Aspects of the phenomenological theory of rubber thermoelasticity

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Some recent work on the phenomenological theory of isothermal rubber elasticity for homogeneous biaxial deformations is extended to the thermoelastic case. Within this phenomenological framework some new general results are established and then applied to consideration of strain induced volume dilation, the notion of anisotropy of compressibility and the energetic contribution to the stress. Certain thermodynamic relations are also examined and reviewed in the light of the phenomenological results.

(Keywords: thermoelasticity; rubbers; deformation; phenomenological theory; compressibility; isotropic elasticity)

(1) INTRODUCTION

In this paper attention is focussed on homogeneous deformations of rubberlike materials subject to biaxial and uniaxial stresses in the presence of hydrostatic pressure. The approach is primarily phenomenological, and it is assumed that the response of rubberlike materials can be described within the framework of *isotropic* thermoelasticity theory on the basis of the Helmholtz free energy function. The formulation of the basic stress–deformation relations appropriate to the isothermal situation given by Ogden[1-3] is generalized to allow for temperature changes. In particular, for any temperature T (>0) general relations between the biaxial stresses t_1, t_2, the pressure P, the volume ratio J and the 'modified' principal stretches $\lambda_1^* \equiv \lambda_1 J^{-1/3}$, $\lambda_2^* \equiv \lambda_2 J^{-1/3}$ are obtained, where λ_1, λ_2 are principal stretches relative to an arbitrary reference configuration. These relations embrace those given by Chadwick[4] and Chadwick and Creasy[5], who were concerned principally with the case of uniaxial stress.

For a general (isotropic) form of the Helmholtz free energy function we analyse the volume dilation accompanying deformation and the strain-induced anisotropy of compressibility for both biaxial and uniaxial states of stress, generalizing previous results described by Ogden[1,6] and references therein. The notion of isotropy of compressibility, which arose initially from thermodynamic considerations[7,8] relating to the contribution to the stress from the internal energy, is shown to be independent of reference configuration. We emphasize that the expression that we give for the anisotropy factor of Elliott and Lippmann[7] is valid for an arbitrary form of Helmholtz free energy function, and can be specialized for any particular model of the network response function.

The energetic contribution to the stress is a quantity which has received much attention in the literature (see, for example, the review by Shen and Croucher[9]). It is expressible in terms of experimentally determinable thermodynamic quantities, but only after certain assumptions have been made; in particular, a specific form for the anisotropy factor has to be either chosen or derived on the basis of a specific model. For the case of uniaxial stress Creasy[10] has shown that the energetic contribution can be derived alternatively by using an explicit phenomenological model of rubber thermoelasticity. Further discussion of this approach is contained in Chadwick and Creasy[5]. Here we examine the energetic contribution to biaxial states of stress and we derive a number of general formulae. These formulae are then used to obtain results for particular phenomenological models, including the modified entropic model of Chadwick and Creasy[5].

The importance of the interplay between the thermodynamic and phenomenological approaches is emphasized and the need for additional experimental data, particularly biaxial data, is highlighted.

(2) THERMOELASTIC DEFORMATIONS

We consider a cuboidal specimen of homogeneous material unstressed at a uniform temperature T_0. We denote this natural configuration by N_0. Suppose that the material is heated to a uniform temperature T, and deformed homogeneously parallel to the edges of the cuboid; let the principal stretches λ_1, λ_2, λ_3 represent the (positive) ratios of the lengths of the deformed edges of the cuboid to the corresponding lengths in N_0. The associated principal Cauchy stresses (per unit deformed area of cross-section) are denoted by t_1, t_2, t_3.

Material which is *isotropic* relative to N_0 is characterized by the Helmholtz free energy $A(\lambda_1,\lambda_2,\lambda_3,T)$ per unit mass, which depends symmetrically on λ_1, λ_2, λ_3.

Let N denote the current (deformed) configuration at temperature T. Then, the densities ρ_0, ρ of the material in N_0 and N respectively are related by

$$\rho = \rho_0 J^{-1} \tag{1}$$

where

$$J = \lambda_1 \lambda_2 \lambda_3 \tag{2}$$

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The principal Cauchy stresses are given by

$$t_i=\rho\lambda_i\frac{\partial A}{\partial\lambda_i}\qquad i=1,2,3 \tag{3}$$

and the entropy S by

$$S=-\frac{\partial A}{\partial T} \tag{4}$$

The internal energy U (per unit mass) is related to A and S by

$$A=U-TS \tag{5}$$

so that equation (3) may also be written

$$t_i=\rho\lambda_i\frac{\partial U}{\partial\lambda_i}-\rho T\lambda_i\frac{\partial S}{\partial\lambda_i}\qquad i=1,2,3 \tag{6}$$

where, in general, U and S each depend on λ_1, λ_2, λ_3 and T.

In order to distinguish the dilatational and distortional parts of the deformation we define the *modified stretches*

$$\lambda_i^*=J^{-1/3}\lambda_i\qquad i=1,2,3 \tag{7}$$

as in the isothermal case[1], so that

$$\lambda_1^*\lambda_2^*\lambda_3^*=1 \tag{8}$$

Since only two of the modified stretches are independent, we now regard λ_1^*, λ_2^*, J and T as the independent variables and define

$$\hat{A}(\lambda_1^*,\lambda_2^*,J,T)\equiv A(J^{1/3}\lambda_1^*,J^{1/3}\lambda_2^*,J^{1/3}\lambda_1^{*-1}\lambda_2^{*-1},T)$$

It then follows that

$$t_1-t_3=\rho\lambda_1^*\frac{\partial\hat{A}}{\partial\lambda_1^*},\qquad t_2-t_3=\rho\lambda_2^*\frac{\partial\hat{A}}{\partial\lambda_2^*}, \tag{9}$$

$$\tfrac{1}{3}(t_1+t_2+t_3)=\rho J\frac{\partial\hat{A}}{\partial J}, \tag{10}$$

and

$$S=-\frac{\partial\hat{A}}{\partial T} \tag{11}$$

In the natural configuration N_0 we must have

$$\hat{A}(1,1,1,T_0)=0,\quad \frac{\partial\hat{A}}{\partial\lambda_\alpha^*}(1,1,1,T_0)=0,\quad \alpha=1,2 \tag{12}$$

$$\frac{\partial^2\hat{A}}{\partial\lambda_1^*\partial\lambda_2^*}(1,1,1,T_0)=2\frac{\mu_0}{\rho_0},\ \frac{\partial^2\hat{A}}{\partial\lambda_\alpha^{*2}}(1,1,1,T_0)=4\frac{\mu_0}{\rho_0}\quad \alpha=1,2 \tag{13}$$

$$\frac{\partial\hat{A}}{\partial J}(1,1,1,T_0)=0,\qquad \frac{\partial^2\hat{A}}{\partial J^2}(1,1,1,T_0)=\frac{\kappa_0}{\rho_0} \tag{14}$$

where μ_0 and κ_0 denote respectively the shear modulus and bulk modulus in N_0.

For any fixed temperature, $\hat{A}$, and hence A, can be determined from triaxial experiments in which λ_1^*, λ_2^*, J are varied independently, with t_1-t_3, t_2-t_3 and $\frac{1}{3}(t_1+t_2+t_3)$ as dependent variables. Since t_1-t_3 and t_2-t_3 are unaffected by a superposed pressure P we may alternatively set $t_3=0$ and take t_1, t_2 and P as dependent variables. The appropriate stress–deformation relations are then

$$t_1=\rho\lambda_1^*\frac{\partial\hat{A}}{\partial\lambda_1^*},\qquad t_2=\rho\lambda_2^*\frac{\partial\hat{A}}{\partial\lambda_2^*} \tag{15}$$

and

$$\tfrac{1}{3}(t_1+t_2)-P=\rho J\frac{\partial\hat{A}}{\partial J} \tag{16}$$

Instead of t_1, t_2 it will sometimes be preferable to make use of the corresponding components of nominal (or engineering) stress s_1, s_2 (measured per unit cross-sectional area in N_0). These are given by

$$s_1=J\lambda_1^{-1}t_1=\rho J^{2/3}\frac{\partial\hat{A}}{\partial\lambda_1^*}$$
$$s_2=J\lambda_2^{-1}t_2=\rho J^{2/3}\frac{\partial\hat{A}}{\partial\lambda_2^*} \tag{17}$$

For the special case of uniaxial tension with $t_2=0$ and $\lambda_2^*=\lambda_1^{*-\frac{1}{2}}$ equations (15)–(17) specialize to

$$t_1=\rho\lambda_1^*\frac{\partial\tilde{A}}{\partial\lambda_1^*},\qquad \tfrac{1}{3}t_1-P=\rho J\frac{\partial\tilde{A}}{\partial J} \tag{18}$$

$$s_1=\rho J^{2/3}\frac{\partial\tilde{A}}{\partial\lambda_1^*} \tag{19}$$

where

$$\tilde{A}(\lambda_1^*,J,T)=\hat{A}(\lambda_1^*,\lambda_1^{*-\frac{1}{2}},J,T) \tag{20}$$

For purely isothermal deformations full details of the derivations of the equations which are generalized by equations (9)–(20) can be found in refs. 1–3.

Now let $\bar{N}$ be an arbitrary configuration at temperature T, related to N_0 by a pure dilatation. If $\bar{\lambda}_1$, $\bar{\lambda}_2$, $\bar{\lambda}_3$ denote the stretches in N relative to $\bar{N}$ then

$$\bar{\lambda}_i=\bar{J}^{-1/3}\lambda_i \tag{21}$$

and

$$\bar{\lambda}_1\bar{\lambda}_2\bar{\lambda}_3=J/\bar{J}=\bar{\rho}/\rho \tag{22}$$

where $\bar{\rho}$ is the density in $\bar{N}$ and

$$\bar{J}=\rho_0/\bar{\rho} \tag{23}$$

Relative to $\bar{N}$ the modified stretches are given by

$$\bar{\lambda}_i^*=(J/\bar{J})^{-1/3}\bar{\lambda}_i=J^{-1/3}\lambda_i=\lambda_i^*$$

Thus they are independent of the choice of reference configuration $\bar{N}$. Since equations (15) and (16) are unaffected by replacing J by $J/\bar{J}$ their structure is likewise independent of $\bar{N}$.

If $\bar{N}$ is a natural configuration then it follows from equation (16) that

$$\frac{\partial \hat{A}}{\partial J}(1,1,\bar{J},T)=0 \qquad (24)$$

This equation determines $\bar{J}$ as a function of T subject to $\bar{J}=1$ when $T=T_0$.

For a material which is mechanically incompressible at any fixed temperature T we have $J=\bar{J}$ for all deformations, and $\bar{\rho}$ depends on T through equations (23) and (24).

The shear bulk moduli μ and κ in $\bar{N}$ at temperature T are given by

$$\bar{\rho}\frac{\partial^2 \hat{A}}{\partial \lambda_\alpha^{*2}}(1,1,\bar{J},T)=2\bar{\rho}\frac{\partial^2 \hat{A}}{\partial \lambda_1^*\partial \lambda_2^*}(1,1,\bar{J},T)=4\mu \quad \alpha=1,2$$
$$\bar{\rho}\bar{J}^2\frac{\partial^2 \hat{A}}{\partial J^2}(1,1,\bar{J},T)=\kappa \qquad (25)$$

with $\mu=\mu_0$, $\kappa=\kappa_0$ when $T=T_0$ and $\bar{\rho}=\rho_0$.

Relative to N_0 the components s_1, s_2 of nominal stress are given by (17). It follows that the corresponding components $\bar{s}_1$, $\bar{s}_2$ relative to $\bar{N}$ are

$$\bar{s}_1=\bar{J}^{-2/3}s_1, \qquad \bar{s}_2=\bar{J}^{-2/3}s_2 \qquad (26)$$

(3) STRAIN-INDUCED VOLUME DILATION

From equations (15) and (16) we obtain

$$\tfrac{1}{3}\rho_0 J^{-1}\lambda_\beta^*\frac{\partial \hat{A}}{\partial \lambda_\beta^*}-P=\rho_0\frac{\partial \hat{A}}{\partial J} \qquad (27)$$

where summation from 1 to 2 is implied by repetition of the index β. This equation provides an expression for P in terms of λ_1^*, λ_2^*, J and T. When T and P are fixed, however, (27) describes (implicitly) the dependence of the volume ratio J on the distortional part of the deformation, λ_1^*, λ_2^*, or equivalently on λ_1, λ_2.

How J varies with deformation under biaxial stress can be determined by differentiating (27) with respect to λ_α^* to obtain

$$\left(\frac{\partial J}{\partial \lambda_\alpha^*}\right)_{T,P}=\frac{\left(\tfrac{1}{3}J^{-1}\lambda_\beta^*\dfrac{\partial^2 \hat{A}}{\partial \lambda_\beta^*\partial \lambda_\alpha^*}+\tfrac{1}{3}J^{-1}\dfrac{\partial \hat{A}}{\partial \lambda_\alpha^*}-\dfrac{\partial^2 \hat{A}}{\partial J\partial \lambda_\alpha^*}\right)}{\left(\dfrac{\partial^2 \hat{A}}{\partial J^2}-\tfrac{1}{3}J^{-1}\lambda_\beta^*\dfrac{\partial^2 \hat{A}}{\partial \lambda_\beta^*\partial J}+\tfrac{1}{3}J^{-2}\lambda_\beta^*\dfrac{\partial \hat{A}}{\partial \lambda_\beta^*}\right)} \quad \alpha=1,2 \qquad (28)$$

This generalizes a result given by Ogden[1] for the purely isothermal case with $P=0$.

For a pure dilatation ($\lambda_\alpha^*=1$) equation (28) reduces to

$$\left(\frac{\partial J}{\partial \lambda_\alpha^*}\right)_{T,P}=\tfrac{1}{3}J^{-1}\left\{\frac{\partial^2 \hat{A}}{\partial \lambda_1^*\partial \lambda_\alpha^*}(1,1,J,T)+\frac{\partial^2 \hat{A}}{\partial \lambda_2^*\partial \lambda_\alpha^*}(1,1,J,T)\right\}\Big/\frac{\partial^2 \hat{A}}{\partial J^2}(1,1,J,T)$$

and, in the configuration $\bar{N}$, use of (25) shows that

$$\left(\frac{\partial J}{\partial \lambda_\alpha^*}\right)_{T,P}=\frac{2\mu\bar{J}}{\kappa} \qquad \alpha=1,2 \qquad (29)$$

On specializing to the uniaxial case equation (28) becomes

$$\left(\frac{\partial J}{\partial \lambda_1^*}\right)_{T,P}=\frac{\left(\dfrac{1}{3}J^{-1}\lambda_1^*\dfrac{\partial^2 \tilde{A}}{\partial \lambda_1^{*2}}+\dfrac{1}{3}J^{-1}\dfrac{\partial \tilde{A}}{\partial \lambda_1^*}-\dfrac{\partial^2 \tilde{A}}{\partial J\partial \lambda_1^*}\right)}{\left(\dfrac{\partial^2 \tilde{A}}{\partial J^2}-\dfrac{1}{3}J^{-1}\lambda_1^*\dfrac{\partial^2 \tilde{A}}{\partial J\partial \lambda_1^*}+\dfrac{1}{3}J^{-1}\lambda_1^*\dfrac{\partial \tilde{A}}{\partial \lambda_1^*}\right)}, \qquad (30)$$

and this reduces to $\mu\bar{J}/\kappa$ in $\bar{N}$.

For rubberlike materials μ/κ is of order 10^{-4} so that volume changes accompanying distortion are small. In the isothermal context the mathematical consequences of the assumption that $(\partial J/\partial \lambda_\alpha^*)_{T,P}$ remains of order μ/κ as distortion proceeds under biaxial or uniaxial stress have been fully explored by Ogden[1,6]. In particular, for uniaxial stress particular forms of the strain–energy function have been used to examine equations (27) and (30) in detail (with the temperature fixed at T_0 throughout). We shall not therefore discuss this aspect of the theory further in this paper.

It is instructive to relate the above to corresponding formulae which arise in the thermodynamic approach, in which different variables are used. Let V and V_0 denote the volume of the material in the current and reference configurations, N and N_0 respectively, and L_α and $L_{0\alpha}$ the lengths of the sides in N and N_0 such that

$$V=JV_0,\ L_\alpha=\lambda_\alpha L_{0\alpha} \qquad \alpha=1,2 \qquad (31)$$

At fixed P and T the *strain-induced volume dilation coefficient* $(\partial V/\partial L_\alpha)_{P,T}$ is expressible in terms of the phenomenological variables through

$$\frac{L_\alpha}{V}\left(\frac{\partial V}{\partial L_\alpha}\right)_{P,T}=\frac{\lambda_\alpha}{J}\left(\frac{\partial J}{\partial \lambda_\alpha}\right)_{P,T} \qquad \alpha=1,2 \qquad (32)$$

Moreover, in terms of the modified stretches it can be shown that

$$\left(\frac{\partial J}{\partial \lambda_\alpha}\right)_{P,T}=J^{-1/3}\left(\frac{\partial J}{\partial \lambda_\alpha^*}\right)_{P,T}\Big/\left\{1+\tfrac{1}{3}J^{-1}\lambda_\beta^*\left(\frac{\partial J}{\partial \lambda_\beta^*}\right)_{P,T}\right\} \qquad (33)$$

Hence an explicit expression is obtainable for $(\partial V/\partial L_\alpha)_{P,T}$, by use of equation (30), *for an arbitrary form of Helmholtz free-energy function* when the stresses are biaxial.

For the uniaxial case with $L_1=L$ the above specializes to provide an expression for $(\partial V/\partial L)_{P,T}$, which plays a prominent role in the thermoelastic literature[8,9,11,12]. In particular, equation (33) becomes

$$\left(\frac{\partial J}{\partial \lambda_1}\right)_{P,T}=J^{-1/3}\left(\frac{\partial J}{\partial \lambda_1^*}\right)_{P,T}\Big/\left\{1+\tfrac{1}{3}J^{-1}\lambda_1^*\left(\frac{\partial J}{\partial \lambda_1^*}\right)_{P,T}\right\} \qquad (34)$$

For an analysis of $(\partial V/\partial L)_{P,T}$ in respect of particular material models we refer to the work of Price[11]. It is worth remarking here that Flory[12] considered that theoretical evaluation of $(\partial V/\partial L)_{P,T}$ required commitment to a model. In the light of the above calculation we now emphasize that this is not the case. However, results for any specific model can be obtained in either the uniaxial or biaxial case by appropriate substitution for $\tilde{A}$ or $\hat{A}$ respectively.

(4) ANISOTROPY OF LINEAR COMPRESSIBILITY

In the thermodynamic theory the uniaxial load is usually denoted by f and this is used in conjunction with the variables L, V, P and T. Equation (31) shows how V and L ($=L_1$) are related to J and λ_1. We now note that the connection between f and s_1 is

$$s_1 V_0 = f L_0 \tag{35}$$

The standard thermodynamic identity

$$\left(\frac{\partial V}{\partial L}\right)_{P,T} = \left(\frac{\partial f}{\partial P}\right)_{L,T} \tag{36}$$

is then equivalent to

$$\left(\frac{\partial J}{\partial \lambda_1}\right)_{P,T} = \left(\frac{\partial s_1}{\partial P}\right)_{\lambda_1,T} \tag{37}$$

Equation (36) has been used extensively in the literature[9,11] as a means of estimating the volume dilation coefficient $(\partial V/\partial L)_{P,T}$ in terms of other coefficients which are more easily accessible to experimental determination. In particular, equation (36) can be recast in the form

$$\left(\frac{\partial V}{\partial L}\right)_{P,T} = \tfrac{1}{3}\eta L K_f \left(\frac{\partial f}{\partial L}\right)_{P,T} \tag{38}$$

or as

$$\left(\frac{\partial V}{\partial L}\right)_{P,T} = \tfrac{1}{3}\eta L K_L \left(\frac{\partial f}{\partial L}\right)_{V,T} \tag{39}$$

These are *exact* equations, with

$$K_f = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{f,T}, \qquad K_L = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{L,T} \tag{40}$$

defining the bulk compressibilities at constant f and L respectively and

$$\eta = \frac{3V}{L}\left(\frac{\partial L}{\partial V}\right)_{f,T} = -\frac{3}{L}\left(\frac{\partial L}{\partial P}\right)_{f,T} \Big/ K_f \tag{41}$$

defining the *anisotropy factor* of Elliott and Lippmann[7], where $-L^{-1}(\partial L/\partial P)_{f,T}$ is the *linear compressibility*.

If $\eta = 1$ the linear compressibility is said to be *isotropic*, that is equal to $\frac{1}{3}K_f$. In the reference configuration $\eta = 1$ exactly, but in general this is not the case, although the approximation $\eta = 1$ can be justified for small deformations[8]. Equation (38), with K_f taken as a constant, has been used for the indirect experimental determination of $(\partial V/\partial L)_{P,T}$ (for references, see Price[11]); this requires a knowledge of η and of the elastic modulus $(\partial f/\partial L)_{P,T}$. Expressions for these in respect of a number of different material models have been given in the literature[9,11,12].

As we have seen in the previous section, however, a general expression for $(\partial V/\partial L)_{P,T}$ has been obtained on the basis of the phenomenological theory for an arbitrary form of Helmholtz free energy function. Thus, from the purely theoretical point of view, this obviates the need for employing approximations in relation to identities such as equations (38) and (39). In particular, the need for an approximation to the anisotropy factor η is avoided by this approach. It is worth noting in passing that exact thermomechanical expressions for the volume dilation coefficient which do not involve η can also be given; for example, it can be shown that

$$\left(\frac{\partial V}{\partial L}\right)_{P,T} = -VK_L\left(\frac{\partial f}{\partial V}\right)_{L,T} = VK_L\left(\frac{\partial P}{\partial L}\right)_{V,T} \tag{42}$$

and

$$\left(\frac{\partial V}{\partial L}\right)_{P,T} = V(K_f - K_L)\left(\frac{\partial f}{\partial V}\right)_{P,T} \tag{43}$$

The first two of these have been used by Flory[12] and Creasy[10] amongst others, but equation (43) has not, to this author's knowledge, been seen previously.

Of the coefficients involved on the right-hand sides of equations (38), (39), (42) and (43) it is $(\partial f/\partial L)_{P,T}$ which is the most amenable to experimental determination, but this is coupled with η.

Although this anisotropy factor is not strictly required in the phenomenological context it does arise in connection with the energetic contribution to the stress (as we see in the next section), essentially through use of equation (38). It is useful, therefore, to provide a general formula for η, and this we now do in respect of the phenomenological theory. We remark that, as with $(\partial V/\partial L)_{P,T}$, η does not require a specific model for its evaluation.

First, from equations (31), (41) and equation (7), we have

$$\eta - 1 = 3J\lambda_1^{-1}\left(\frac{\partial \lambda_1}{\partial J}\right)_{s_1,T} - 1 = 3J\lambda_1^{*-1}\left(\frac{\partial \lambda_1^*}{\partial J}\right)_{s_1,T} \tag{44}$$

for uniaxial stress s_1 (with $s_2 = 0$). For fixed s_1 and T equation (19) provides a relation between λ_1^* and J, from which we obtain

$$J\left(\frac{\partial \lambda_1^*}{\partial J}\right)_{s_1,T} = \left(\frac{1}{3}\frac{\partial \tilde{A}^*}{\partial \lambda_1^*} - J\frac{\partial^2 \tilde{A}^*}{\partial J \partial \lambda_1^*}\right) \Big/ \frac{\partial^2 \tilde{A}^*}{\partial \lambda_1^{*2}} \tag{45}$$

The requirement of isotropy of linear compressibility therefore amounts to the vanishing of equation (45). Since, from equation (26), $\bar{s}_1 = \bar{J}^{-2/3}s_1$, and $\bar{J}$ depends only on T, it follows that the formula equation (45) is independent of the choice of reference temperature and configuration. But the actual value of equation (45) does depend on T in general. For $T = T_0$ the result of equation (45) was given by Ogden[6].

For illustration, we choose (relative to $\bar{N}$)

$$\bar{\rho}A(\lambda_1,\lambda_2,\lambda_3,T) = \tfrac{1}{2}\bar{\mu}J^{m-2/3}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) + g(J,T)$$

a modified form of the Gaussian model, where g is a function of J and T, $\bar{\mu}$ depends on T and m is a constant. This yields

$$\eta = 1 + (1-3m)\frac{(\lambda_1^{*3}-1)}{(\lambda_1^{*3}+2)}$$

which reduces to the Gaussian formula[12]

$$\eta = \frac{3}{\lambda_1^{*3}+2}$$

when $m=\frac{2}{3}$.

The resulting equation (45) can be extended to the case of biaxial stresses to determine the coefficients $J(\partial\lambda_\alpha^*/\partial J)_{s_\beta,T}$ for $\alpha=1,2$ at fixed s_β ($\beta=1,2$). For future reference we record that differentiation of equation (17) with respect to J using equation (1) yields

$$J\left(\frac{\partial\lambda_1^*}{\partial J}\right)_{s_\beta,T} = \frac{\dfrac{\partial^2\hat{A}}{\partial\lambda_2^{*2}}\left(\dfrac{1}{3}\dfrac{\partial\hat{A}}{\partial\lambda_1^*} - J\dfrac{\partial^2\hat{A}}{\partial J\partial\lambda_1^*}\right) - \dfrac{\partial^2\hat{A}}{\partial\lambda_1^*\partial\lambda_2^*}\left(\dfrac{1}{3}\dfrac{\partial\hat{A}}{\partial\lambda_2^*} - J\dfrac{\partial^2\hat{A}}{\partial J\partial\lambda_2^*}\right)}{\left\{\dfrac{\partial^2\hat{A}}{\partial\lambda_1^{*2}}\dfrac{\partial^2\hat{A}}{\partial\lambda_2^{*2}} - \left(\dfrac{\partial^2\hat{A}}{\partial\lambda_1^*\partial\lambda_2^*}\right)^2\right\}}$$

in full generality, and similarly for $J(\partial\lambda_2^*/\partial J)_{s_\beta,T}$.

Corresponding expressions for the bulk compressibilities at fixed s_β, λ_β or λ_β^* (generalizations of equation (40) in particular) can be obtained along similar lines. Further, the linear compressibilities at fixed s_β can then be expressed in the form

$$-\frac{1}{\lambda_\alpha}\left(\frac{\partial\lambda_\alpha}{\partial P}\right)_{s_\beta,T} = -\frac{1}{J}\left(\frac{\partial J}{\partial P}\right)_{s_\beta,T}\left\{\frac{1}{3} + \frac{J}{\lambda_\alpha^*}\left(\frac{\partial\lambda_\alpha^*}{\partial J}\right)_{s_\beta,T}\right\}$$

For simplicity we illustrate this in the uniaxial context.

From equation (27) appropriately specialized we obtain

$$-\frac{1}{J}\left(\frac{\partial J}{\partial P}\right)_{\lambda_1^*,T} = \frac{1}{\rho}\left\{J^2\frac{\partial^2\tilde{A}}{\partial J^2} - \frac{1}{3}\lambda_1^* J\frac{\partial^2\tilde{A}}{\partial J\partial\lambda_1^*} + \frac{1}{3}\lambda_1^*\frac{\partial\tilde{A}}{\partial\lambda_1^*}\right\}^{-1} \quad (46)$$

and it can also be shown that

$$\left(\frac{\partial J}{\partial P}\right)_{\lambda_1^*,T} = \left(\frac{\partial J}{\partial P}\right)_{s_1,T}\left\{1 - \left(\frac{\partial J}{\partial\lambda_1^*}\right)_{P,T}\left(\frac{\partial\lambda_1^*}{\partial J}\right)_{s_1,T}\right\}$$

and

$$\left(\frac{\partial J}{\partial P}\right)_{\lambda_1,T} = \left(\frac{\partial J}{\partial P}\right)_{\lambda_1^*,T}\left\{1 + \frac{1}{3}J^{-1}\lambda_1^*\left(\frac{\partial J}{\partial\lambda_1^*}\right)_{P,T}\right\}$$

Since, for rubberlike materials, $(\partial J/\partial\lambda_1^*)_{P,T}$ is of order 10^{-4} we have established in general terms that the bulk compressibilities at fixed s_1, λ_1 and λ_1^* respectively differ only by a term of this order, and for many purposes can be regarded as equivalent. This is the usual practice in the literature. In particular, in equations (38), (39) and (42) the identification $K_L=K_f$ is legitimate, but in equation (43) the difference must be taken into consideration. In the former case it can be seen from equation (46) that each may be approximated as

$$\rho J^2\left(\frac{\partial^2\tilde{A}}{\partial J^2}\right)^{-1}$$

since the remaining terms are of order μ/κ compared with $\partial^2\tilde{A}/\partial J^2$. In the isothermal context this latter approximation has been explored fully and exploited by Ogden[1].

(5) ENERGETIC CONTRIBUTION TO THE STRESS

Suppose that, when expressed in terms of λ_1^*, λ_2^*, J and T, the internal energy and entropy are written as $\hat{U}$ and $\hat{S}$ respectively, analogously to the definition of $\hat{A}$. Then equation (5) becomes

$$\hat{A} = \hat{U} - T\hat{S} \quad (47)$$

and the stress–deformation relations can be written

$$s_\alpha = \rho_0 J^{-1/3}\frac{\partial\hat{A}}{\partial\lambda_\alpha^*} \equiv \rho_0 J^{-1/3}\frac{\partial\hat{U}}{\partial\lambda_\alpha^*} - \rho_0 T J^{-1/3}\frac{\partial\hat{S}}{\partial\lambda_\alpha^*} \qquad \alpha=1,2 \quad (48)$$

in conjunction with

$$P = \frac{1}{3}\rho_0 J^{-1}\lambda_\beta^*\frac{\partial\hat{A}}{\partial\lambda_\beta^*} - \rho_0\frac{\partial\hat{A}}{\partial J} \quad (49)$$

relative to N_0. We recall that summation over β from 1 to 2 is implied in equation (49).

The energetic contribution to the stress in equation (48), s_α^e say, is defined as

$$s_\alpha^e = \rho_0 J^{-1/3}\frac{\partial\hat{U}}{\partial\lambda_\alpha^*} \quad (50)$$

From equations (48) and (50) it therefore follows that

$$s_\alpha^e = s_\alpha - T\left(\frac{\partial s_\alpha}{\partial T}\right)_{J,\lambda_\beta} = s_\alpha - T\left(\frac{\partial s_\alpha}{\partial T}\right)_{J,\lambda_\beta^*} \quad (51)$$

where the subscript λ_β represents (λ_1,λ_2).

Considerable effort has been devoted in the literature to deriving expressions for the ratio s_α^e/s_α for the uniaxial case ($\alpha=1$ with $s_2=0$) and to comparing these with experimental data (much of this work is summarized by Shen and Croucher[9]). Here we obtain some new theoretical results for the biaxial case and we note that their specialization to $s_2=0$ embraces previously established formulae.

Equation (51) can be rewritten in a number of different ways depending on which independent variables are selected. First, we note that

$$s_\alpha^e = s_\alpha - T\left(\frac{\partial s_\alpha}{\partial T}\right)_{P,\lambda_\beta} - \frac{\beta T}{K_\lambda}\left(\frac{\partial J}{\partial\lambda_\alpha}\right)_{P,T} \quad (52)$$

where K_λ is the bulk compressibility and β the thermal expansion coefficient at fixed λ_1, λ_2. Thus

$$K_\lambda = -\frac{1}{J}\left(\frac{\partial J}{\partial P}\right)_{T,\lambda_\beta}, \qquad \beta = \frac{1}{J}\left(\frac{\partial J}{\partial T}\right)_{P,\lambda_\beta} \quad (53)$$

The derivation of equation (52) makes use of the identity

$$\left(\frac{\partial s_\alpha}{\partial P}\right)_{T,\lambda_\beta} = \left(\frac{\partial J}{\partial\lambda_\alpha}\right)_{T,P} \qquad \alpha=1,2$$

which generalizes equation (37). The coefficient $(\partial J/\partial\lambda_\alpha)_{P,T}$ in equation (52) is expressible in terms of biaxial anisotropy factors by means of a generalization of equation (38) to this case, or, alternatively, can be given explicit form through equations (33) and (28).

An equation equivalent to equation (52) which is also exact is

$$s_\alpha^e = s_\alpha - T\left(\frac{\partial s_\alpha}{\partial T}\right)_{P,\lambda_\beta} - \beta T J^{2/3}\left(\frac{\partial P}{\partial \lambda_\alpha^*}\right)_{J,T} \qquad (54)$$

and equation (49) may be used to give the latter term explicit form in terms of $\hat{A}$. The final equivalent form that we mention here is

$$s_\alpha^e = s_\alpha - T\left(\frac{\partial s_\alpha}{\partial T}\right)_{P,\lambda_\beta^*} + \beta^* T J\left(\frac{\partial s_\alpha}{\partial J}\right)_{T,\lambda_\beta^*} \qquad (55)$$

where

$$\beta^* = \frac{1}{J}\left(\frac{\partial J}{\partial T}\right)_{P,\lambda_\beta^*} \qquad (56)$$

We note the connection

$$\beta^* = \beta\left\{1 + \frac{1}{3}J^{-1}\lambda_\beta^*\left(\frac{\partial J}{\partial \lambda_\beta^*}\right)_{P,T}\right\}$$

and hence, in the light of the discussion in Section 3, we deduce the approximation $\beta^* \simeq \beta$, which may be used in equation (55).

We emphasize that equations (52), (54) and (55) are completely general for biaxial stresses in the presence of hydrostatic pressure. The specialization of equation (52) to the uniaxial case yields results noted previously[9-12], but corresponding specializations of equations (54) and (55) with the independent variables used here have not, to this author's knowledge, appeared in the literature before. The uniaxial counterpart of equation (52) and its variants expressed in terms of the modulus $(\partial s_1/\partial\lambda_1)_{P,T}$ and the anisotropy factor or in terms of $(\partial s_1/\partial P)_{T,\lambda_1}$ can be related directly to experimental data[9,11] in order to determine the ratio s_1^e/s_1 for particular ranges of deformation. A more compact expression for this ratio is simply

$$s_1^e/s_1 = \frac{\partial \tilde{U}}{\partial \lambda_1^*}\bigg/\frac{\partial \tilde{A}}{\partial \lambda_1^*}$$

where $\tilde{A}$ is defined by equation (20) and $\tilde{U}$ similarly. However, if the function $\tilde{A}$ is known then

$$\tilde{U} = \tilde{A} - T\frac{\partial \tilde{A}}{\partial T}$$

is determined, and

$$s_1^e/s_1 = 1 - T\frac{\partial^2 \tilde{A}}{\partial T\partial \lambda_1^*}\bigg/\frac{\partial \tilde{A}}{\partial \lambda_1^*} \qquad (57)$$

is described in terms of $\tilde{A}$ and its derivatives. Thus, the phenomenological theory in which the form of the Helmholtz free energy is established can provide a check on the values of s_1^e/s_1 obtained by other means.

For biaxial stresses equation (57) generalizes to

$$s_\alpha^e/s_\alpha = 1 - T\frac{\partial^2 \hat{A}}{\partial T\partial \lambda_\alpha^*}\bigg/\frac{\partial \hat{A}}{\partial \lambda_\alpha^*} \qquad \alpha = 1,2 \qquad (58)$$

We now illustrate the application of equation (58) to some particular forms of $\hat{A}$. First we consider a generalization of the modified Gaussian model used in Section 4: this is given by

$$\rho\hat{A} = \tfrac{1}{2}\mu(J,T)(\lambda_1^{*2} + \lambda_2^{*2} + \lambda_1^{*-2}\lambda_2^{*-2}) + h(J,T) \qquad (59)$$

with J measured relative to N_0 and where $\mu(J,T)$ is defined by

$$2\mu(J,T) = \rho\frac{\partial^2 \hat{A}}{\partial \lambda_1^*\partial \lambda_2^*}(1,1,J,T) \qquad (60)$$

When $J = \bar{J}$ the expression (60) coincides with the μ defined in equation (25), and $\mu(\bar{J},T) = \bar{\mu}(T)$ was used in Section 4.

Substitution of equation (59) into equation (58) yields simply

$$s_\alpha^e/s_\alpha = 1 - \frac{T}{\mu}\frac{\partial \mu}{\partial T} \qquad \alpha = 1,2 \qquad (61)$$

We note that the right-hand side of equation (61) has the same value for each of $\alpha = 1$ and $\alpha = 2$, is independent of the distortion, but depends on J through μ. At constant pressure J depends on T and equation (61) may be rewritten as

$$s_\alpha^e/s_\alpha = 1 - \frac{T}{\mu}\frac{d\mu}{dT} + \frac{T}{\mu}\left(\frac{\partial \mu}{\partial J}\right)_T\left(\frac{\partial J}{\partial T}\right)_{P,\lambda_\beta^*}$$

or, by use of equation (56), as

$$s_\alpha^e/s_\alpha = 1 - \frac{T}{\mu}\frac{d\mu}{dT} + \frac{JT\beta^*}{\mu}\left(\frac{\partial \mu}{\partial J}\right)_T \qquad (62)$$

If μ is proportional to $J^{-1/3}$ the final term in this expression simplifies to $-\frac{1}{3}\beta^* T$ and the result for the neo-Hookean model described by Shen and Croucher[9] is recovered.

We now turn our attention to the modified entropic model of rubber thermoelasticity due to Chadwick and Creasy[5]. For this model it is assumed that the internal energy and entropy can be written in the form

$$U(\lambda_1,\lambda_2,\lambda_3,T) = U_1(\lambda_1,\lambda_2,\lambda_3) + U_2(T)$$

$$S(\lambda_1,\lambda_2,\lambda_3,T) = S_1(\lambda_1,\lambda_2,\lambda_3) + S_2(T)$$

where U_1, S_1 are independent of T and U_2, S_2 depend only on T. A consequence of this is that the free energy is expressible in the form

$$A(\lambda_1,\lambda_2,\lambda_3,T) = A(\lambda_1,\lambda_2,\lambda_3,T_0)\frac{T}{T_0} - U_1(\lambda_1,\lambda_2,\lambda_3)\left(\frac{T}{T_0} - 1\right) + A_2(T) - A_2(T_0)\frac{T}{T_0} \qquad (63)$$

where

$$A_2(T) = U_2(T) - TS_2(T).$$

In the notation $\hat{A}$, $\hat{U}$ with $\hat{A}_0 \equiv \hat{A}(\lambda_1^*, \lambda_2^*, J, T_0)$ equations (48) become

$$s_\alpha = \rho_0 J^{-1/3} \frac{T}{T_0} \frac{\partial \hat{A}_0}{\partial \lambda_\alpha^*} - \rho_0 J^{-1/3} \left(\frac{T}{T_0} - 1 \right) \frac{\partial \hat{U}}{\partial \lambda_\alpha^*} \quad (64)$$

with s_α^e as in equation (50). It follows that

$$s_\alpha^e / s_\alpha = \frac{\tau_\alpha}{[(1 - \tau_\alpha) T / T_0 + \tau_\alpha]} \qquad \alpha = 1,2 \quad (65)$$

where

$$\tau_\alpha = \frac{\partial \hat{U}}{\partial \lambda_\alpha^*} \bigg/ \frac{\partial \hat{A}_0}{\partial \lambda_\alpha^*} \qquad \alpha = 1,2 \quad (66)$$

is *independent* of T, but in general dependent on J and λ_α^*.

Equation (65) generalizes the uniaxial formula given by Chadwick and Creasy[5] to the biaxial case. Chadwick and Creasy have discussed the energetic contribution to the stress in some detail for the extension of a cylinder within the setting of their phenomenological model. In particular, they have examined experimental data in relation to specific forms of the functions $\hat{U}_1$ and $\hat{A}_0$ specialized to the considered deformation. We refer to their paper for details of their calculations and for an assessment of the experimental data. In broad terms there is good agreement between theory and experiment, but the extent of the data is somewhat limited. There is clearly a need for more experimental results for the case of uniaxial stress for both large and small deformations. More importantly, there is a need for some attempt to be made to obtain biaxial data which can then be assessed within the general phenomenological framework described here. Experimental determination of the ratio s_α^e/s_α can be direct, on the basis of equation (51), or indirect, through measurement of thermodynamic coefficients such as occur in equations (52), (54) or (55). The simplest general theoretical form of the ratio is equation (58), and this can be related to the data for any chosen form of $\hat{A}$. This connection between the phenomenological theory and the thermodynamic approach is emphasized since there is much to be gained by a dual attack on the underlying objective, namely the characterization of the thermoelastic properties of rubberlike materials by means of the Helmholtz free energy function.

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