , has the solution

$$J = \mathcal{J} - \frac{\eta F_J(\mathcal{J}, \Lambda) + (\Pi T_0/\kappa T)}{g''(\mathcal{J}) - \alpha T_0\{1 - (T_0/T)\}h''(\mathcal{J})} + O(\eta^2), \quad (25)$$

provided that  $\Pi \ll \kappa(T/T_0)$ ,  $\mathcal{J}$  being defined as a function of  $T$  only by the volume–temperature relation (15). It is assumed in the remainder of this section that the pressure acting on the cylinder is atmospheric ( $\Pi = 1.01 \times 10^2$  kPa). The proviso  $\Pi \ll \kappa(T/T_0)$  is then satisfied over the entire temperature range within which rubberlike behaviour is encountered and equation (25) supplies the approximation  $J = \mathcal{J}$  to leading order in powers of  $\eta$ .

In the subsections which follow we examine the response of the cylinder under isothermal, isometric, isotonic and isentropic conditions (in which  $T$ ,  $\Lambda$ ,  $\sigma$  and  $S$  are in turn held fixed), and it is convenient to set down here the inequalities

$$(d/d\Lambda) \{ \Lambda F_\Lambda(1, \Lambda) \} > -F_{J\Lambda}(1, \Lambda) > 0 \quad \text{for } \Lambda > 0 \quad (26)$$

to which repeated reference is made. When  $J = \Lambda = 1$  (i.e. in the natural state  $N_0$ ),  $F$ ,  $F_J$  and  $F_\Lambda$  each vanish and the normalization conditions (14), applied to the definition (19), give

$$F_{JJ}(1, 1) = \frac{1}{3}, \quad F_{J\Lambda}(1, 1) = -1, \quad F_{\Lambda\Lambda}(1, 1) = 3. \quad (27)$$

The inequalities (26) are evidently consistent with (27) and they imply that

$$\left. \begin{aligned} F(1, \Lambda) > 0, \quad F_J(1, \Lambda) > 0, \quad F_\Lambda(1, \Lambda) < 0 \quad \text{for } 0 < \Lambda < 1, \\ F(1, \Lambda) > 0, \quad F_J(1, \Lambda) < 0, \quad F_\Lambda(1, \Lambda) > 0 \quad \text{for } \Lambda > 1. \end{aligned} \right\} \quad (28)$$

#### (a) Isothermal behaviour

We consider first the variation of the nominal applied traction  $s$  with the extension of the cylinder at different fixed values of the temperature  $T$ . In experiments of this kind the measured axial stretch,  $\tilde{\Lambda}$ , is reckoned from the natural state  $N$  of the specimen at the ambient temperature  $T$  and, recalling the penultimate paragraph of §3*b*,  $\tilde{\Lambda}$  is connected to  $\Lambda$ , the axial stress relative to  $N_0$ , by the relation  $\Lambda = \mathcal{J}^{\frac{1}{3}}\tilde{\Lambda}$ . Thus, from equation (24),

$$s = \mu F_\Lambda(J, \mathcal{J}^{\frac{1}{3}}\tilde{\Lambda}) (T/T_0), \quad (29)$$

$J$  and  $\mathcal{J}$  being given by equations (21) and (15) respectively. As pointed out above,  $J$  and  $\mathcal{J}$  differ only by a term of order  $\eta$  in tests performed at atmospheric pressure and because of the comparative smallness of  $\alpha T_0$  it follows from equation (15) that  $\mathcal{J}$  is weakly temperature dependent.† Axial stress–stretch isothermals computed from equation (29) therefore fan out from the origin in the first quadrant of the  $(s, \tilde{\Lambda})$ -plane, the initial gradient increasing with  $T$  (cf. Anthony *et al.* 1942, p. 834; Treloar 1958, p. 30 and figure 4 below).

† Using the data listed in table 1,  $\alpha T_0 = 0.190$ . A discussion of the volume–temperature relation (15) is included in §5*b* below; see, in particular, the first two columns of table 2.

At the reference temperature  $T_0$ ,  $\mathcal{J} = 1$  and  $\tilde{\Lambda} = \Lambda$ . In the leading approximation equation (22) then reduces to

$$\sigma = \mu \Lambda F_{\Lambda}(1, \Lambda), \quad (30)$$

and, to terms of order one in  $\eta$ ,

$$J = \hat{J} - \eta F_J(1, \Lambda), \quad (31)$$

where  $\hat{J} = 1 - (II/\kappa) + O(\eta^2)$  specifies the compression arising from the action of atmospheric pressure at temperature  $T_0$ . It is a matter of common experience with rubberlike materials that  $\sigma$  is an increasing function of  $\Lambda$ , negative when  $0 < \Lambda < 1$  and positive when  $\Lambda > 1$ , but the determination of the variation with extension of the volume change  $J - \hat{J}$  calls for sensitive experimental techniques. Several series of measurements have been carried out (see Gee *et al.* 1950; Hewitt & Anthony 1958; Allen *et al.* 1963), each demonstrating that  $J - \hat{J}$  increases monotonically with  $\Lambda$  through positive values which are of the same order of magnitude as  $\eta$  over the range of extensions investigated (up to 120 %; see figure 5 below). The inequalities (26), with their corollaries (28), are seen to guarantee that, to the stated orders of accuracy, equations (30) and (31) reproduce the properties which have just been described. These inequalities may therefore be interpreted as sufficient conditions for the rubberlike material under consideration to exhibit physically realistic response in simple extension at the reference temperature  $T_0$ .

(b) *Isometric behaviour*

We turn next to the variation with temperature of the axial stress  $s$  when the length of the cylinder is held fixed, that is for a specified value of the axial stretch  $\Lambda$  relative to  $N_0$ . This variation is given by equation (24) with  $J$  defined implicitly by (21). For tests at atmospheric pressure  $J$  can be replaced by  $\mathcal{J}$  and in view of the weak temperature dependence of  $\mathcal{J}$ , pointed out in §4*a*,  $s$  is nearly proportional to  $T$ . This property is confirmed experimentally (see Meyer & Ferri 1935, p. 578; Anthony *et al.* 1942, p. 831 and Shen *et al.* 1967, p. 794), isometric curves being obtained which are indistinguishable from straight lines. The gradient  $\partial s / \partial T$  is found to increase monotonically with  $\Lambda$  from negative values at extensions below about 10 % to positive values at higher stretches. This is an example of the anomalous thermoelastic behaviour, mentioned in §1, which is a characteristic feature of rubberlike materials and we now look into the possibility of an inversion of the sign of  $\partial s / \partial T$  being predicted by equations (24) and (21).

If, to a close approximation, there is an isometric curve on which  $s$  is constant the derivative  $\partial s / \partial T$ , computed from equations (24) and (21) and evaluated at  $T = T_0$ , vanishes for some value of  $\Lambda$  exceeding unity. This requirement is easily shown to take the form

$$F_{\Lambda}(J, \Lambda) + F_{J\Lambda}(J, \Lambda) \frac{\alpha T_0 h'(J) + \eta \mu^{-1} II}{g''(J) + \eta F_{JJ}(J, \Lambda)} = 0 \quad (32)$$

with  $J$  satisfying

$$\eta \{F_J(J, \Lambda) + \mu^{-1} II\} + g'(J) = 0. \quad (33)$$

To leading order in powers of  $\eta$  equations (33) and (16)<sub>2</sub> give  $J = 1$  and, with use of (16)<sub>3,5</sub>, equation (32) reduces to

$$F_{\Lambda}(1, \Lambda) + \alpha T_0 F_{J\Lambda}(1, \Lambda) = 0. \quad (34)$$

If  $F$  satisfies the inequalities (26) (and hence (28)) the two terms on the left side of equation (34) are of opposite sign when  $\Lambda > 1$  and, by virtue of (27)<sub>2</sub>, their sum is negative when  $\Lambda = 1$ . It follows that equation (34) has a root exceeding unity if  $\alpha T_0$  is sufficiently small. More precisely,

$$\Lambda \approx 1 + \frac{1}{3} \alpha T_0,$$



with error of order  $(\alpha T_0)^2$ , and on using the data given in table 1 inversion is found to occur at an extension of about 6 %, in fair agreement with the quoted experiments. When  $0 < \lambda < 1$ , corresponding to uniaxial compression of the cylinder, both terms on the left of equation (34) are negative, indicating that the stress-temperature coefficient  $\partial s/\partial T$  is of one sign. Physical considerations supporting this conclusion have been put forward by Gee *et al.* (1950, p. 1106). As in §4*a* the inequalities (26) therefore ensure that the response of the cylinder is in accord with experience and the emerging significance of these conditions is underlined further in §§4*c* and *d*.

(c) *Isotonic behaviour*

Under this heading we study the variation with temperature of the axial stretch  $\lambda$  and the dimensionless specific volume  $J$  when the stress  $\sigma$  (and the pressure  $II$ ) are fixed. Of particular interest are the gradients of the  $\lambda$ - $T$  and  $J$ - $T$  curves which determine the linear coefficients of thermal expansion relative to the deformed configuration of the cylinder in the axial and transverse directions. These coefficients,  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  respectively, are defined by

$$\gamma_{\parallel} = \lambda^{-1}(\partial\lambda/\partial T), \quad \gamma_{\perp} = (J\lambda^{-1})^{-\frac{1}{2}}\{\partial(J\lambda^{-1})^{\frac{1}{2}}/\partial T\} = \frac{1}{2}\{J^{-1}(\partial J/\partial T) - \gamma_{\parallel}\}, \quad (35)$$

the derivatives being evaluated with  $\sigma$  and  $II$  held constant.

We proceed to calculate  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  at the reference temperature  $T_0$ . On differentiating equations (21) and (22) with respect to  $T$  in the appropriate manner, evaluating at  $T = T_0$  and using the definitions (35), a pair of linear relations between the expansion coefficients is obtained, namely

$$\left. \begin{aligned} \{\eta J F_{JJ}(J, \lambda) + \eta \lambda F_{J\lambda}(J, \lambda) + J g''(J)\} \gamma_{\parallel} + 2\{\eta J F_{JJ}(J, \lambda) + J g''(J)\} \gamma_{\perp} &= \alpha h'(J) + \eta \mu^{-1} T_0^{-1} II, \\ \{J F_{J\lambda}(J, \lambda) + \lambda F_{\lambda\lambda}(J, \lambda)\} \gamma_{\parallel} + 2\{J F_{J\lambda}(J, \lambda) - F_{\lambda\lambda}(J, \lambda)\} \gamma_{\perp} &= -T_0^{-1} F_{\lambda}(J, \lambda). \end{aligned} \right\} \quad (36)$$

When the extension  $\lambda$  is specified,  $J$  is given by equation (33) (the result of setting  $T = T_0$  in (21)) and the values of  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  are then found by solving equations (36). In the leading approximation employed in the analyses of isothermal and isometric response,  $J = 1$  and the terms in equation (36)<sub>1</sub> containing  $\eta$  are negligible. With use of the normalization conditions (16)<sub>3,5</sub> equations (36) then lead to the expressions

$$\left. \begin{aligned} \gamma_{\parallel} &= [T_0(d/d\lambda)\{\lambda F_{\lambda}(1, \lambda)\}]^{-1}\{-(1 - \alpha T_0)F_{\lambda}(1, \lambda) - \alpha T_0 F_{J\lambda}(1, \lambda)\}, \\ \gamma_{\perp} &= [2T_0(d/d\lambda)\{\lambda F_{\lambda}(1, \lambda)\}]^{-1}\{(1 - \alpha T_0)F_{\lambda}(1, \lambda) + \alpha T_0[(d/d\lambda)\{\lambda F_{\lambda}(1, \lambda)\} + F_{J\lambda}(1, \lambda)]\}, \end{aligned} \right\} \quad (37)$$

for the expansion coefficients. When  $\lambda = 1$  equations (37) refer to the natural state  $N_0$  and the expected equality of  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  to  $\frac{1}{3}\alpha$  is easily verified with the aid of equations (27)<sub>2,3</sub>.

Data compiled by Flory (1953, p. 437) from experimental results tabulated by Joule (1859, p. 106) show that for  $\lambda \geq 1$ ,  $\gamma_{\parallel}$  decreases steadily as the axial stretch increases, ultimately through negative values (see figure 7 below). This is a further manifestation of the anomalous thermo-elastic behaviour of rubberlike materials, the inversion in the sign of  $\gamma_{\parallel}$  occurring at an extension of about 8 %. According to James & Guth (1943, p. 465)  $\gamma_{\perp}$  is positive, their arguments being based upon expressions resembling (37) in which the counterpart of the response function  $F$  is derived from a statistical theory of the network adopting a Gaussian form for the entropy of the molecular chains. In compression ( $0 < \lambda < 1$ ) the axial expansion coefficient displays no inversion effect (see Meyer & van der Wyk 1946, pp. 1842-1843).

When the inequalities (26) and (28) hold and  $\alpha T_0$  is sufficiently small it is apparent from equations (37) that the variations with  $\lambda$  of  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  are fully consistent with the foregoing account, the axial stretch at which  $\gamma_{\parallel} = 0$  being given by

$$(1 - \alpha T_0) F_{\lambda}(1, \lambda) + \alpha T_0 F_{J\lambda}(1, \lambda) = 0. \quad (38)$$

This equation, like (34), yields  $\lambda = 1 + \frac{1}{3}\alpha T_0 + O((\alpha T_0)^2)$  and the inversion point of about 6% calculated from the data contained in table 1 is satisfactorily close to the experimental value.

(d) *Isentropic behaviour*

When the cylinder is extended without change of entropy equation (23) holds with  $S$  taking the constant value

$$\hat{S} = -(\kappa/\rho_0 T_0) \{g(\hat{J}) - \alpha T_0 h(\hat{J})\} = -(\alpha II/\rho_0) \{1 + O(\eta)\},$$

and the resulting relation, in conjunction with equation (21), enables us to determine  $J$  and  $T$  when the stretch  $\lambda$  and the pressure  $II$  are specified. The axial stress needed to maintain the deformation is then given by equation (22) (or (24)). Experiments on the isentropic extension of cylindrical specimens of rubberlike materials are directed towards the measurement of the variation with  $\lambda$  of the temperature change  $T - T_0$  at atmospheric pressure (see Joule 1859, pp. 105, 124; James & Guth 1943, p. 475; Flory 1953, pp. 436–439; Treloar 1958, pp. 38–43 and figure 8 below). Initially, as  $\lambda$  increases from unity, the temperature falls, as would be expected in a ‘conventional’ material in view of the dilatation which occurs (see equation (40)<sub>2</sub> below). At about 7% extension, however, the temperature passes through a minimum and subsequently it rises with increasing rapidity, positive values of  $T - T_0$  being observed at stretches exceeding about 13%. In compression a steady increase in temperature is observed. Here, therefore, is a third example of anomalous thermoelastic behaviour occurring in the extension of a cylinder, but not in compression.

In order to investigate the variation of temperature with axial stretch on the approximate theoretical basis adopted in the earlier parts of this section expansions of  $J - 1$  and  $T - T_0$  in direct powers of  $\eta$  are substituted into equations (21) and (23) (with  $S = \hat{S}$ ) and the leading terms obtained by equating coefficients of like powers. In applying this procedure it must be recognized, however, that the dimensionless quantity  $\rho_0 c_0 T_0/\kappa$ , where  $c_0 = c(T_0)$ , is  $O(1)$  and not of the first order in  $\eta$  as might appear†. With this gloss it is found that

$$\frac{T - T_0}{T_0} = \frac{\mu}{\rho_0 c_0 T_0 (1 + \epsilon)} \{F(1, \lambda) + \alpha T_0 F_J(1, \lambda)\} \quad (39)$$

in which the error is  $O(\eta^2)$  and  $\epsilon = \alpha^2 T_0 \kappa / \{\rho_0 c_0 (1 + \frac{4}{3}\eta)\}$  is the thermoelastic coupling constant† of the material relative to  $N_0$ . On writing down the condition for  $(\partial T/\partial \lambda)_S$  to vanish we recover equation (34) and it follows from the discussion of that equation given in §4*b* that if the inequalities (26) and (28) hold and  $\alpha T_0$  is sufficiently small the stretch dependence of the temperature predicted by equations (21) and (23) follows the trends observed experimentally. The extension at which inversion of the sign of  $(\partial T/\partial \lambda)_S$  occurs, estimated with the aid of the data given in table 1, agrees closely with the measured value.

An exact calculation of the temperature–stretch and volume–stretch coefficients  $(\partial T/\partial \lambda)_S$  and  $(\partial J/\partial \lambda)_S$  based upon equations (21) and (23) shows that, in the natural state  $N_0$ ,

$$(\partial T/\partial \lambda)_S = -(\alpha T_0 \kappa/\rho_0 c_0) (\partial J/\partial \lambda)_S = -\alpha T_0 E [3\rho_0 c_0 \{1 + 2\epsilon(1 - \nu)\}]^{-1}, \quad (40)$$

† The values of  $\rho_0 c_0 T_0/\kappa$  and  $\epsilon$  derived from the data listed in table 1 are 0.225 and 0.160 respectively.

where

$$E = 3\mu/(1 + \frac{1}{3}\eta) \quad \text{and} \quad \nu = \frac{1}{2}(1 - \frac{2}{3}\eta)/(1 + \frac{1}{3}\eta)$$

are respectively the isothermal Young modulus and the isothermal Poisson ratio of the material relative to  $N_0$ . Equation (40) agrees with results obtained by the writer in a study of the propagation of thermoelastic disturbances in a thin rod (see Chadwick 1962, in particular, equation (35)).

(e) *Discussion*

Thermoelastic inversion phenomena in rubberlike materials are accounted for physically by the competing influences of the chain molecules and the secondary intermolecular actions. The latter respond to a rise in temperature by an increase in pressure at constant volume and by expansion at constant pressure, while an increase of volume at constant entropy is accompanied by a fall in temperature. On the other hand, the pattern of behaviour associated with the chain molecules is 'unconventional'. The individual links of the chains execute random thermal motions and the overall state of disorder is reduced by tension and by uncoiling and increased by heating. The effect of a rise in temperature is therefore to increase the tension at constant end-to-end distance and to decrease the separation of terminal points at constant tension, while elongation under isentropic conditions (in which the state of disorder is preserved) causes the temperature to rise. These opposing tendencies explain the three inversion effects encountered in §§ 4 *b-d*. Because the values of the mean normal stress attained in the experimental situations considered are much smaller than the bulk modulus of the material, volume changes, which are associated with intermolecular forces, are almost entirely due to thermal expansion. Adequate account of secondary forces is therefore taken by allowing for the positive thermal expansivity of the material in its unstressed state. At small extensions thermal expansion effects are dominant and the locations of the actual inversion points are substantially determined by the value of the appropriate expansion coefficient (see Anthony *et al.* 1942, pp. 833, 836 and Treloar 1958, p. 29, 1971, pp. 52-53).

In the theoretical treatment of the extension of a cylinder which has been given in the preceding subsections the collective response of the chain molecules is represented by the function  $F$  and intermolecular actions by the volumetric response functions  $g$  and  $h$ , and the role of the expansion coefficient  $\alpha$  in determining the axial stretch at which the contending effects are in balance is clearly displayed in equations (34) and (38). The results obtained therefore lend considerable support to the physical basis of the model of rubberlike thermoelasticity constructed in § 3 and confidence in the theory is further increased by the mildness of the hypotheses which have been made regarding the forms of the response functions  $F$ ,  $g$  and  $h$ . In fact nothing has been assumed about the volumetric response functions  $g$  and  $h$ , and it is apparent from the details of the analysis that the results are rendered insensitive to the precise nature of these functions by the smallness of the volume changes and hence by the disparity between the shear and isothermal bulk moduli in the natural state  $N_0$ . The network response function  $F$  has been restricted only by the constitutive inequalities (26) which, subject to  $\alpha T_0$  being sufficiently small, secure qualitative agreement between theory and experiment over the whole range of behaviour investigated. It may be concluded, in particular, that a qualitatively correct account of the thermoelastic response of rubberlike materials can be developed without making explicit appeal to microscopic considerations, much less to a specific type of molecular statistics.

Quantitative evaluation of the theoretical model in relation to experimental results depends of course upon the availability of more detailed information about the response functions  $f$ ,  $g$  and  $h$ , the requirements in respect of  $f$  being much more stringent than in the cases of  $g$  and  $h$  for the

reason stated in the last paragraph. Granted a comprehensive understanding of the structure of a given rubberlike material and of the forces operating within it, one might look to the statistical theory of polymers for a means of determining these functions. Unfortunately, results obtained to date are far from complete and calculations of the network response function  $f$  are in satisfactory agreement with experiment only over rather limited ranges of deformation.† In seeking functional forms of  $f$ ,  $g$  and  $h$  for use in the remainder of this work we are therefore obliged to proceed on an empirical basis. In §5*a* expressions for the volumetric response functions  $g$  and  $h$  are adduced from the results of experiments involving isothermal compression at different temperatures, and in §5*c* a form of the network response function  $f$  is adopted which is closely related to an isothermal strain–energy function for incompressible rubberlike materials recently proposed by Ogden (1972*a*). Utilizing these functions we pursue numerically in §6 the various aspects of the behaviour of a cylindrical test-piece in extension which have been introduced in §§4*a–d*.

## 5. EMPIRICAL FORMS OF THE RESPONSE FUNCTIONS

### (a) *The volumetric response functions $g$ and $h$*

The response of a rubberlike material to volume changes is studied experimentally by the application of pressure under isothermal conditions. To a close approximation the strain produced in the test-piece (relative to the reference configuration  $N_0$ ) is a uniform dilatation, that is a homogeneous deformation in which the principal stretches are all equal.‡ A theoretical account of compression tests is therefore obtained by entering into equations (11) the expressions

$$a_1 = a_2 = a_3 = J^{\frac{1}{3}}, \quad \sigma_1 = \sigma_2 = \sigma_3 = -P$$

for the principal stretches and stresses. Here  $P$  is the applied pressure and the specimen is maintained in equilibrium by this traction without the intervention of body forces. In view of the conditions (12)<sub>1–3</sub> we arrive directly at the pressure–volume–temperature relation

$$P/\kappa = -g'(J) (T/T_0) + \alpha h'(J) (T - T_0). \quad (41)$$

At the reference temperature  $T_0$  equation (41) assumes the simple form

$$P/\kappa = -g'(J) \quad (42)$$

which is appropriate for comparison with the results of compression tests carried out at room temperature. Experiments of this kind have been widely reported in the literature and much use has been made of an observation of Murnaghan (1951, pp. 71–79) that measurements on certain metals can be accurately fitted by taking

$$g(J) = \frac{1}{m} \left( J + \frac{1}{m-1} J^{-m+1} - \frac{m}{m-1} \right) \quad (m > 1). \quad (43)$$

This response function, which is suggestive of an intermolecular force potential, is seen to satisfy the normalization conditions (16)<sub>1–3</sub>. A close agreement between curves computed from equations (42) and (43) and the results of compression tests on a variety of vulcanized rubbers at pressures

† Recent developments in the statistical theory of rubber elasticity are described in papers by Gee (1966) and Edwards (1971).

‡ Equation (41) also applies in the case of a cylindrical specimen confined within a rigid, tight-fitting sleeve and subjected to pressure on one or both of its end-faces, provided that the smallness of  $\eta$  is held to justify the neglect of the first term on the right of equation (11) (cf. Ogden 1972*b*, pp. 575–576).



up to about  $5 \times 10^6$  kPa (= 50 kbar) has been exhibited by Blatz (1969, pp. 27–29), the value of  $m$  lying between 8 and 12 depending upon the composition of the material.

A variant of equation (44), preferred by Ogden (1972*b*, §3), is

$$g(J) = m^{-2}(m \ln J + J^{-m} - 1) \quad (m > 1) \quad (44)$$

which also meets the requirements (16)<sub>1–3</sub>. The expressions for  $g'(J)$  derived from (43) and (44) differ by a factor of  $J$  which varies only between 1 and about 0.8 over the range of pressures for which experimental results are available. The effectiveness of the empirical form (43) in accurately representing experimental data on rubberlike materials is therefore equalled by (44)<sup>†</sup>, as is evident from the excellent agreement displayed in figure 1 of Ogden's paper between results for three different rubbers and the variation of  $mP/\kappa$  with  $1 - J$  given by equations (42) and (44) with  $m = 9$ .

Isothermal compression tests in which the temperature can be set at different values are more difficult to perform, but results for rubbers of carefully controlled composition have been published and some measurements of Wood & Martin (1964) on samples of the peroxide-cured vulcanizate of natural rubber referred to in §3*d* have been selected for detailed study. The ranges of pressure and temperature spanned by these experiments are quite modest, the pressure varying between zero and  $5 \times 10^4$  kPa (= 0.5 kbar) and the temperature between 0 and 25 °C, but success in accurately representing the results in the form (41) is found to depend rather sensitively on the shape ascribed to the second volumetric response function  $h$ . The following procedure was adopted.

The reference temperature in the experiments of Wood & Martin is 25 °C and the values of  $\kappa$  and  $\alpha$  are as shown in table 1. With  $\kappa = 1.95 \times 10^6$  kPa and  $m = 9$  equations (42) and (43) provide a  $J$ – $P$  curve closely fitting the measurements at  $T = T_0$ . The remainder of the experimental data were then used in conjunction with equations (41) and (43) and the stated values of  $\kappa$ ,  $\alpha$  and  $m$  to prepare a plot of  $h'(J)$  against  $J$ . The points corresponding to the 18 measurements of specific volume are too scattered for the nature of the function  $h'$  to be clearly revealed by this exercise, but it can be concluded with reasonable certainty that  $0 < h'(J) \leq 1$  and  $h''(J) > 0$  over the range of values of  $J$  attained in the tests ( $0.964 \leq J \leq 1$ ). The simplest functional form which meets these conditions is  $h'(J) = J^p$ , where  $p > 0$ , and the experimental results offer scant support for more elaborate possibilities. Observing the normalization conditions (16)<sub>4,5</sub>, we are therefore led to the expression

$$h(J) = n^{-1}(J^n - 1) \quad (n > 1) \quad (45)$$

for  $h$  and hence, in view of our earlier use of (43), to the form

$$\frac{P}{\kappa} = -\frac{T}{mT_0}(1 - J^{-m}) + \alpha(T - T_0)J^{n-1} \quad (46)$$

of the pressure–volume–temperature relation. Estimates of the exponents  $m$  and  $n$  appearing in equations (43) and (45) were next obtained by evaluating the derivatives of the isothermal bulk

<sup>†</sup> A third form of the volumetric response function  $g$ , recommended by Wood & Martin (1964, §9), is

$$g(J) = m^{-2}[\exp\{m(1-J)\} - 1 - m(1-J)] \quad (m > 0).$$

The pressure–volume relation obtained by substituting this expression into equation (42) is known as the Tait equation (cf. Tait 1889, §VII).



modulus with respect to pressure and temperature in the reference configuration  $N_0$ . The formulae for these coefficients which follow from equation (41) are

$$-g'''(1) - 1 \quad \text{and} \quad \kappa T_0^{-1}[1 + \alpha T_0\{g'''(1) - h''(1) + 1\}] \quad (47)$$

respectively and, with use of (43) and (45), the expressions

$$m \quad \text{and} \quad -\kappa T_0^{-1}\{\alpha T_0(m+n-1) - 1\}$$

are obtained. The values of the two coefficients computed from the experimental data by the method proposed by Wood & Martin in §3 of their paper are 8.06 and  $-7.84 \times 10^3 \text{ kPa K}^{-1}$ , leading to the estimates  $m = 8.1$ ,  $n = 4.6$ . With these exponents and the values of  $\kappa$  and  $\alpha$  given in table 1, equation (46) provides  $P$ - $J$  curves which agree well with the full set of experimental results. It was evident at this stage, however, that some adjustment of the values of  $m$  and  $n$  would provide an improved fit and after further computation the final choice  $m = 9$ ,  $n = \frac{5}{2}$  was made, giving the satisfactory representation of the experimental data shown in figure 2.

An attempt to fit theoretical curves to the measurements of Wood & Martin has also been made by Besseling & Voetman (1968, §4). The pressure-volume-temperature relation adopted by these authors is of the form (41) with

$$\left. \begin{aligned} g(J) &= \frac{(\alpha T_0)^2}{2n\alpha T_0 - 1} \ln \left\{ 1 + \frac{2n\alpha T_0 - 1}{n\alpha T_0} (J^n - 1) \right\} + \frac{\alpha T_0}{n} (J^n - 1), \\ h(J) &= n^{-1}(J^n - 1), \end{aligned} \right\} \quad (48)$$

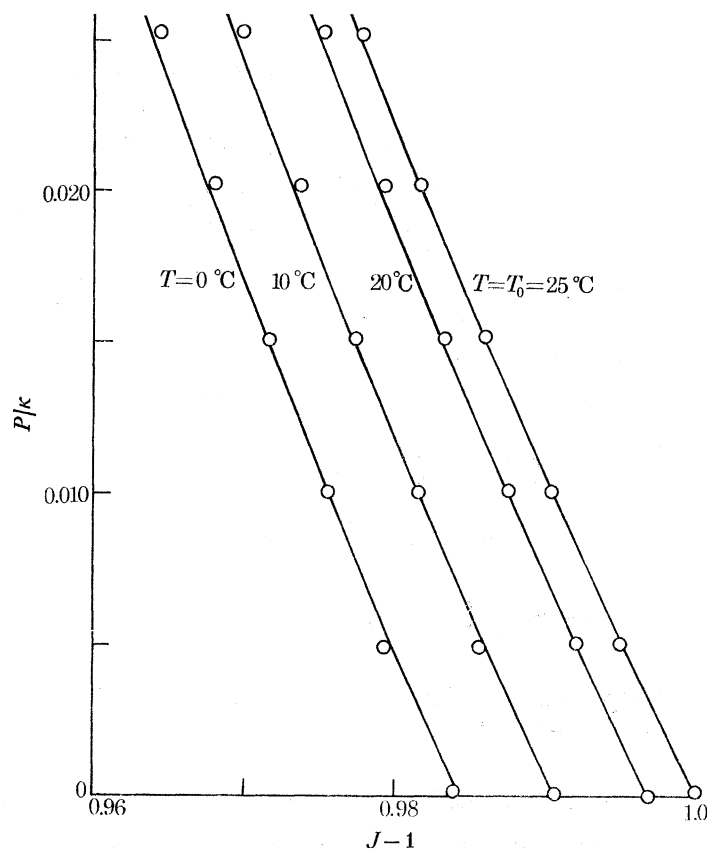


FIGURE 2. Experimental results of Wood & Martin  $\circ$  compared with theoretical curves based upon the pressure-volume-temperature relation (46) with data from (57) (i), (ii).

and 
$$n = \frac{1}{2}\{(1/\alpha T_0) + (\alpha\kappa/\rho_0 c_0)\}. \quad (49)$$

Thus the exponent  $n$  is not an independent material constant as in equation (45)†. The agreement between theory and experiment shown in figure 1 of the paper is not close and from this Besseling & Voetman infer first that the dependence of the internal energy upon volume has a more complicated form than is represented by their equations, and secondly that it is necessary to take into account the temperature dependence of the specific heat at constant deformation  $c$ . These conclusions are not supported by the present work since the internal energy function obtained by combining equations (10) and (45) is much simpler than Besseling & Voetman's equation (3.3), while the pressure–volume–temperature relation (46) is independent of  $c$  on account of assumption II. The deficiencies in the internal energy function of Besseling & Voetman must therefore be attributed to an inappropriate choice of those terms which give rise to the coefficient of  $T$  in the pressure–volume–temperature relation. In particular, it follows from equations (48) that

$$g'''(1) = 5n - 3 - 2n^2\alpha T_0 - 2(\alpha T_0)^{-1}, \quad h''(1) = n - 1,$$

and, with use of equation (49) and the data given in table 1, the values of the pressure and temperature coefficients of the isothermal bulk modulus, calculated from (47), are found to be 0.803 and  $2.99 \times 10^3$  kPa K<sup>-1</sup> respectively. Compared with the values derived from the experimental results of Wood & Martin (quoted above), the first of these coefficients is an order of magnitude too small and the second one has the wrong sign.

The considerations outlined in this subsection indicate that a variety of empirical forms of the first volumetric response function  $g$  (of which (43) and (44) are two) can be used with confidence over the whole of the observed range of compressions, but that the expression (45) for the second function  $h$  is likely to have a much more limited range of applicability. It is fortunate that, in the solution of particular problems, the influence of  $h$  is muted first by the smallness of  $\eta$  and then by the comparative smallness of  $\alpha T_0$ .

(b) *The pressure–volume–temperature relation (46)*

In equation (46),  $\kappa$ ,  $\alpha$  and  $T_0$  are positive constants and the exponents  $m$  and  $n$  each exceed unity. The temperature is therefore uniquely determined when  $P$  and  $J$  are known and the pressure when  $T$  and  $J$  are given, but the existence of a solution for  $J$  corresponding to assigned values of  $P$  and  $T$  calls for a brief discussion.

Recasting equation (46) in the form  $\varphi(J) = 0$ , where

$$\varphi(J) = 1 - J^{-m} - m\alpha(T_0/T)(T - T_0)J^{n-1} + m(PT_0/\kappa T)$$

and

$$\varphi'(J) = mJ^{-m-1} - m(n-1)\alpha(T_0/T)(T - T_0)J^{n-2},$$

we note first that  $\varphi(J) \rightarrow -\infty$  as  $J \rightarrow 0$ , and that  $\varphi(J) \rightarrow \infty$ ,  $1 + mP/\kappa$  or  $-\infty$  as  $J \rightarrow \infty$  according as  $T < T_0$ ,  $T = T_0$  or  $T > T_0$ . Since  $\varphi'(J) > 0$  for all  $J > 0$  when  $T \leq T_0$  it follows that equation (46) has a unique solution for  $J$  if  $T < T_0$  or  $T = T_0$  and  $P > -m^{-1}\kappa$ . When  $T > T_0$ ,  $\varphi'$  has a single positive zero  $J^*$ , given by

$$J^* = \{(n-1)\alpha(T_0/T)(T - T_0)\}^{-(m+n-1)^{-1}},$$

and the number of positive zeros of  $\varphi$  is therefore two, one or none according as  $\varphi(J^*)$  is positive, zero or negative. We conclude that the region of validity of the pressure–volume–temperature

† In conjunction with the data listed in table 1, equation (49) gives  $n = 3.1$ , in fair agreement with the value of 2.5 adopted above.

relation (46) is delimited by the curve in the  $(P, T)$ -plane sketched in figure 3. Since in practice interest is confined to positive pressures and a range of temperatures bounded below by the glass transition zone of the material considered ( $T/T_0 \approx 0.7$ , say) and extending about  $150^\circ\text{C}$  above the reference level ( $T/T_0 \approx 1.5$ ), this limitation, which is devoid of physical significance, presents no difficulty. Of the two positive zeros possessed by  $\varphi$  in the portion of the region of validity for which  $T > T_0$  (shown shaded in figure 3), the smaller one decreases and the larger one increases with pressure at a fixed temperature. The larger solution of equation (46) is thus associated with unphysical behaviour and must be rejected.

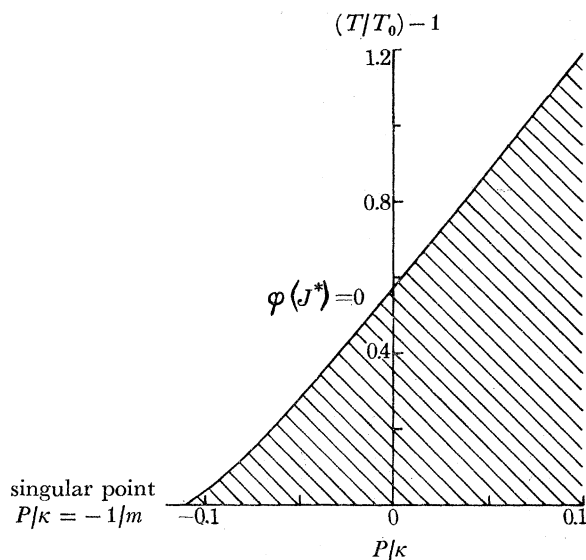


FIGURE 3. Region of validity of the pressure–volume–temperature relation (46) (data from (57) (i), (ii)).

TABLE 2. VALUES OF  $J$  SATISFYING THE PRESSURE–VOLUME–TEMPERATURE RELATION (46) FOR VARIOUS PRESSURES AND TEMPERATURES (data from (57) (i), (ii))

$\frac{T - T_0}{^\circ\text{C}}$	$P/\kappa = 0$ ( $\tilde{J}$ )	$P/\kappa = 0.001$	$P/\kappa = 0.01$	$P/\kappa = 0.02$	$P/\kappa = 0.05$
120	1.0961	1.0938	1.0759	1.0595	1.0231
100	1.0748	1.0730	1.0583	1.0442	1.0117
80	1.0569	1.0554	1.0427	1.0303	1.0007
60	1.0410	1.0397	1.0285	1.0174	0.9902
40	1.0265	1.0253	1.0152	1.0051	0.9799
20	1.0130	1.0119	1.0026	0.9933	0.9697
0	1.0000	0.9990	0.9905	0.9818	0.9596
-20	0.9874	0.9865	0.9786	0.9704	0.9494
-40	0.9751	0.9742	0.9668	0.9591	0.9391
-60	0.9628	0.9620	0.9550	0.9477	0.9286
$T^* - T_0/^\circ\text{C}$	170.0	171.8	187.9	206.0	260.9

Numerical values of  $J$  for pressures and temperatures in the ranges

$$0 \leq P/\kappa \leq 0.05, \quad -60^\circ\text{C} \leq T - T_0 \leq 120^\circ\text{C}$$

are set out in table 2. The results given in the first two columns represent the solution  $\tilde{J}(T)$  of the volume–temperature relation

$$1 - \tilde{J}^{-m} - m\alpha T_0 \{1 - (T_0/T)\} \tilde{J}^{n-1} = 0, \quad (50)$$

obtained by setting  $P = 0$  and replacing  $J$  by  $\tilde{J}$  in (46) (or, alternatively, by combining equations (43) and (45) with (15)). These figures are seen to uphold the statement, made in §4*a*, that  $\tilde{J}$  is a slowly varying function of  $T$  and, indeed, this property is observed to apply to  $J$  at each of the pressures for which calculations have been made. At the foot of each column of table 2 appears the maximum value of the temperature change  $T - T_0$  for which equation (46) can be solved for  $J$  at the indicated value of  $P/\kappa$ . These entries correspond to points on the limiting curve shown in figure 3.

(c) *The network response function  $f$*

The nature of the remaining response function  $f$  is most clearly revealed by experiments at the reference temperature  $T_0$  in which the variation of stress (or load) with deformation is measured over an extended range of strain and in circumstances in which the proportional contribution of volume changes to the stress is  $O(\eta)$ . One such situation, the extension of a cylinder, has been considered in §4*a*, the stress–stretch relation (30) being obtained by retaining only the leading term in the expansion of the axial stress  $\sigma$  in powers of  $\eta$ , and it can easily be verified, by appeal to the constitutive equations (11), that the error incurred in neglecting volume changes is likewise  $O(\eta)$  in any homogeneous deformation for which one or two of the principal stresses are equal to the atmospheric pressure  $\Pi$  (or to zero). Three deformations meeting this requirement (uniaxial extension, pure shear and equibiaxial extension) have been utilized by Treloar (1944) in tests on samples of a vulcanized natural rubber containing 8% of sulphur, the experiments involving the imposition of extension ratios up to about 7.5.

In a recent study of the correlation of theory and experiment for rubberlike solids Ogden (1972*a, b*) has proposed a family of isothermal strain-energy functions for *incompressible* elastic materials in the form of a linear combination of sums of like powers of the principal stretches, and figure 4 of his first paper displays an excellent agreement between curves based upon a three-term function of this type and the experimental data obtained by Treloar for the three deformations mentioned above. Ogden's work provides a simple, yet acceptable, empirical form of the network response function  $f$  appropriate to the special case of isochoric deformations ( $J = 1$ ). In the present, more general, context, it must be modified so as to comply with the requirement that  $f = 0$  when  $a_1 = a_2 = a_3$  (see equation (4)) and this is most readily accomplished† by adopting the expression

$$f(\mathbf{a}) = \sum_r (\mu_r / \mu \alpha_r) (a_1^{\alpha_r} + a_2^{\alpha_r} + a_3^{\alpha_r} - 3J^{\frac{1}{3}\alpha_r}) \quad (51)$$

which satisfies the normalization conditions (14) provided that

$$\sum_r \mu_r \alpha_r = 2\mu. \quad (52)$$

In equations (51) and (52)  $\alpha_r$  and  $\mu_r$  ( $r = 1, 2, \dots$ ) are material constants,  $\alpha_r$  being dimensionless and  $\mu_r$  having the dimensions of stress. For theoretical purposes the number of terms to which the summations extend need not be specified, but in practice it is such as to secure an accurate representation of experimental force–extension data for the material at hand. The analysis of Treloar's results given by Ogden (1972*a*, §4) suggests that three terms will usually suffice and

† In his second paper Ogden (1972*b*, §2) has constructed an isothermal strain–energy function for compressible rubberlike solids by adding to the form proposed for incompressible materials a function of the dimensionless specific volume  $J$ . The resulting theory differs in motivation and in detail from the treatment of isothermal deformations at  $T = T_0$  based upon equations (11) and (51). As regards the homogeneous deformations realized in Treloar's tests, however, the discrepancies between the force–extension relations supplied by the two approaches are only  $O(\eta)$  and in neither case, therefore, is there appreciable interference with the very close agreement between theory and experiment to which reference has just been made (cf. Ogden 1972*b*, p. 573).

that the goodness of fit is not particularly sensitive to the choice of values of  $\alpha_r$  and  $\mu_r$ , an expedient property also possessed by the response functions (43) and (44) in respect of the exponent  $m$  and the bulk modulus  $\kappa$ .

When the expression (51) for  $f$  is entered into the definition (19) the form of the network response function appropriate to a biaxial state of strain is found to be

$$F(J, A) = \sum_r (\mu_r / \mu \alpha_r) (2J^{\frac{1}{2}\alpha_r} A^{-\frac{1}{2}\alpha_r} + A^{\alpha_r} - 3J^{\frac{1}{3}\alpha_r}). \quad (53)$$

A simple calculation gives

$$(d/dA) \{AF_A(1, A)\} + F_{JA}(1, A) = \sum_r (\mu_r \alpha_r / \mu) A^{\alpha_r - 1}, \quad -F_{JA}(1, A) = \sum_r (\mu_r \alpha_r / 2\mu) A^{-\frac{1}{2}\alpha_r - 1},$$

and it follows that the constitutive inequalities (26) are satisfied if

$$\mu_r \alpha_r > 0 \quad \text{for each } r. \quad (54)$$

These conditions on the material constants  $\alpha_r$  and  $\mu_r$  have been shown by Ogden (1972*a*, §6; 1972*b*, §4) to arise from more general considerations affecting the realistic mechanical behaviour of elastic materials, and their implications have been studied in a variety of situations involving non-homogeneous deformations of incompressible rubberlike solids (see Ogden & Chadwick 1972; Chadwick & Haddon 1972 and Ogden *et al.* 1973). The results obtained in §4 reinforce the substantial evidence presented by these papers in favour of (54) as the basic restrictions applying to the material constants when the contribution of the polymer network to the isothermal strain energy of a rubberlike material is given an empirical representation of the type proposed by Ogden.

The material constants derived by Ogden from the experimental results of Treloar are

$$\left. \begin{aligned} \alpha_1 &= 1.3, & \alpha_2 &= 5.0, & \alpha_3 &= -2.0, \\ \mu_1 &= 6.3, & \mu_2 &= 0.012, & \mu_3 &= -0.1, \end{aligned} \right\} \quad (55)$$

the values of  $\mu_r$  here being in units of  $\text{kgf cm}^{-2}$ . These values are seen to meet the requirements (54) and, when substituted into the normalization condition (52), to fix the shear modulus relative to the natural state  $N_0$  at  $4.225 \text{ kgf cm}^{-2}$  ( $= 4.143 \times 10^2 \text{ kPa}$ ), in good agreement with the second entry in table 1.

We conclude this section with a further comment on the theory of Besseling & Voetman (1968). On using equations (3.3) and (3.6) of their paper to calculate the Helmholtz free energy  $A(F, T)$  then applying the definition (4) to the resulting expression, a complicated form of the network response function is obtained of which the dominant part (normalized in accordance with (14) and converted to the present notation) is

$$f(\mathbf{a}) = \frac{1}{2}(\frac{1}{2} + \beta_1) \{J^{-\frac{2}{3}}(a_1^2 + a_2^2 + a_3^2) - 3\} + \frac{1}{2}(\frac{1}{2} - \beta_1) \{J^{\frac{2}{3}}(a_1^{-2} + a_2^{-2} + a_3^{-2}) - 3\}. \quad (56)$$

Recognizable as a variant of the Mooney strain-energy function, the right side of equation (56) contains a single (dimensionless) material constant  $\beta_1$  which is assumed by Besseling & Voetman to satisfy the conditions  $-\frac{1}{2} \leq \beta_1 \leq \frac{1}{2}$  (cf. Truesdell & Noll 1965, pp. 350–352). It follows from (56), via the definition (19), that

$$(d/dA) \{AF_A(1, A)\} = -3F_{JA}(1, A) = (\frac{1}{2} + \beta_1) (2A + A^{-2}) + (\frac{1}{2} - \beta_1) (1 + 2A^{-3}).$$

The network response function (56) therefore complies with the constitutive inequalities (26) and the qualitatively correct account of thermoelastic inversion effects given in the final section of Besseling & Voetman's paper can be foreseen.



## 6. EXTENSION OF A CYLINDER: NUMERICAL RESULTS

Relations linking the axial stretch  $\Lambda$ , the specific volume  $J$  and the temperature  $T$  of an extended cylinder to the applied axial stress  $\sigma$  and the ambient pressure  $\Pi$  are obtained by substituting into equations (21) and (22) the empirical forms (43), (45) and (53) of the response functions, and the additional connexion between  $\Lambda$ ,  $J$  and  $T$  which holds when the deformation is performed isentropically is supplied by equation (23) (with  $S = \hat{S}$ ). No difficulty is encountered in basing numerical calculations directly on these exact equations, but the proportional error incurred in using the approximate formulae derived in §§4*a-d* is in all cases of the same order of magnitude as  $\eta$  ( $\approx 2 \times 10^{-4}$ ), indicating a level of accuracy entirely adequate for purposes of graphical display. We therefore employ the approximate results in conjunction with the expressions (43), (45) and (53) and note that the volumetric response functions enter the calculations only through the volume-temperature relation (50). The reader is reminded that the solution  $\hat{J}(T)$  of this relation, computed with the aid of the data summarized below in (57), appears in the first two columns of table 2.

The numerical results presented in this section and in §7 are based upon

$$\left. \begin{array}{l} \text{(i) the constants listed in table 1,} \\ \text{(ii) the exponents } m = 9, n = \frac{5}{2} \text{ determined in §5a,} \\ \text{(iii) the values (55) of } \alpha_r \text{ and } \mu_r. \end{array} \right\} \quad (57)$$

and

The manner in which these data have been assembled compels us to regard them as specifying a hypothetical material and it would of course be preferable to work with constants referring to an actual rubberlike solid whose thermo-mechanical response has been studied experimentally. This would be feasible, however, only if compression and extension tests of the kinds discussed in §§5*a* and 5*c* had been applied to samples of the chosen substance and no instance has been found in the literature of a single material being subjected to such detailed investigation.

## (a) Isothermal behaviour

To leading order in powers of  $\eta$  the dependence of the nominal axial stress  $s$  upon the axial stretch  $\tilde{\Lambda}$  relative to  $N$ , the natural state at temperature  $T$ , is specified by equation (29) with  $J = \hat{J}$ . On entering into this equation the expression (53) for the network response function we obtain

$$s = \sum_r \mu_r \hat{J}^{\frac{1}{2}(\alpha_r-1)} (\tilde{\Lambda}^{\alpha_r-1} - \tilde{\Lambda}^{-\frac{1}{2}\alpha_r-1}) (T/T_0). \quad (58)$$

Isothermal stress-stretch curves, computed from equation (58), are shown in figure 4, and a comparison of this plot with sets of experimentally determined isothermals given by Anthony *et al.* (1942, p. 834) and Treloar (1958, p. 30) reveals an exact formal similarity.

The approximate formula for the dilatation accompanying isothermal extension at the reference temperature  $T_0$ , derived from equations (31) and (53), is

$$J - \hat{J} = \eta \sum_r (\mu_r/\mu) (1 - \Lambda^{-\frac{1}{2}\alpha_r}). \quad (59)$$

The variation of volume change with axial stretch represented by this equation is compared in figure 5 with measurements reported by Gee *et al.* (1950), Hewitt & Anthony (1958) and Allen *et al.* (1963). The theoretical curve evidently matches the trend of the experimental results and predicts volume changes of the true order of magnitude.

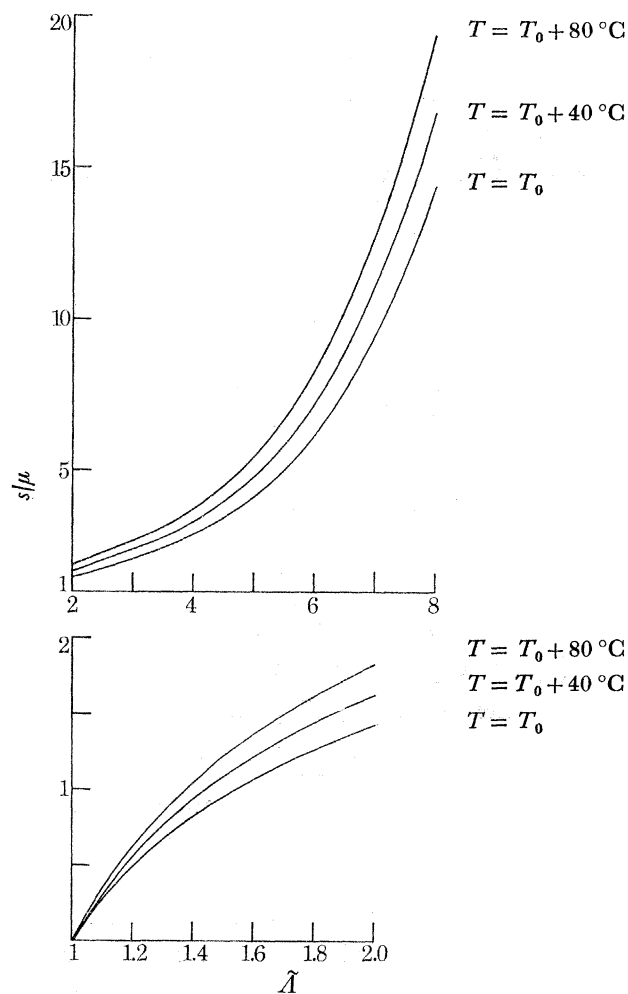


FIGURE 4. Isothermal behaviour of an extended cylinder. Variation of the nominal axial stress with the axial stretch (relative to the natural state  $N$ ) at different temperatures (equation (58); data from (57)).

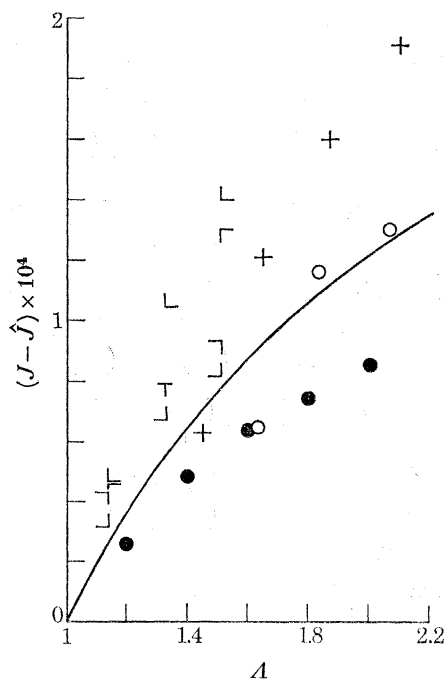


FIGURE 5. Isothermal behaviour of an extended cylinder. Experimental results of Gee *et al.* (○, +), Hewitt & Anthony (└, ▮, ▯, ▭) and Allen *et al.* (●) compared with the theoretically predicted variation of the volume change with the axial stretch at the reference temperature  $T_0$  (equation (59); data from (57)).

*(b) Isometric behaviour*

In the leading approximation the equation which governs the variation with temperature of the nominal axial stress  $s$  at fixed axial stretch  $\lambda$  relative to  $N_0$  is found by substituting from equation (53) into (24) and setting  $J = \bar{J}$  (or, more directly, by replacing  $\bar{\lambda}$  by  $\bar{J}^{-\frac{1}{2}}\lambda$  in equation (58)). The result is

$$s = \sum_r \mu_r (\lambda^{\alpha_r - 1} - \bar{J}^{\frac{1}{2}\alpha_r} \lambda^{-\frac{1}{2}\alpha_r - 1}) (T/T_0), \quad (60)$$

and isometric stress-temperature curves computed from this equation appear in figure 6. This diagram reproduces the essential features of experimental data presented graphically by Meyer & Ferri (1935, p. 578), Anthony *et al.* (1942, p. 831) and Shen *et al.* (1967, p. 794).

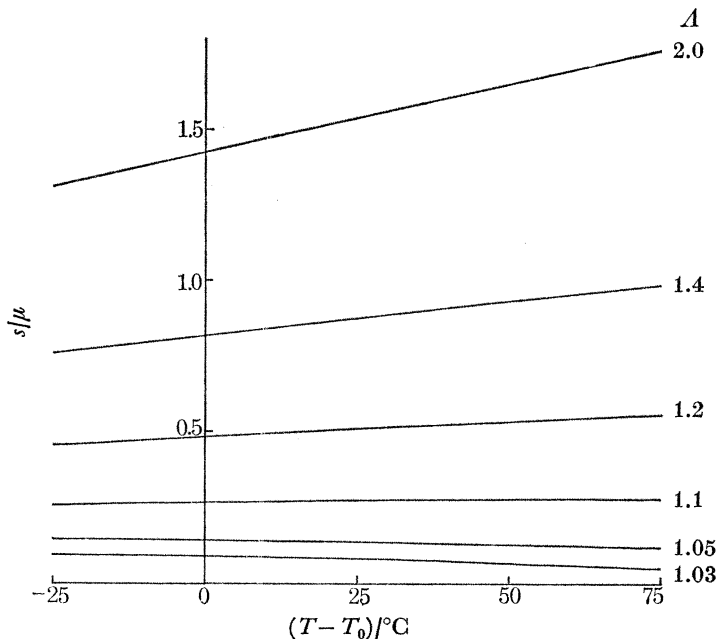


FIGURE 6. Isometric behaviour of an extended cylinder. Variation of the nominal axial stress with the temperature at different values of the axial stretch (equation (60); data from (57)).

From equation (34), in combination with (53), the isometric curve having zero gradient at  $T = T_0$  is found to correspond to an extension of 6.16% which is somewhat smaller than the inversion level indicated by the experimental results. However, the numerical results upon which figure 6 is based show that  $s$  decreases monotonically over the indicated range of temperatures when  $\lambda = 1.05$  and increases monotonically when  $\lambda = 1.11$ , while for intervening values of  $\lambda$  the isometric curve has a maximum which increases as  $\lambda$  increases. For the rubberlike material specified in (57), and with reference to the temperature interval  $-25^\circ\text{C} \leq T - T_0 \leq 75^\circ\text{C}$ , the inversion of the gradient of the isometric curves therefore occurs at extensions between 5 and 11%, the location of an inversion 'point' depending on the manner in which it is defined.

*(c) Isotonic behaviour*

The approximate formulae for the axial and transverse coefficients of thermal expansion obtained by introducing the network response function (53) into equations (37) are

$$\gamma_{\parallel} = [T_0 \sum_r \mu_r \alpha_r (\lambda^{\alpha_r} + \frac{1}{2} \lambda^{-\frac{1}{2}\alpha_r})]^{-1} \sum_r \mu_r \left[ -(1 - \alpha T_0) \lambda^{\alpha_r} + \left\{ 1 + \frac{1}{2} \alpha T_0 (\alpha_r - 2) \right\} \lambda^{-\frac{1}{2}\alpha_r} \right], \quad (61)$$

$$\gamma_{\perp} = \frac{1}{2} (\alpha - \gamma_{\parallel}).$$

The variations of  $\gamma_{\parallel}$  and  $\gamma_{\perp}$  with the axial stretch  $A$  are represented graphically in figure 7, and marked on this diagram are points corresponding to measurements of the axial coefficient made by Joule (1859, p. 106; see also Flory 1953, p. 437). It is again apparent that the observed behaviour of the specimen is correctly portrayed by the theory and the agreement between the computed curves and the experimental points is quite satisfactory. The extension at which  $\gamma_{\parallel} = 0$  is found to be 7.55 %.

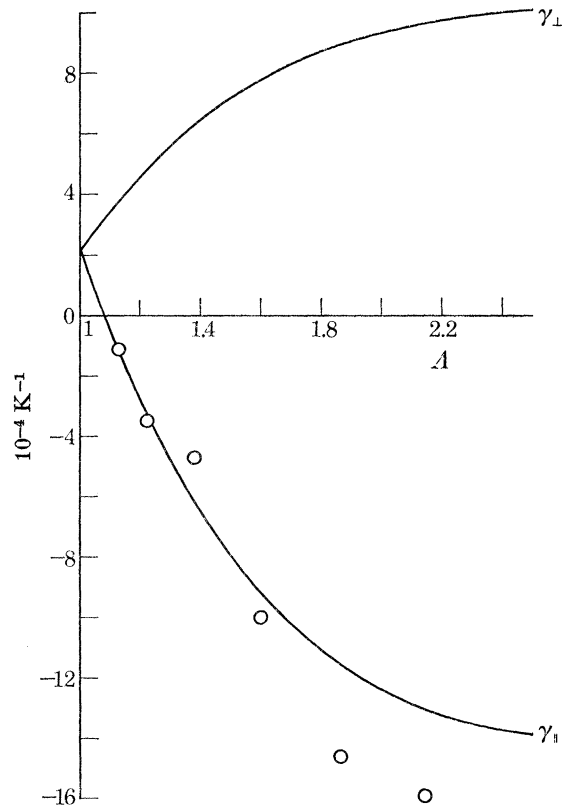


FIGURE 7. Isotonic behaviour of an extended cylinder. Experimental results of Joule ( $\circ$ ) compared with the theoretically predicted variation of the axial and transverse coefficients of thermal expansion with the axial stretch at the reference temperature  $T_0$  (equation (61); data from (57)).

(d) *Isentropic behaviour*

Equation (39), in combination with (53), yields the approximate expression

$$T - T_0 = \{\rho_0 c_0 (1 + \epsilon)\}^{-1} \sum_r (\mu_r / \alpha_r) (1 - A^{-\frac{1}{2}\alpha_r}) \{(A^{\frac{1}{2}\alpha_r} - 1)(A^{\frac{1}{2}\alpha_r} + 2) - \alpha T_0 \alpha_r\} \quad (62)$$

for the change in temperature resulting from extension of the cylinder under isentropic conditions. Figure 8 shows the temperature-stretch curve computed from equation (62) together with points representing experimental data due to Joule (1859, p. 105) and Dart (see James & Guth 1943, p. 475). As in the preceding subsections there is complete qualitative accord between theory and observation and, bearing in mind possible differences between the physical constants of the rubbers used in the tests and those listed in (57), the agreement is quantitatively as close as could be expected. The minimum point on the theoretical curve corresponds to an extension of 6.16 % and the extension at which the temperature change alters sign is 12.61 %.

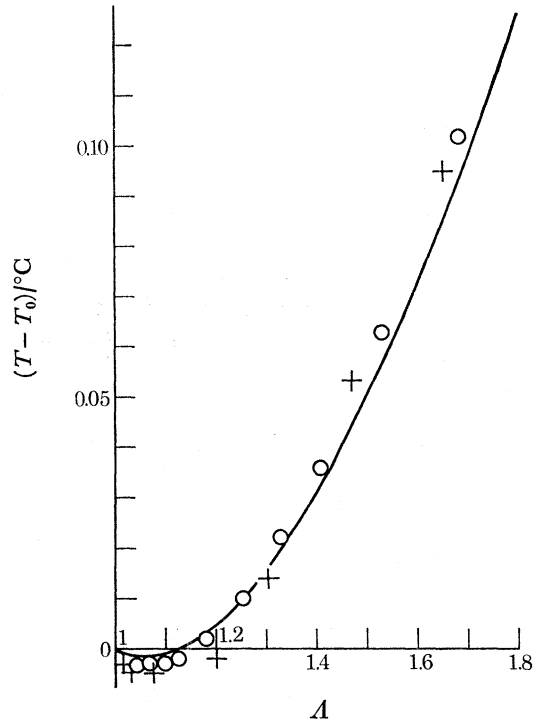


FIGURE 8. Isentropic behaviour of an extended cylinder. Experimental results of Dart (O) and Joule (+) compared with the theoretically predicted variation of the temperature change with the axial stretch (equation (62); data from (57)).

### 7. ISOTHERMAL DEFORMATIONS OF INCOMPRESSIBLE RUBBERLIKE MATERIALS

Extensive use has been made in §§ 4–6 of the fact that, for rubberlike materials and with reference to the natural configuration  $N_0$ , the isothermal bulk modulus  $\kappa$  greatly exceeds the shear modulus  $\mu$ . In isothermal deformations at the reference temperature  $T_0$  such a material can, for most practical purposes, be regarded as incompressible and, as first demonstrated by Rivlin (1948, 1949*a*, *b*), far-reaching developments in the analytical solution of particular problems are then made possible. But the incompressibility condition  $J = 1$  is physically inappropriate in circumstances in which the temperature departs from the uniform value  $T_0$  since volume changes due to thermal expansion are then precluded. The seemingly natural step of replacing  $J = 1$  by a constraint of the form  $J = \phi(T)$  has been shown by Beevers (1969) to lead to equations which, when linearized and applied to the study of small amplitude body waves, yield unacceptable results, and in the same connexion Green *et al.* (1970, p. 899) have encountered difficulties in proving that solutions of initial-boundary value problems governed by the linearized equations are unique. The discussion which now follows is concerned only with deformations occurring under isothermal conditions and it is found possible, in this restricted context, to satisfactorily incorporate into the model of rubberlike thermoelasticity formulated in §3 the concept of mechanical incompressibility.



(a) *Isothermal deformations at  $T = T_0$* 

When the temperature is everywhere fixed at the reference point  $T_0$  the principal stress–stretch relations provided by equations (11) are

$$\sigma_i = \mu J^{-1} a_i \frac{\partial f}{\partial a_i} + \kappa g'(J). \quad (63)$$

The assumption that the material under consideration can undergo no volume change in deformations at temperature  $T_0$  is associated with a formal limiting process in which  $\kappa \rightarrow \infty$  and  $J \rightarrow 1$  (implying, via (16)<sub>2</sub>, that  $g'(J) \rightarrow 0$ ) in such a way that  $\kappa g'(J)$  approaches a finite limit  $-q$ . Equations (63) are then replaced by

$$\sigma_i = \mu a_i \frac{\partial f}{\partial a_i} - q \quad \text{with} \quad a_1 a_2 a_3 = 1. \quad (64)$$

The quantity  $q$ , interpretable as a pressure, is not a specified function of the deformation.

On substituting into (64) the form (51) of the network response function and setting  $\hat{p} = q + \sum_r \mu_r$  we obtain

$$\sigma_i = \sum_r \mu_r a_i^{\alpha_r} - \hat{p} \quad \text{with} \quad a_1 a_2 a_3 = 1. \quad (65)$$

These are the principal stress–stretch relations corresponding to the isothermal strain–energy function for incompressible rubberlike materials proposed by Ogden (1972*a*; see equation (14)). Solutions of problems involving non-homogeneous deformations of circular cylinders and tubes have been obtained, on the basis of equations (65), by Ogden & Chadwick (1972), Chadwick & Haddon (1972) and Ogden *et al.* (1973), and spherically symmetric deformations and motions governed by these equations have been studied by Ogden (1972*a*, §5) and Chadwick (1974).

(b) *Isothermal deformations at  $T \neq T_0$* 

It has been shown in §3*b* that, in the absence of applied forces, a uniform temperature change from  $T_0$  to a value  $T$  in the interval  $\mathcal{T}$  gives rise to thermal expansion represented by the conformal deformation  $N_0 \rightarrow N$  in which each of the principal stretches is equal to  $\mathcal{J}^{\frac{1}{3}}$  where  $\mathcal{J}$  satisfies the volume–temperature relation (15). If the material is assumed to be mechanically incompressible volume changes can only be brought about by thermal expansion and isothermal deformations at temperature  $T$  are subject to the constraint  $a_1 a_2 a_3 = \mathcal{J}$ . There is associated with this assumption a formal limiting process in which  $\kappa \rightarrow \infty$  and  $J \rightarrow \mathcal{J}$  in such a way that the product of  $\kappa$  with the expression on the left of equation (15) approaches a finite limit  $-\tilde{q}$ , and the principal stress–stretch–temperature relations (11) then assume the form

$$\sigma_i = \left( \mu \mathcal{J}^{-1} a_i \frac{\partial f}{\partial a_i} - \tilde{q} \right) \frac{T}{T_0} \quad \text{with} \quad a_1 a_2 a_3 = \mathcal{J}. \quad (66)$$

At a representative particle the value of  $\tilde{q}$  depends upon  $a_i$  and  $T$  but the relation is not specified *a priori* as part of the characterization of the material; in short,  $\tilde{q}$  is not a response function.

The result of entering the expression (51) for  $f$  into equations (66) and putting

$$\tilde{\hat{p}} = (\tilde{q} + \sum_r \mu_r \mathcal{J}^{\frac{1}{3}\alpha_r - 1})(T/T_0)$$

is

$$\sigma_i = \sum_r \mu_r \mathcal{J}^{-1} a_i^{\alpha_r} (T/T_0) - \tilde{\hat{p}} \quad \text{with} \quad a_1 a_2 a_3 = \mathcal{J}.$$

These equations have a formal similarity with (65) which is most clearly exhibited by introducing the principal stretches  $\tilde{a}_i = J^{-\frac{1}{3}}a_i$  measured from the natural state  $N$  and defining

$$\tilde{\mu}_r = \mu_r J^{\frac{1}{3}\alpha_r - 1} (T/T_0) \quad (r = 1, 2, \dots), \quad 2\tilde{\mu} = \sum_r \tilde{\mu}_r \alpha_r. \quad (67)$$

Then 
$$\sigma_i = \sum_r \tilde{\mu}_r \tilde{a}_i^{\alpha_r} - \tilde{p} \quad \text{with} \quad \tilde{a}_1 \tilde{a}_2 \tilde{a}_3 = 1, \quad (68)$$

and we conclude, on comparing (65) and (68), that the analysis of isothermal deformations of a mechanically incompressible rubberlike material at a temperature different from  $T_0$  can be deduced from the theory of isothermal deformations at the reference temperature by simply regarding the principal stretches as reckoned from  $N$  and interpreting  $\tilde{\mu}_r$  in accordance with equation (67)<sub>1</sub>. The resemblance between equations (67)<sub>2</sub> and (52) suggests that  $\tilde{\mu}$  should be the shear modulus of the material relative to the thermally expanded configuration  $N$  and it is not difficult to confirm that this is indeed the case. Equation (13)<sub>1</sub>, in conjunction with (11) and (12), furnishes the expression

$$\frac{3}{4}\mu J^{-\frac{1}{3}}(\partial^2 f / \partial a_i^2)_{a_1=a_2=a_3=J^{-\frac{1}{3}}}(T/T_0)$$

for the shear modulus relative to  $N$  and this is found to equal  $\tilde{\mu}$  when use is made of equation (51) and the definitions (67).

As a simple application of the analogy which has just been set up we return once more to the problem of the extension of a cylinder illustrated in figure 1. The connexion between the axial stress  $\sigma$  and the axial stretch  $\Lambda$  in deformations at the reference temperature  $T_0$  is established by making the substitutions (18) (with  $J = 1$ ) in the constitutive equations (65) and eliminating  $p$ . The result obtained is

$$\sigma = \sum_r \mu_r (\Lambda^{\alpha_r} - \Lambda^{-\frac{1}{2}\alpha_r})$$

(cf. Ogden 1972 *a*, p. 572). On replacing  $\mu_r$  by  $\tilde{\mu}_r$  and  $\Lambda$  by  $\tilde{\Lambda}$  the analogous relation for isothermal deformations at temperature  $T$  is found to be

$$\sigma = \sum_r \mu_r J^{\frac{1}{3}\alpha_r - 1} (\tilde{\Lambda}^{\alpha_r} - \tilde{\Lambda}^{-\frac{1}{2}\alpha_r}) (T/T_0), \quad (69)$$

and equation (58) is recovered on observing that  $s = J^{\frac{2}{3}}\tilde{\Lambda}^{-1}\sigma$ , the cross-sectional area of the cylinder in the natural state  $N$  being  $J^{\frac{2}{3}}$  times its value in  $N_0$ .

The choice of a single-term network response function of the form (51) in which  $\alpha_1 = 2$  corresponds, in relation to mechanically incompressible materials, to the adoption of the neo-Hookean strain-energy function for deformations at the reference temperature  $T_0$ . Equation (58) then reduces to

$$s = \mu J^{\frac{1}{3}}(\tilde{\Lambda} - \tilde{\Lambda}^{-2}) (T/T_0) = \mu(\Lambda - J\Lambda^{-2}) (T/T_0), \quad (70)$$

a result which differs (by a factor of  $J^{\frac{2}{3}}$  on the right) from the force-extension relation for this problem given by Blatz (1969, equation (149)†). Blatz's derivation of equation (70) is based upon a theory of mechanically incompressible rubberlike materials which proceeds from first principles and regards the principal stretches  $\tilde{a}_i$  relative to  $N$  and the temperature  $T$  as independent variables. The theory yields an analogy between the principal stress-stretch relations governing isothermal deformations at temperatures  $T_0$  and  $T(\neq T_0)$  (see Blatz 1969, equation (134))

† Blatz's article contains some misprints. In the cited equation the first minus sign should indicate equality and in the first exponent  $\partial$  should be replaced by 2.

which, applied to equations (65), reproduces (68) but with  $(67)_1$  replaced by  $\tilde{\mu}_r = \mu_r J^{-1}(T/T_0)$ . This difference accounts for the discrepancy noted above. In fact the variables chosen by Blatz are not independent, owing to the dependence of the  $\tilde{a}_i$  upon  $T$ , and it is basically for this reason that the treatment of rubberlike thermoelasticity given in his article is judged, in the light of the present work, to be defective.

(c) *Combined torsion and extension of a circular cylinder*

As a more substantial application of the theory developed in §7*b* we consider in this concluding subsection a non-homogeneous deformation for which experimental results, obtained under isothermal conditions and at different temperatures, are available. The tests in question were carried out by Boyce & Treloar (1970) and the solution of the corresponding problem in finite elastostatics has been obtained, on the basis of the constitutive equations (65), by Ogden & Chadwick (1972, §2).

In the experimental situation a circular cylindrical test-piece is maintained at a fixed uniform temperature and deformed first by the application of a uniaxial extension, then by twisting about the axis of symmetry. The variation with temperature of the torque needed to maintain a specified angular displacement of one end of the cylinder relative to the other was measured by Boyce & Treloar and found to be linear with positive gradient throughout the ranges of torsional and extensional strain investigated and for samples of various vulcanizates of natural rubber.

The theoretical work of Ogden & Chadwick refers to combined torsion and extension at the reference temperature  $T_0$  of a circular cylinder composed of an incompressible rubberlike material conforming to the principal stress–stretch relations (65). It is assumed that the curved surface of the cylinder is stress-free† and that tractions are applied to the end-faces which ensure that the cylindrical form of the bounding surface is preserved in the deformation. Under these conditions the cylinder is held in equilibrium solely by the action of the surface tractions and the resultant torque which must be exerted on each end-face in order to support the deformation is given by

$$M = 2\pi\tau^{-3} \sum_r \mu_r \lambda^{\frac{1}{2}\alpha_r - \frac{3}{2}} \{F(\lambda^{\frac{3}{2}}, a; \alpha_r + 2) + F(\lambda^{\frac{3}{2}}, a; \alpha_r - 2) - (\lambda^{\frac{3}{2}} + \lambda^{-\frac{3}{2}}) F(\lambda^{\frac{3}{2}}, a; \alpha_r)\}, \quad (71)$$

where 
$$a = \frac{1}{2} \{ \lambda^{\frac{1}{2}} (\tau R)^2 + (\lambda^{\frac{3}{2}} + \lambda^{-\frac{3}{2}})^2 \}^{\frac{1}{2}} + \frac{1}{2} \{ \lambda^{\frac{1}{2}} (\tau R)^2 + (\lambda^{\frac{3}{2}} - \lambda^{-\frac{3}{2}})^2 \}^{\frac{1}{2}} \quad (72)$$

and 
$$F(x, y; \alpha) = (y^\alpha + y^{-\alpha} - x^\alpha - x^{-\alpha})/\alpha, \quad F(x, y; 0) = 0$$

(see Ogden & Chadwick 1972, equations (27) and (26)). Here  $\lambda$  is the axial stretch,  $\tau$  the twist per unit extended length and  $R$  the radius of the cylinder in the natural state  $N_0$ . The angle through which one end-face is turned relative to the other is hence  $\tau\lambda L$  radians where  $L$  is the length of the cylinder in  $N_0$ .

In order to deduce from equation (71) a formula for the torque required to maintain a deformation of the cylinder at uniform temperature  $T \in \mathcal{T}$  in which the length and the total twist retain their former values ( $\lambda L$  and  $\tau\lambda L$ ) we follow the procedure laid down in §7*b*. The  $\mu_r$  are replaced by the  $\tilde{\mu}_r$  (defined by equation (67)<sub>1</sub>), the strain parameters  $\lambda$ ,  $\tau$  by  $\tilde{\lambda}$ ,  $\tilde{\tau}$ , their counterparts measured in relation to the natural configuration  $N$ , and the dimensions  $R$ ,  $L$  by  $\tilde{R} = J^{\frac{1}{3}}R$ ,  $\tilde{L} = J^{\frac{1}{3}}L$ , the radius and length of the cylinder in  $N$ . Since  $\tilde{\lambda}\tilde{L} = \lambda L$  and  $\tilde{\tau}\tilde{L} = \tau\lambda L$  it follows that

† In the laboratory this surface is subject to atmospheric pressure, but since attention is confined here to the torque acting on the cylinder no correction is needed.

$\tilde{\lambda} = \mathcal{J}^{-\frac{1}{2}}\lambda$  and  $\tilde{\tau} = \tau$ , and the required equation representing the variation of torque with temperature at constant strain is therefore

$$M = 2\pi\tau^{-3} \sum_r \mu_r \mathcal{J}^{\frac{1}{2}\alpha_r - \frac{1}{2}} \lambda^{\frac{1}{2}\alpha_r - \frac{3}{2}} \{F(\mathcal{J}^{-\frac{1}{2}}\lambda^{\frac{1}{2}}, \tilde{a}; \alpha_r + 2) + F(\mathcal{J}^{-\frac{1}{2}}\lambda^{\frac{1}{2}}, \tilde{a}; \alpha_r - 2) - (\mathcal{J}^{-\frac{1}{2}}\lambda^{\frac{1}{2}} + \mathcal{J}^{\frac{1}{2}}\lambda^{-\frac{3}{2}}) F(\mathcal{J}^{-\frac{1}{2}}\lambda^{\frac{1}{2}}, \tilde{a}; \alpha_r)\} (T/T_0), \quad (73)$$

where

$$\tilde{a} = \frac{1}{2} \{(\mathcal{J}\lambda)^{\frac{1}{2}} (\tau R)^2 + (\mathcal{J}^{-\frac{1}{2}}\lambda^{\frac{1}{2}} + \mathcal{J}^{\frac{1}{2}}\lambda^{-\frac{3}{2}})^2\}^{\frac{1}{2}} + \frac{1}{2} \{(\mathcal{J}\lambda)^{\frac{1}{2}} (\tau R)^2 + (\mathcal{J}^{-\frac{1}{2}}\lambda^{\frac{1}{2}} - \mathcal{J}^{\frac{1}{2}}\lambda^{-\frac{3}{2}})^2\}^{\frac{1}{2}} \quad (74)$$

and  $\mathcal{J}$  is given by the volume-temperature relation (50).

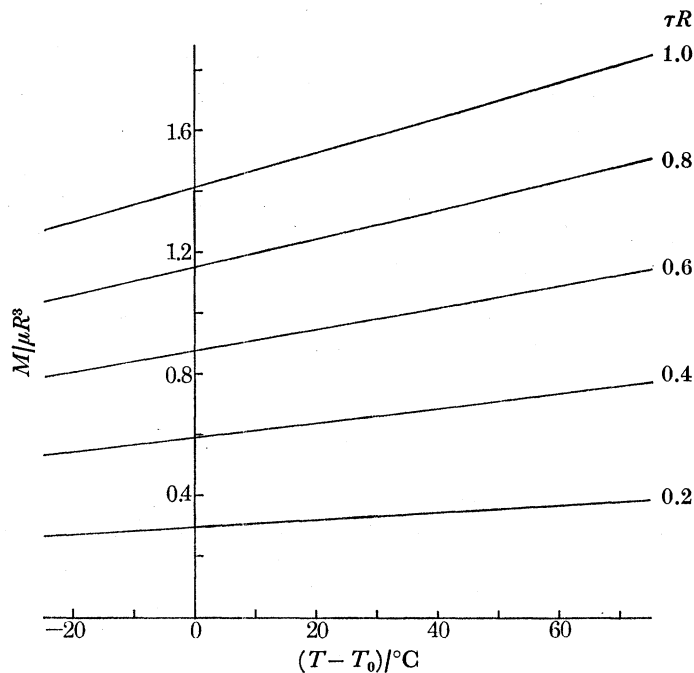


FIGURE 9. Combined torsion and extension of a circular cylinder. Variation of the torque with the temperature at indicated values of the torsional strain parameter and at 25% extension (equation (73); data from (57)).

The special form of equation (73) obtained by adopting the 'neo-Hookean' single-term network response function with  $\alpha_1 = 2$  is

$$M = \frac{1}{2} \pi \mu \mathcal{J} \tau R^4 (T/T_0) = \frac{1}{2} \pi \mu \mathcal{J}^{-\frac{1}{2}} \tau \tilde{R}^4 (T/T_0), \quad (75)$$

a result which may appropriately be compared with a theoretical torque-temperature relation derived by Treloar (1969*b*, equation (32)). Treloar's formula, which is based upon constitutive equations associated with a modified form of the statistical theory of Gaussian networks, differs from equation (75)<sub>2</sub> only by a factor on the right representing the effect of cross-linking on the mean-square end-to-end length of the network chains (see Treloar 1969*a*, p. 280). It follows from (75)<sub>1</sub> that

$$\partial M / \partial T = (M/T) (1 + \tilde{\alpha} T),$$

where  $\tilde{\alpha} = \mathcal{J}^{-1} \partial \mathcal{J} / \partial T$  is the volume coefficient of thermal expansion relative to  $N$ . The torque is therefore a monotonically increasing function of the temperature for all values of the torsional and extensional strain parameters and no thermoelastic inversion effect is in evidence (cf. Treloar 1969*b*, p. 300).

In the general solution (73) the value of  $MT_0/T$  corresponding to specified values of  $\tau$  and  $\lambda$  is approximately constant on account of the weak dependence of  $\bar{J}$  upon  $T$  indicated by the first two columns of table 2. In fact  $MT_0/T$  is approximately equal to the expression on the right of equation (71) which, as pointed out by Ogden & Chadwick (1972, figure 1), increases monotonically with  $\tau$  at a fixed value of the axial extension  $\lambda$ . These features are confirmed by numerical calculations based upon equation (73), with (74) and (50), and the data summarized in (57). A selection of the results is presented graphically in figure 9 which correctly reproduces the pattern of torque-temperature curves determined experimentally by Boyce & Treloar (1970, figure 4). In both the computations and the measurements the coefficient  $\partial M/\partial T$ , evaluated at constant deformation, is of one sign, suggesting that the absence of anomalous thermoelastic behaviour, noted above in connexion with the special temperature-torque relation (75), is a typical property of rubberlike materials.

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