Arch. Mech., 33, 4, pp. 523-539, Warszawa 1981

On a thermodynamic theory of fiber-reinforced thermoelastic materials with thermo-kinematic constraints

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A NEW METHOD for the indirect introduction of thermo-kinematic constraints into a thermodynamic continuum theory of fiber-reinforced thermoelastic materials is presented. It is applicable to all materials for which the symmetry class and hence the representations of the constitutive functions are known. Detailed results are given for the unidirectionally and the bidirectionally fiber-reinforced materials subject to the constraints of incompressibility with purely thermal volume expansion and of inextensibility in the fiber directions with thermal expansion of the fibres. Some applications to rubber-elasticity are reported. It is shown, in particular, that the energy-elastic effect of rubber can be explained in quantitative agreement with experiments.

Przedstawiono metodę pośredniego wprowadzenia więzów termokinematycznych do termodynamicznej teorii kontynualnej materiałów termosprężystych zbrojonych włóknami. Stosuje się ona do wszelkich materiałów, dla których znane są klasy symetrii, a więc i reprezentacje funkcji konstytutywnych. Podano wyniki szczegółowe dla materiałów zbrojonych jedno- i dwukierunkowo poddanych więzom nieściśliwości, przy czysto termicznych odkształceniach objętościowych, oraz więzom nierozciągliwości w kierunku zbrojenia przy termicznych wydłużeniach włókien. Omówiono pewne zastosowania dotyczące sprężystości materiałów gumopodobnych. Pokazano w szczególności, że energosprężyste zjawiska w gumie przebiegają w ilościowej zgodności z wynikami doświadczeń.

Представлен метод косвенного введения термокинематических связей в термодинамическую континуальную теорию термоупругих материалов армированных волокнами. Применяется он к всяким материалам, для которых известны классы симметрии, значит и представления определяющих функций. Приведены детальные результаты для материалов, армированных одно- и двухнапрявленно, подвергнутых связям несжимаемости, при чисто термических объемных деформациях, а также связям нерастяжимаемости в направлении армирования, при термических удлинениях волокон. Обсуждены некоторые применения, касающиеся упругости резиноподобных материалов. Показано в частности, что энергоупругие явления в резине происходят в количественном совпадении с результатами экспериментов.

1. Introduction

THE DIRECT consideration of thermo-kinematic constraints in a thermodynamic continuum theory of fiber-reinforced materials requires some modifications of the basic principles of thermodynamics and a complicated analysis so as to arrive at detailed results; [1, 2, 3].

In this approach a different, rather simple, method for the introduction of constraints is presented. It is applicable to all thermoelastic materials for which the symmetry class and hence the representations are known. It starts from the well-known thermodynamic constitutive theory of elastic bodies and introduces the thermokinematic constraints by a limiting process, after interchange of certain deformations with their thermodynamic conjugate stresses. This method has two essential advantages compared to the direct one:

1. It is simple. 2. It shows explicitly the action of constraints in the thermodynamic relations.

Detailed results are presented for the unidirectionally and the bidirectionally fiber-reinforced materials subject to the constraints of incompressibility with purely thermal volume expansion and of inextensibility in the fiber directions with thermal extension of the fibers.

Some applications to rubber-elasticity are reported.

2. Reinforced thermoelastic materials without constraints

Thermoelastic materials which are reinforced by two families of fibers are defined by the constitutive equations

$$C = \mathscr{C}(x^k_{;K}, T, T_{,K}; N^K_\alpha, \varrho_R) \tag{2.1}$$

for the stress tensor, the internal energy, the heat flux and the entropy; where $x^k_{;K} := \frac{\partial x^k(\mathbf{X}, t)}{\partial X^K}$ denotes the deformation gradient with respect to an undistorted reference configuration R at temperature T_R and pressure p_R, T denotes the (absolute) temperature and $T_{,K} := \frac{\partial T(\mathbf{X}, t)}{\partial X^K}$ its gradient with respect to the configuration R, $N^K_\alpha = N^K_\alpha(\mathbf{X})$ ($\alpha = 1, 2$) are *unit* tangent vectors in the two-fiber directions in the configuration R and ϱ_R is the mass density in that configuration.([1])

By a thermodynamic treatment, according to MÜLLERS's [4] or COLEMAN's [5] entropy principle, it can be shown that the stress, the internal energy and the entropy are independent of the temperature gradient. This means that the *bidirectionally reinforced thermoelastic materials without constraints* are given by the constitutive functions

$$\eta = \eta(T, I_0, I_1, I_2, J_1, J_2, \ldots, J_6; \varrho_R),$$
$$\varepsilon = \varepsilon(T, I_0, I_1, I_2, J_1, J_2, \ldots, J_6, \varrho_R),$$
$$t^{kl} = -pg^{kl} + \sum_{\alpha=1}^{2} t_\alpha \frac{n^k_\alpha n^l_\alpha}{I_\alpha} + \hat{t}^{kl}, \tag{2.2}$$
$$\hat{t}^{kl} = \frac{1}{J}\Big[M_0 g^{kl} + (K_1 + J_1 K_2)B^{kl} - K_2(\mathbf{B}^2)^{kl} + M_1 \frac{n^k_1 n^l_1}{I_1} + K_3 n_1^{(k}(\mathbf{B}\mathbf{n}_1)^{l)}$$
$$+ M_2 \frac{n^k_2 n^l_2}{I_2} + K_4 n_2^{(k}(\mathbf{B}\mathbf{n}_2)^{l)} + K_5 \cos\phi\, n_1^{(k} n_2^{l)} + K_6 \cos\phi\big(n_1^{(k}(\mathbf{B}\mathbf{n}_2)^{l)} + n_2^{(k}(\mathbf{B}\mathbf{n}_1)^{l)}\big)\Big]$$

([1]) I use stationary metric coordinate systems with the coordinates X^K ($K = 1, 2, 3$) and the metric tensor $g_{KM}(\mathbf{X})$ for the description of the reference configuration R and the coordinates x^k ($k = 1, 2, 3$) and a different metric tensor $g_{km}(\mathbf{x})$ for the description of the deformed configuration in some observer frame. Both coordinate systems are fixed in an inertial frame. g^{KM} and g^{km} denote the inverse metric tensors. The summation convention is applied according to which summation over diagonally repeated indices has to be performed. The partial derivative with respect to X^K is denoted by a comma, e.g. $T_{,K} := \frac{\partial T}{\partial X^K}$; the covariant derivative with respect to X^K is denoted by a semicolon in front of coordinate indices, an exception is $x^k_{;K} := \frac{\partial x^k(\mathbf{X}, t)}{\partial \mathbf{X}^K}$.

Round brackets enclosing tensor indices indicate symmetrization, squared brackets antisymmetrization with respect to the enclosed indices.

for the specific entropy η, the specific internal energy ε and the Cauchy stress t^{kl}; cf. [3]. $B^{kl}:=g^{KL}x^k_{;K}\,x^l_{;L}$ is the left Cauchy–Green deformation tensor and $n^k_\alpha:=x^k_{;K}N^K_\alpha(\alpha==1,2)$ are tangent vectors in the actual fiber directions. I_0, I_1, I_2 and $J_1, J_2, \ldots, J_6$ denote the following invariants:

$$
\begin{aligned}
&I_0:=\det\mathbf{B}=\det\mathbf{C}=J^2,\\
&I_1:=(\mathbf{n}_1\cdot\mathbf{n}_1)=(\mathbf{N}_1\cdot\mathbf{C}\mathbf{N}_1),\\
&I_2:=(\mathbf{n}_2\cdot\mathbf{n}_2)=(\mathbf{N}_2\cdot\mathbf{C}\mathbf{N}_2);
\end{aligned}
\tag{2.3}
$$

$$
\begin{aligned}
&J_1:=\operatorname{tr}\mathbf{B}=\operatorname{tr}\mathbf{C},\\
&J_2:=\frac{1}{2}[(\operatorname{tr}\mathbf{B})^2-\operatorname{tr}\mathbf{B}^2]=\frac{1}{2}[(\operatorname{tr}\mathbf{C})^2-\operatorname{tr}\mathbf{C}^2],\\
&J_3:=\frac{1}{2}(\mathbf{n}_1\cdot\mathbf{B}\mathbf{n}_1)=\frac{1}{2}(\mathbf{N}_1\cdot\mathbf{C}^2\mathbf{N}_1),\\
&J_4:=\frac{1}{2}(\mathbf{n}_2\cdot\mathbf{B}\mathbf{n}_2)=\frac{1}{2}(\mathbf{N}_2\cdot\mathbf{C}^2\mathbf{N}_2),\\
&J_5:=\cos\phi(\mathbf{n}_1\cdot\mathbf{n}_2)=\cos\phi(\mathbf{N}_1\cdot\mathbf{C}\mathbf{N}_2),\\
&J_6:=\cos\phi(\mathbf{n}_1\cdot\mathbf{B}\mathbf{n}_2)=\cos\phi(\mathbf{N}_1\cdot\mathbf{C}^2\mathbf{N}_2);
\end{aligned}
\tag{2.4}
$$

where $C_{KL}:=g_{kl}x^k_{;K}x^l_{;L}$ is the right Cauchy–Green deformation tensor and $\cos\phi:=:=(\mathbf{N}_1\cdot\mathbf{N}_2)$ defines the angle between the fiber directions in the reference configuration R.

The stress coeffcients $p, t_1, t_2, M_0, M_1, M_2, K_1, K_2, \ldots, K_6$ are functions of T, ϱ_K and the invariants (2.3) and (2.4). p denotes the pressure, t_1 and t_2 are the stresses in the fiber directions and the coefficients M_0, M_1, M_2 in $\hat{t}^{kl}$ obey the conditions $\hat{t}^k_k=0$, $n_{\alpha k}\hat{t}^{kl}n_{\alpha l}=0$ $(\alpha=1,2)$ so that the decomposition of Eq. $(2.2)_3$ is unique:

$$
\begin{aligned}
&K_1\cdot J_1+K_2\cdot 2J_2+K_3\cdot 2J_3+K_4\cdot 2J_4+K_5\cdot J_5+K_6\cdot 2J_6+3M_0+M_1+M_2=0,\\
&K_1\cdot 2J_3+K_2\cdot(J_2I_1-I_0)+K_3\cdot 2J_3I_1+K_4\cdot\frac{J_5J_6}{\cos^2\phi}+K_5\cdot J_5I_1\\
&\qquad+K_6\cdot(J_6I_1+2J_3J_5)+M_0\cdot I_1+M_1\cdot I_1+M_2\cdot\frac{1}{I_2}\frac{J_5^2}{\cos^2\phi}=0,\\
&K_1\cdot 2J_4+K_2\cdot(J_2I_2-I_0)+K_3\cdot\frac{J_5J_6}{\cos^2\phi}+K_4\cdot 2J_4I_2+K_5\cdot J_5I_2\\
&\qquad+K_6\cdot(J_6I_2+2J_4J_5)+M_0\cdot I_2+M_1\cdot\frac{1}{I_1}\frac{J_5^2}{\cos^2\phi}+M_2\cdot I_2=0.
\end{aligned}
\tag{2.5}
$$

Finally, the thermodynamic relations for the unconstrained bidirectionally reinforced material follow from $d\eta=\dfrac{1}{T}\left(d\varepsilon-\dfrac{1}{2\varrho_R}t^{KL}dC_{KL}\right)$, where

$$
\begin{aligned}
t^{KL}&:=JX^K_{;k}X^L_{;l}t^{kl}\\
&=-pJ(\overline{\mathbf{C}}^{-1})^{KL}+\sum_{\alpha=1}^{2}t_\alpha J\frac{N^K_\alpha N^L_\alpha}{I_\alpha}+M_0(\overline{\mathbf{C}}^{-1})^{KL}+(K_1+J_1K_2)g^{KL}-K_2C^{KL}\\
&\quad+M_1\frac{N^K_1N^L_1}{I_1}+K_3N_1^{(K}(\mathbf{C}\mathbf{N}_1)^{L)}+M_2\frac{N^K_2N^L_2}{I_2}+K_4N_2^{(K}(\mathbf{C}\mathbf{N}_2)^{L)}\\
&\quad+K_5\cos\phi N_1^{(K}N_2^{L)}+K_6\cos\phi\big(N_1^{(K}(\mathbf{C}\mathbf{N}_2)^{L)}+N_2^{(K}(\mathbf{C}\mathbf{N}_1)^{L)}\big)
\end{aligned}
$$

is the second Kirchhoff–Piola stress:

$$
\begin{aligned}
&\frac{\partial\eta}{\partial T} = \frac{1}{T}\frac{\partial\varepsilon}{\partial T},\\
&\frac{\partial\eta}{\partial I_0} = \frac{1}{T}\left[\frac{\partial\varepsilon}{\partial I_0} - \frac{1}{2\varrho_R}(M_0 - pJ)\frac{1}{I_0}\right],\\
&\frac{\partial\eta}{\partial I_\alpha} = \frac{1}{T}\left[\frac{\partial\varepsilon}{\partial I_\alpha} - \frac{1}{2\varrho_R}(M_\alpha + t_\alpha J)\frac{1}{I_\alpha}\right] \quad (\alpha = 1, 2),\\
&\frac{\partial\eta}{\partial J_A} = \frac{1}{T}\left[\frac{\partial\varepsilon}{\partial J_A} - \frac{1}{2\varrho_R}K_A\right] \quad (A = 1, 2, \ldots, 6).
\end{aligned}
\tag{2.6}
$$

These relations imply the following integrability conditions for the entropy:

$$
\begin{aligned}
&\frac{1}{I_0}\left(\frac{\partial M_0}{\partial I_\alpha} - \frac{\partial p}{\partial I_\alpha}J\right) = \frac{1}{I_\alpha}\left(\frac{\partial M_\alpha}{\partial I_0} + \frac{\partial t_\alpha}{\partial I_0}J + \frac{t_\alpha}{2J}\right) \quad (\alpha = 1, 2),\\
&\frac{1}{I_0}\left(\frac{\partial M_0}{\partial J_A} - \frac{\partial p}{\partial J_A}J\right) = \frac{\partial K_A}{\partial I_0} \quad (A = 1, 2, \ldots, 6),\\
&\frac{1}{I_1}\left(\frac{\partial M_1}{\partial I_2} + \frac{\partial t_1}{\partial I_2}J\right) = \frac{1}{I_2}\left(\frac{\partial M_2}{\partial I_1} + \frac{\partial t_2}{\partial I_1}J\right),\\
&\frac{1}{I_\alpha}\left(\frac{\partial M_\alpha}{\partial J_A} + \frac{\partial t_\alpha}{\partial J_A}J\right) = \frac{\partial K_A}{\partial I_\alpha} \quad (\alpha = 1, 2), \quad (A = 1, 2, \ldots, 6),\\
&\frac{\partial K_A}{\partial J_B} = \frac{\partial K_B}{\partial J_A} \quad (A, B = 1, 2, \ldots, 6;\ A \neq B),\\
&2\varrho_R\frac{\partial\varepsilon}{\partial I_0} = \frac{1}{I_0}\left(M_0 - T\frac{\partial M_0}{\partial T}\right) - \frac{1}{J}\left(p - T\frac{\partial p}{\partial T}\right),\\
&2\varrho_R\frac{\partial\varepsilon}{\partial I_\alpha} = \frac{1}{I_\alpha}\left(M_\alpha - T\frac{\partial M_\alpha}{\partial T}\right) + \frac{J}{I_\alpha}\left(t_\alpha - T\frac{\partial t_\alpha}{\partial T}\right) \quad (\alpha = 1, 2),\\
&2\varrho_R\frac{\partial\varepsilon}{\partial J_A} = K_A - T\frac{\partial K_A}{\partial T} \quad (A = 1, 2, \ldots, 6).
\end{aligned}
\tag{2.7}
$$

The unidirectionally reinforced and the isotropic unreinforced materials are included as special cases. The relations for the *unidirectionally reinforced material* are obtained by omitting the invariants I_2, J_4, J_5, J_6 and the relation $(2.5)_3$ and by setting $t_2 = 0$ $M_2 = 0$, $K_4 = K_5 = K_6 = 0$. The unreinforced *isotropic material* is included, if in addition the invariants I_1 and J_3 and the relation $(2.5)_2$ are omitted and the stress coefficients $t_1 = 0$, $M_1 = 0$, $K_3 = 0$ are set equal to zero.

3. Introduction of thermo-kinematic constraints

Many reinforced materials, especially those with a highly deformable matrix (as rubber) between strong fibers, are almost inextensible in the fiber directions up to moderate stresses They are, moreover, almost incompressible up to moderate pressure. Thus they obey approximately the constraints of incompressibility and inextensibility in the fiber directions at constant temperature. The thermal volume expansion and the thermal expansion in the fiber directions, however, cannot be neglected. Thus they obey the thermo-kinematic constraints

$$\det \mathbf{B} = \left(\frac{\varrho_R}{\varrho}\right)^2 = I_0 = f_0(T), \quad f_0(T_R) = 1;$$
$$(3.1) \qquad (\mathbf{n}_\alpha \cdot \mathbf{n}_\alpha) = (\mathbf{N}_\alpha \cdot \mathbf{C}\mathbf{N}_\alpha) = I_\alpha = f_\alpha(T), \quad f_\alpha(T_R) = 1 \quad (\alpha = 1, 2).$$

These constraints can be introduced into the relations of Sect. 2, if the pressure p and the fiber tractions t_α ($\alpha = 1, 2$) are taken as independent variables instead of the volume I_0 and the fiber extensions I_α ($\alpha = 1, 2$), respectively. Assuming that the constitutive equations $p = p\ (T, I_0, I_\alpha, J_A; \varrho_R)$ for the pressure and $t_\alpha = t_\alpha\ (T, I_0, I_\alpha, J_A; \varrho_R)$ for the fiber tractions of the unconstrained material are invertible with respect to I_0 and I_α, respectively, one has

$$(3.2) \qquad \begin{aligned} I_0 &= \tilde{F}_0(T, p, t_\beta, J_A; \varrho_R) \quad (\alpha, \beta = 1, 2), \\ I_\alpha &= \tilde{F}_\alpha(T, p, t_\beta, J_A; \varrho_R) \quad (A = 1, 2, \ldots, 6), \end{aligned}$$

and can eliminate I_0 and I_α from Eqs. (2.6) and (2.7). With the notation

$$(3.3) \qquad \varepsilon(T, I_0, I_\alpha, J_A; \varrho_R) = \tilde{\varepsilon}(T, p, t_\alpha, J_A; \varrho_R) \quad \text{etc.}$$

it thus follows after some calculation:

$$\frac{\partial\tilde{\eta}}{\partial T} = \frac{1}{T}\left[\frac{\partial\tilde{\varepsilon}}{\partial T} - \frac{1}{2\varrho_R}\left\langle\left(\tilde{M}_0 - p\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_0}\frac{\partial\tilde{F}_0}{\partial T} + \sum_{\beta=1}^{2}\left(M_\beta + t_\beta\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_\beta}\frac{\partial\tilde{F}_\beta}{\partial T}\right\rangle\right],$$

$$\frac{\partial\tilde{\eta}}{\partial p} = \frac{1}{T}\left[\frac{\partial\tilde{\varepsilon}}{\partial p} - \frac{1}{2\varrho_R}\left\langle\left(\tilde{M}_0 - p\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_0}\frac{\partial\tilde{F}_0}{\partial p} = \sum_{\beta=1}^{2}\left(M_\beta + t_\beta\sqrt{\tilde{F}_0}\right)\frac{1}{\hat{F}_\beta}\frac{\partial\tilde{F}_\beta}{\partial p}\right\rangle\right],$$

$$(3.4) \qquad \frac{\partial\tilde{\eta}}{\partial t_\alpha} = \frac{1}{T}\left[\frac{\partial\tilde{\varepsilon}}{\partial t_\alpha} - \frac{1}{2\varrho_R}\left\langle\left(\tilde{M}_0 - p\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_0}\frac{\partial\tilde{F}_0}{\partial t_\alpha} + \sum_{\beta=1}^{2}\left(M_\beta + t_\beta\sqrt{\tilde{F}_0}\right)\frac{1}{\hat{F}_\beta}\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}\right\rangle\right] \quad (\alpha = 1, 2),$$

$$\frac{\partial\tilde{\eta}}{\partial J_A} = \frac{1}{T}\left[\frac{\partial\tilde{\varepsilon}}{\partial J_A} - \frac{1}{2\varrho_R}\left\langle\tilde{K}_A + \left(\tilde{M}_0 - p\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_0}\frac{\partial\tilde{F}_0}{\partial J_A}\right.\right.$$
$$\left.\left. + \sum_{\beta=1}^{2}\left(M_\beta + t_\beta\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_\beta}\frac{\partial\tilde{F}_\beta}{\partial J_A}\right\rangle\right] \quad (A = 1, 2, \ldots, 6),$$

and the integrability conditions for the entropy transform into

$$(3.5) \qquad \frac{1}{\sqrt{\tilde{F}_0}}\left(\frac{\partial\tilde{F}_0}{\partial t_\alpha} + \frac{\tilde{F}_0}{\tilde{F}_\alpha}\frac{\partial\tilde{F}_\alpha}{\partial p}\right) = \frac{1}{\tilde{F}_0}\left(\frac{\partial\tilde{F}_0}{\partial t_\alpha}\frac{\partial\tilde{M}_0}{\partial p} - \frac{\partial\tilde{F}_0}{\partial p}\frac{\partial\tilde{M}_0}{\partial t_\alpha}\right) + \sum_{\beta=1}^{2}\frac{1}{\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}\frac{\partial\tilde{M}_\beta}{\partial p}\right.$$
$$\left. - \frac{\partial\tilde{F}_\beta}{\partial p}\frac{\partial\tilde{M}_\beta}{\partial t_\alpha}\right) + \sum_{\beta=1}^{2}\frac{t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}\frac{\partial\tilde{F}_0}{\partial p} - \frac{\partial\tilde{F}_\beta}{\partial p}\frac{\partial\tilde{F}_0}{\partial t_\alpha}\right) \quad (\alpha = 1, 2),$$

(3.5) [cont.]

$$\frac{\partial\tilde{K}_A}{\partial p}-\frac{1}{\sqrt{\tilde{F}_0}}\frac{\partial\tilde{F}_0}{\partial J_A}=\frac{1}{\tilde{F}_0}\left(\frac{\partial\tilde{F}_0}{\partial p}\frac{\partial\tilde{M}_0}{\partial J_A}-\frac{\partial\tilde{F}_0}{\partial J_A}\frac{\partial\tilde{M}_0}{\partial p}\right)+\sum_{\beta=1}^{2}\frac{1}{\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial p}\frac{\partial\tilde{M}_\beta}{\partial J_A}\right.$$

$$\left.-\frac{\partial\tilde{F}_\beta}{\partial J_A}\frac{\partial\tilde{M}_\beta}{\partial p}\right)+\sum_{\beta=1}^{2}\frac{t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial p}\frac{\partial\tilde{F}_0}{\partial J_A}-\frac{\partial\tilde{F}_\beta}{\partial J_A}\frac{\partial\tilde{F}_0}{\partial p}\right)\quad(A=1,2,\ldots,6),$$

$$\sqrt{\tilde{F}_0}\left(\frac{1}{\tilde{F}_1}\frac{\partial\tilde{F}_1}{\partial t_2}-\frac{1}{\tilde{F}_2}\frac{\partial\tilde{F}_2}{\partial t_1}\right)=-\frac{1}{\tilde{F}_0}\left(\frac{\partial\tilde{F}_0}{\partial t_2}\frac{\partial\tilde{M}_0}{\partial t_1}-\frac{\partial\tilde{F}_0}{\partial t_1}\frac{\partial\tilde{M}_0}{\partial t_2}\right)$$

$$-\sum_{\beta=1}^{2}\frac{1}{\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_2}\frac{\partial\tilde{M}_\beta}{\partial t_1}-\frac{\partial\tilde{F}_\beta}{\partial t_1}\frac{\partial\tilde{M}_\beta}{\partial t_2}\right)-\sum_{\beta=1}^{2}\frac{t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_2}\frac{\partial\tilde{F}_0}{\partial t_1}-\frac{\partial\tilde{F}_\beta}{\partial t_1}\frac{\partial\tilde{F}_0}{\partial t_2}\right),$$

$$\frac{\partial\tilde{K}_A}{\partial t_\alpha}+\frac{\sqrt{\tilde{F}_0}}{\tilde{F}_\alpha}\frac{\partial\tilde{F}_\alpha}{\partial J_A}=\frac{1}{\tilde{F}_0}\left(\frac{\partial\tilde{F}_0}{\partial t_\alpha}\frac{\partial\tilde{M}_0}{\partial J_A}-\frac{\partial\tilde{F}_0}{\partial J_A}\frac{\partial\tilde{M}_0}{\partial t_\alpha}\right)+\sum_{\beta=1}^{2}\frac{1}{\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}\frac{\partial\tilde{M}_\beta}{\partial J_A}\right.$$

$$\left.-\frac{\partial\tilde{F}_\beta}{\partial J_A}\frac{\partial\tilde{M}_\beta}{\partial t_\alpha}\right)+\sum_{\beta=1}^{2}\frac{t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}\frac{\partial\tilde{F}_0}{\partial J_A}-\frac{\partial\tilde{F}_\beta}{\partial J_A}\frac{\partial\tilde{F}_0}{\partial t_\alpha}\right)$$

$$(\alpha=1,2)\quad(A=1,2,\ldots,6),$$

$$\frac{\partial\tilde{K}_A}{\partial J_B}-\frac{\partial\tilde{K}_B}{\partial J_A}=\frac{1}{\tilde{F}_0}\left(\frac{\partial\tilde{F}_0}{\partial J_B}\frac{\partial\tilde{M}_0}{\partial J_A}-\frac{\partial\tilde{F}_0}{\partial J_A}\frac{\partial\tilde{M}_0}{\partial J_B}\right)+\sum_{\beta=1}^{2}\frac{1}{\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial J_B}\frac{\partial\tilde{M}_\beta}{\partial J_A}\right.$$

$$\left.-\frac{\partial\tilde{F}_\beta}{\partial J_A}\frac{\partial\tilde{M}_\beta}{\partial J_B}\right)+\sum_{\beta=1}^{2}\frac{t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial J_B}\frac{\partial\tilde{F}_0}{\partial J_A}-\frac{\partial\tilde{F}_\beta}{\partial J_A}\frac{\partial\tilde{F}_0}{\partial J_B}\right)$$

$$(A,B=1,2,\ldots,6;\ A\neq B),$$

$$2\varrho_R\frac{\partial\tilde{\varepsilon}}{\partial p}=-\frac{T}{\sqrt{\tilde{F}_0}}\frac{\partial\tilde{F}_0}{\partial T}+(\tilde{M}_0-p\sqrt{\tilde{F}_0})\frac{1}{\tilde{F}_0}\frac{\partial\tilde{F}_0}{\partial p}-\frac{T}{\tilde{F}_0}\left(\frac{\partial\tilde{F}_0}{\partial p}\frac{\partial\tilde{M}_0}{\partial T}-\frac{\partial\tilde{F}_0}{\partial T}\frac{\partial\tilde{M}_0}{\partial p}\right)$$

$$+\sum_{\beta=1}^{2}\left[(\tilde{M}_\beta+t_\beta\sqrt{\tilde{F}_0})\frac{1}{\tilde{F}_\beta}\frac{\partial\tilde{F}_\beta}{\partial p}-\frac{T}{\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial p}\frac{\partial\tilde{M}_\beta}{\partial T}-\frac{\partial\tilde{F}_\beta}{\partial T}\frac{\partial\tilde{M}_\beta}{\partial p}\right)\right.$$

$$\left.-\frac{T\cdot t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial p}\frac{\partial\tilde{F}_0}{\partial T}-\frac{\partial\tilde{F}_\beta}{\partial T}\frac{\partial\tilde{F}_0}{\partial p}\right)\right]$$

$$2\varrho_R\frac{\partial\tilde{\varepsilon}}{\partial t_\alpha}=+T\frac{\sqrt{\tilde{F}_0}}{\tilde{F}_\alpha}\frac{\partial\tilde{F}_\alpha}{\partial T}+(\tilde{M}_0-p\sqrt{\tilde{F}_0})\frac{1}{\tilde{F}_0}\frac{\partial\tilde{F}_0}{\partial t_\alpha}-\frac{T}{\tilde{F}_0}\left(\frac{\partial\tilde{F}_0}{\partial t_\alpha}\frac{\partial\tilde{M}_0}{\partial T}\right.$$

$$\left.-\frac{\partial\tilde{F}_0}{\partial T}\frac{\partial\tilde{M}_0}{\partial t_\alpha}\right)+\sum_{\beta=1}^{2}\left[(\tilde{M}_\beta+t_\beta\sqrt{\tilde{F}_0})\frac{1}{\tilde{F}_\beta}\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}-\frac{T}{\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}\frac{\partial\tilde{M}_\beta}{\partial T}-\frac{\partial\tilde{F}_\beta}{\partial T}\frac{\partial\tilde{M}_\beta}{\partial t_\alpha}\right)\right.$$

$$\left.-\frac{T\cdot t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial\tilde{F}_\beta}{\partial t_\alpha}\frac{\partial\tilde{F}_0}{\partial T}-\frac{\partial\tilde{F}_\beta}{\partial T}\frac{\partial\tilde{F}_0}{\partial t_\alpha}\right)\right]\quad(\alpha=1,2)$$

(3.5) [cont.]
$$2\varrho_R \frac{\partial \tilde{\varepsilon}}{\partial J_A} = \left(\tilde{K}_A - T\frac{\partial \tilde{K}_A}{\partial T}\right) + \left(\tilde{M}_0 - p\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_0}\frac{\partial \tilde{F}_0}{\partial J_A} - \frac{T}{\tilde{F}_0}\left(\frac{\partial \tilde{F}_0}{\partial J_A}\frac{\partial \tilde{M}_0}{\partial T} - \frac{\partial \tilde{F}_0}{\partial T}\frac{\partial \tilde{M}_0}{\partial J_A}\right) + \sum_{\beta=1}^{2}\left[\left(\tilde{M}_\beta + t_\beta\sqrt{\tilde{F}_0}\right)\frac{1}{\tilde{F}_\beta}\frac{\partial \tilde{F}_\beta}{\partial J_A} - \frac{T}{\tilde{F}_\beta}\left(\frac{\partial \tilde{F}_\beta}{\partial J_A}\frac{\partial \tilde{M}_\beta}{\partial T} - \frac{\partial \tilde{F}_\beta}{\partial T}\frac{\partial \tilde{M}_\beta}{\partial J_A}\right) - \frac{T\cdot t_\beta}{2\sqrt{\tilde{F}_0}\tilde{F}_\beta}\left(\frac{\partial \tilde{F}_\beta}{\partial J_A}\frac{\partial \tilde{F}_0}{\partial T} - \frac{\partial \tilde{F}_\beta}{\partial T}\frac{\partial \tilde{F}_0}{\partial J_A}\right)\right] \quad (A = 1, 2, \ldots, 6).$$

The constitutive relations (3.2) become the constraints (3.1) if $\tilde{F}_0$, $\tilde{F}_\alpha$ are independent of p, t_α and J_A. Hence the *incompressible* and *in the fiber directions inextensible material* is contained in Eqs. (3.4) and (3.5) as a special case for

(3.6)
$$\tilde{F}_0 = f_0(T), \quad \tilde{F}_\alpha = f_\alpha(T) \quad (\alpha = 1, 2).$$

Hence insertion into Eqs. (3.4) and (3.5) yields:

1. The stress coefficients are independent of the pressure and the fiber tractions:

(3.7)
$$\tilde{K}_A = \hat{K}_A(T, J_1, J_2, \ldots, J_0; \varrho_A) \quad (A = 1, 2, \ldots, 6).$$

2. The same follows from Eqs. (2.5) for the coefficients:

(3.8)
$$\tilde{M}_0 = \hat{M}_0(T, J_1, J_2, \ldots, J_6; \varrho_R),$$
$$\tilde{M}_\alpha = \hat{M}_\alpha(T, J_1, J_2, \ldots, J_6; \varrho_R) \quad (\alpha = 1, 2).$$

3. The entropy and the internal energy are additively decomposed according to

(3.9)
$$\tilde{\eta} = \bar{\eta}(T, p, t_\alpha) + \hat{\eta}(T, J_A; \varrho_R),$$
$$\tilde{\varepsilon} = \bar{\varepsilon}(T, p, t_\alpha) + \hat{\varepsilon}(T, J_A; \varrho_R),$$

where the pressure and the fiber tractions depending parts are given by

(3.10)
$$\bar{\eta} = \frac{\sqrt{f_0(T)}}{2\varrho_R}\left[-p\frac{f_0'(T)}{f_0(T)} + \sum_{\alpha=1}^{2} t_\alpha \frac{f_\alpha'(T)}{f_\alpha(T)}\right],$$
$$\bar{\varepsilon} = T\frac{\sqrt{f_0(T)}}{2\varrho_R}\left[-p\frac{f_0'(T)}{f_0(T)} + \sum_{\alpha=1}^{2} t_\alpha \frac{f_\alpha'(T)}{f_\alpha(T)}\right]$$

and the constitutive parts satisfy the relations

(3.11)
$$\frac{\partial \hat{\eta}}{\partial T} = \frac{1}{T}\left[\frac{\partial \hat{\varepsilon}}{\partial T} - \frac{1}{2\varrho_R}\left(\hat{M}_0\frac{f_0'(T)}{f_0(T)} + \sum_{\alpha=1}^{2}\hat{M}_\alpha\frac{f_\alpha'(T)}{f_\alpha(T)}\right)\right],$$
$$\frac{\partial \hat{\eta}}{\partial J_A} = \frac{1}{T}\left[\frac{\partial \hat{\varepsilon}}{\partial J_A} - \frac{1}{2\varrho_R}\hat{K}_A\right] \quad (A = 1, 2, \ldots, 6)$$

and

(3.12)
$$\frac{\partial \hat{K}_A}{\partial J_B} = \frac{\partial \hat{K}_B}{\partial J_A} \quad (A, B = 1, 2, \ldots, 6; A \neq B),$$
$$\frac{\partial \hat{\varepsilon}}{\partial J_A} = \frac{1}{2\varrho_R}\left(\hat{K}_A - T\frac{\partial \hat{K}_A}{\partial T}\right) + \frac{T}{2\varrho_R}\left[\frac{f_0'(T)}{f_0(T)}\frac{\partial \hat{M}_0}{\partial J_A} + \sum_{\alpha=1}^{2}\frac{f_\alpha'(T)}{f_\alpha(T)}\frac{\partial \hat{M}_\alpha}{\partial J_A}\right] \quad (A = 1, 2, \ldots, 6).$$

These are just the results which are obtained by a direct thermodynamic theory of fiber reinforced thermoelastic materials subject to incompressibility and fiber inextensibility with thermal volume expansion and thermal fiber extensions, cf. [2, 3]. The present derivation, however, is much simpler and has in addition the advantage of showing how the constraints act in each thermodynamic relation. Moreover, generalizations of constraints of the types (3.6) can easily be considered.

4. Introduction of thermal convective deformation measures

The thermal expansions due to the constraints (3.1) cannot be suppressed by the application of forces. Hence all constrained thermoelastic materials react to a change of temperature with a thermal deformation that cannot be suppressed. In order to have a deformation measure, which can be varied independently of the temperature, a new deformation measure must be introduced. This can be done by a decomposition of the deformation gradient according to

$$x^k_{;K} = \hat{F}^k_{.L}\bar{F}^L_{.K} \tag{4.1}$$

into a thermal deformation $\bar{F}^L_{.K}$ of the (locally) prescribed thermal expansions due to the constraints, and a thermal convective deformation $\hat{F}^k_{.L}$ relative to the (local) thermal expanded configuration of the body. I call $\hat{F}^k_{.L}$ a thermal convective deformation since the thermal expanded configuration changes with changing temperature. The decomposition (4.1) is meaningful only if it is unique. It can be made unique by the requirement that $\bar{F}^K_{.L}$ is determined *only* by the (locally) prescribed constraints (3.1), namely

$$\det\|\bar{C}^K_L\| = f_0(T), \quad N^K_\alpha\bar{C}_{KL}N^L_\alpha = f_\alpha(T) \quad (\alpha = 1, 2), \tag{4.2}$$

where

$$\bar{C}_{KL}: = g_{MN}\bar{F}^M_{.K}\bar{F}^N_{.L} \tag{4.3}$$

is the right Cauchy–Green deformation tensor of the prescribed thermal expansions.

The relation between the right and the left Cauchy–Green deformation tensors with the thermal deformation is, according to Eq. (4.1),

$$C_{KL} = \bar{F}^M_{.K}\hat{C}_{MN}\bar{F}^N_{.L}, \quad B^{kl} = \hat{F}^k_{.K}\bar{B}^{KL}\hat{F}^l_{.L}, \tag{4.4}$$

where $\hat{C}_{KL}$ and $\bar{B}^{KL}$ are defined as follows:

$$\hat{C}_{KL}: = g_{kl}\hat{F}^k_{.K}\hat{F}^l_{.L}, \quad \bar{B}^{KL}: = g^{MN}\bar{F}^K_{.M}\bar{F}^L_{.N}. \tag{4.5}$$

$\hat{C}_{KL}$ is the thermal convective right Cauchy–Green deformation tensor and $\bar{B}^{KL}$ is the left Cauchy–Green tensor of the (locally) prescribed thermal deformation. If one finally defines through

$$\bar{n}^K_\alpha: = \frac{1}{\sqrt{f_\alpha(T)}}\bar{F}^K_{.L}N^L_\alpha \quad (\alpha = 1, 2) \tag{4.6}$$

unit vectors in the direction of the thermally deformed fibers, the constraints (3.1) yield with Eqs. (4.2) and (4.4)

$$\det\|\hat{C}^K_L\| = 1, \quad \bar{n}^K_\alpha\hat{C}_{KL}\bar{n}^L_\alpha = 1. \quad (\alpha = 1, 2). \tag{4.7}$$

Hence the constrained material behaves like an incompressible and in the fiber directions inextensible one at all temperatures if the thermal convective deformation measure is used.

The thermal expansion of the anisotropic fiber-reinforced material with different thermal expansions of the fiber and the matrix materials is itself anisotropic. Every spherical piece of such a material deforms in a general ellipsoid if the temperature is changed uniformly and the material has free boundaries. Hence the thermal deformation under these conditions is given by

$$\bar{F}^K_{\cdot L} = \mu_0 \delta^K_L + \sum_{\alpha=1}^{2} \mu_\alpha N^K_\alpha N_{\alpha L}. \tag{4.8}$$

From Eq. (4.6) it follows then that the thermally deformed fiber directions

$$\begin{aligned} \bar{n}^K_1 &= \frac{1}{\sqrt{f_1(T)}} [(\mu_0+\mu_1)N^K_1 + \mu_2 \cos\phi N^K_2], \\ \bar{n}^K_2 &= \frac{1}{\sqrt{f_2(T)}} [\mu_1 \cos\phi N^K_1 + (\mu_0+\mu_2)N^K_2] \end{aligned} \tag{4.9}$$

are rotated against the fiber directions N^K_1, N^K_2 in the reference configuration R. Moreover, the angle between the fibers is changed during the thermal deformation:

$$\bar{n}^K_1 \bar{n}_{2K} := \cos\bar{\varphi} = \frac{\cos\phi}{\sqrt{f_1 f_2}} [(\mu_0+\mu_1+\mu_2)^2 - \mu_1\mu_2 \sin^2\phi]. \tag{4.10}$$

To determine the coefficients μ_0, μ_α from f_0, f_α we need the tensor $\bar{C}_{KL}$ of the thermal expansions. Insertion of Eq. (4.8) into Eq. (4.3) yields

$$\bar{C}_{KL} = \mu_0^2 g_{KL} + \mu_1(2\mu_0+\mu_1)N_{1K}N_{1L} + \mu_2(2\mu_0+\mu_2)N_{2K}N_{2L} + 2\mu_1\mu_2\cos\phi N_{1(K}N_{2L)}. \tag{4.11}$$

From the constraints (4.2) we thus obtain the relations

$$\begin{aligned} \det\|\bar{C}^K_L\| &= \mu_0^2[\mu_0^2 + \mu_0(\mu_1+\mu_2) + \mu_1\mu_2\sin^2\phi]^2 = f_0(T), \\ N^K_1 \bar{C}_{KL} N^L_1 &= (\mu_0+\mu_1)^2 \sin^2\phi + (\mu_0+\mu_1+\mu_2)^2\cos^2\phi = f_1(T), \\ N^K_2 \bar{C}_{KL} N^L_2 &= (\mu_0+\mu_2)^2 \sin^2\phi + (\mu_0+\mu_1+\mu_2)^2\cos^2\phi = f_2(T) \end{aligned} \tag{4.12}$$

for the determination of $\mu_0(T;\phi)$, $\mu_\alpha(T,\phi)$ $(\alpha = 1, 2)$. The solution of Eqs. (4.12) is unique; hence μ_0, μ_α can be used equivalently to describe the thermal deformation of the constrained fiber reinforced material.

The expression (4.8) is the thermal deformation of constrained fiber-reinforced materials with free boundaries and at uniform temperature. If, however, the temperature is non-uniform and/or if the surface of the body is not free, the thermal deformation is different from Eq. (4.8). This additional deformation is not known, unless a combined boundary value problem for the fields of displacement and temperature has been solved. It seems therefore meaningless to decompose the total deformation $x^k_{;L}$ into the parts $\hat{F}^k_{\cdot K}$ and $\bar{F}^K_{\cdot L}$. However, it is always possible to split off that part of the thermal deformation, namely $\bar{F}^K_{\cdot L} = \mu_0 \delta^K_L + \sum_{\alpha=1}^{2} \mu_\alpha N^K_\alpha N_{\alpha L}$ which, due to the constraints (4.2), cannot be suppressed by application of forces. This part is then, in general, not the total thermal deformation (as usually defined) but it is an important part of it. If the remaining part of this deformation is associated with $\hat{F}^k_{\cdot K}$, the decomposition (4.1) is *unique* under all conditions. Hence the decomposition

$$x^k_{;L} = \hat{F}^k_{\cdot K}\bar{F}^K_{\cdot L} = \hat{F}^k_{\cdot K}\Big(\mu_0\,\delta^K_L + \sum_{\alpha=1}^{2}\mu_\alpha N^K_\alpha N_{\alpha L}\Big) \tag{4.13}$$

defines uniquely the thermal convective deformation $\hat{F}^k_{\cdot K}$.

An important observation must be noted: In general the deformations

$$\hat{F}^k_{\cdot K} \quad \text{and} \quad \bar{F}^K_{\cdot L} = \mu_0(T;\phi)\,\delta^K_L + \sum_{\alpha=1}^{2}\mu_\alpha(T;\phi)N^K_\alpha N_{\alpha L}$$

are not gradients of displacement fields. This follows from the integrability conditions for the total displacement

$$\begin{aligned} x^k_{;[LM]} &= \hat{F}^k_{\cdot K}\bar{F}^K_{\cdot[L;M]} + \hat{F}^k_{\cdot[K;M]}\bar{F}^K_{\cdot L} \\ &= \hat{F}^k_{\cdot K}\Bigg[\Big(\frac{\partial\mu_0}{\partial T}\,\delta^K_{[L} + \sum_{\alpha=1}^{2}\frac{\partial\mu_\alpha}{\partial T}N^K_\alpha N_{\alpha[L}\Big)T_{,M]} + \Big(\frac{\partial\mu_0}{\partial\phi}\,\delta^K_{[L} + \sum_{\alpha=1}^{2}\frac{\partial\mu_\alpha}{\partial\phi}N^K_\alpha N_{\alpha[L}\Big)\phi_{,M]} \\ &\quad + \sum_{\alpha=1}^{2}\mu_\alpha(N^K_\alpha N_{\alpha[L;M]} + N_{\alpha[L}N^K_{\alpha;M]})\Bigg] + \hat{F}^k_{\cdot[K;M]}\Big(\mu_0\,\delta^K_L + \sum_{\alpha=1}^{2}\mu_\alpha N^K_\alpha N_{\alpha L}\Big) = 0. \end{aligned} \tag{4.14}$$

It follows that both deformations $\hat{F}^k_{\cdot K}$ and $\bar{F}^K_{\cdot L}$ are gradients of displacement fields only if the fibers in the reference configuration R are straight and if the temperature is uniform. This has important consequences for the application of the theory to experiments.

5. Application to isotropic incompressible materials

The introduction of the thermal convective deformation measure into the thermodynamic relations for fiber reinforced materials is easily performed; however, it is very laborious. The results are published in [3].

For the purpose of simplification and in view of application to rubberlike materials, I shall consider in the sequel only the isotropic incompressible material. This is included in the foregoing results as a special case which is obtained by setting $t_\alpha = 0$, $M_\alpha = 0$, $f_\alpha = 0$, $\mu_\alpha = 0$ ($\alpha = 1, 2$) and $K_3 = K_4 = K_5 = K_6 = 0$ and by omitting Eqs. $(2.5)_{2,3}$ and $(4.12)_{2,3}$:

$$\begin{aligned} \hat{M}_0 &= -\frac{1}{3}(\hat{K}_1\cdot J_1 + \hat{K}_2\cdot 2J_2), \\ t^{kl} &= -pg^{kl} + \frac{1}{\sqrt{f_0}}[\hat{M}_0 g^{kl} + (\hat{K}_1 + \hat{K}_2 J_1)B^{kl} - \hat{K}_2(\mathbf{B}^2)^{kl}] \end{aligned} \tag{5.1}$$

for the Cauchy-stress;

$$(5.2)\qquad \begin{aligned}\eta &= -\frac{p}{2\varrho_R}\frac{f_0'(T)}{\sqrt{f_0(T)}}+\hat{\eta}(T, J_1, J_2; \varrho_R),\\ \varepsilon &= -\frac{p}{2\varrho_R}\frac{Tf_0'(T)}{\sqrt{f_0(T)}}+\hat{\varepsilon}(T, J_1, J_2; \varrho_R)\end{aligned}$$

with

$$(5.3)\qquad \begin{aligned}\frac{\partial\hat{\eta}}{\partial T} &= \frac{1}{T}\left(\frac{\partial\hat{\varepsilon}}{\partial T}-\frac{1}{2\varrho_R}\hat{M}_0\frac{f_0'(T)}{f_0(T)}\right),\\ \frac{\partial\hat{\eta}}{\partial J_a} &= \frac{1}{T}\left(\frac{\partial\hat{\varepsilon}}{\partial J_a}-\frac{1}{2\varrho_R}\hat{K}_a\right)\quad (a = 1, 2)\end{aligned}$$

and

$$(5.4)\qquad \frac{\partial\hat{K}_1}{\partial J_2} = \frac{\partial\hat{K}_2}{\partial J_1},\qquad \frac{\partial\hat{\varepsilon}}{\partial J_a} = \frac{1}{2\varrho_R}\left(\hat{K}_a - T\frac{\partial\hat{K}_a}{\partial T}\right)+\frac{T}{2\varrho_R}\frac{f_0'(T)}{f_0(T)}\frac{\partial\hat{M}_0}{\partial J_a}\quad (a = 1, 2)$$

for the specific entropy and the specific internal energy where $\hat{K}_a = \hat{K}_a\,(T, J_1, J_2; \varrho_R)$. Equation (4.13) reduces to

$$(5.5)\qquad x^k_{;K} = \mu_0(T)\hat{F}^k_{\cdot K},\quad \mu_0(T) = \sqrt[6]{f_0(T)},$$

and the relations between the left Cauchy–Green deformation tensor of the total B^{kl} and the thermal convective $\hat{B}^{kl} := g^{KL}\hat{F}^k_{\cdot K}\hat{F}^l_{\cdot L}$ deformation and its main invariants are

$$(5.6)\qquad B^{kl} = \mu_0^2(T)\hat{B}^{kl};\quad J_1 = \mu_0^2\hat{J}_1,\quad J_2 = \mu_0^4\hat{J}_2,$$

where

$$(5.7)\qquad \hat{J}_1 := \mathrm{tr}\,\hat{\mathbf{B}},\quad \hat{J}_2 := \frac{1}{2}[(\mathrm{tr}\,\mathbf{B})^2-\mathrm{tr}\,\mathbf{B}^2].$$

With these relations the Cauchy-stress (5.1) can be rewritten as follows:

$$(5.8)\qquad t^{kl} = -pg^{kl}+\frac{1}{\sqrt{f_0}}\left[-\frac{1}{3}(\hat{L}_1\hat{J}_1+\hat{L}_2\cdot 2\hat{J}_2)g^{kl}+(\hat{L}_1+\hat{L}_2\hat{J}_1)\hat{B}^{kl}-\hat{L}_2(\hat{\mathbf{B}}^2)^{kl}\right],$$

where the abbreviations

$$(5.9)\qquad \hat{L}_1 := \mu_0^2\hat{K}_1,\quad \hat{L}_2 := \mu_0^4\hat{K}_2$$

have been used and the coefficients $\hat{L}_1, \hat{L}_2$ of the constitutive part of the stress are functions of $T, \hat{J}_1, \hat{J}_2$ and ϱ_R. Furthermore, the constitutive parts of the entropy $\hat{\eta} = \hat{\eta}(T, \hat{J}_1, \hat{J}_2; \varrho_R)$ and the internal energy $\hat{\varepsilon} = \hat{\varepsilon}(T, \hat{J}_1, \hat{J}_2; \varrho_R)$ satisfy, after transformation of Eqs. (5.3) and (5.4) to the thermal convective deformation, the simplified relations

$$(5.10)\qquad \frac{\partial\hat{\eta}}{\partial T} = \frac{1}{T}\frac{\partial\hat{\varepsilon}}{\partial T},\qquad \frac{\partial\hat{\eta}}{\partial\hat{J}_a} = \frac{1}{T}\left(\frac{\partial\hat{\varepsilon}}{\partial\hat{J}_a}-\frac{1}{2\varrho_R}\hat{L}_a\right)\quad (a = 1, 2)$$

and

$$5.11)\qquad \frac{\partial\hat{L}_1}{\partial\hat{J}_2} = \frac{\partial\hat{L}_2}{\partial\hat{J}_1},\qquad \frac{\partial\hat{\varepsilon}}{\partial\hat{J}_a} = \frac{1}{2\varrho_R}\left(\hat{L}_a - T\frac{\partial\hat{L}_a}{\partial T}\right)\quad (a = 1, 2).$$

Equations (5.8), (5.10) and (5.11) are the general results for isotropic incompressible thermoelastic materials with thermal volume expansion expressed by the thermal convective deformation measure.

In these relations the thermal convective deformation $\hat{B}^{kl}$ and its invariants $\hat{J}_1$ and $\hat{J}_2$ can be held constant at different temperatures, hence the appearing scalar functions can be determined from thermo-mechanical experiments. Furthermore, the specific heat capacity c_p at constant pressure p_R in the *thermal convective reference configuration* is measurable as a function of temperature at one pressure:

$$(5.12) \qquad c_p(T, p_R) = \left.\frac{\partial h}{\partial T}\right|_{\substack{p=p_R \\ \hat{J}_1=\hat{J}_2=3}} = -\frac{p_R \cdot T}{2\varrho_R}\frac{d}{dT}\left[\frac{f_0'(T)}{\sqrt{f_0(T)}}\right] + \left.\frac{\partial \hat{\varepsilon}}{\partial T}\right|_{\hat{J}_1=\hat{J}_2=3},$$

where $h = \varepsilon + p/\varrho$ is the specific enthalpy.

If in addition the thermal volume expansion $f_0(T)$ is known as a function of the temperature, the set (5.10) and (5.11) can be integrated and the total entropy and the total internal energy are given by the relations

$$\eta = \eta_R + \int_{T_R}^{T} \frac{c_p(T', p_R)}{T'}\,dT' + \frac{p_R}{\varrho_R}\left[\sqrt{f_0(T)}-1\right] - \frac{p_R}{2\varrho_R}\left[\frac{f_0'(T)}{\sqrt{f_0(T)}} - \frac{f_0'(T_R)}{1}\right]$$
$$-\frac{1}{2\varrho_R}\frac{f_0'(T)}{\sqrt{f_0(T)}}(p-p_R) - \frac{1}{2\varrho_R}\frac{\partial}{\partial T}\left[\int_3^{\hat{J}_1} \hat{L}_1(T, \hat{J}_1', \hat{J}_2; \varrho_R)\,d\hat{J}_1' + \int_3^{\hat{J}_2} \hat{L}_2(T, 3, \hat{J}_2'; \varrho_R)\,d\hat{J}_2'\right],$$

(5.13)

$$\varepsilon = \varepsilon_R + \int_{T_R}^{T} c_p(T', p_R)\,dT' - \frac{p_R}{\varrho_R}\left[\sqrt{f_0(T)}-1\right] - \frac{T}{2\varrho_R}\frac{f_0'(T)}{\sqrt{f_0(T)}}(p-p_R)$$
$$+\frac{1}{2\varrho_R}\left(1 - T\frac{\partial}{\partial T}\right)\left[\int_3^{\hat{J}_1} \hat{L}_1(T, \hat{J}_1', \hat{J}_2; \varrho_R)\,d\hat{J}_1' + \int_3^{\hat{J}_2} \hat{L}_2(T, 3, \hat{J}_2'; \varrho_R)\,d\hat{J}_2'\right],$$

where the integration constants η_R and ε_R are the specific total entropy and the specific total internal energy, respectively, in the reference configuration R at temperature T_R and pressure p_R.

The results (5.13) and the expression (5.8) for the Cauchy stress contain the unknown field $p = p(\mathbf{x}, t)$ for the reaction pressure. This pressure can be determined by solving a boundary value problem. Hence the total stress, the entropy and the internal energy are known whenever a boundary value problem has been solved.

6. Specialization to rubberlike materials

All high polymers possess in a temperature interval of about 120°C well above the glass transition temperature T_G a domain of rubberlike elasticity. This domain is characterized by the following experimental facts:

(i) The amorphous high polymers are isotropic highly deformable elastic materials up to deformations of medium order of magnitude, [7]; they are almost incompressible at constant temperature for pressures up to 100 bar, [8].

Hence the theory for constrained thermoelastic materials is applicable.

(ii) The specific volume is a linear function of the (absolute) temperature, [9], p. 73, [10]: $v = v_R[1+\alpha_0(T-T_R)]$.

From Eq. $(3.1)_1$ it follows then:

$$\frac{d}{dT}\sqrt{f_0(T)} = \frac{f_0'(T)}{2\sqrt{f_0(T)}} = \alpha. \tag{6.1}$$

(iii) The specific heat capacity c_p is independent of the temperature for $T \geqslant T_R > T_G$, [11], p. 175:

$$c_p = \text{constant}. \tag{6.2}$$

(iv) From isothermal experiments in simple extension and in two-dimensional extension, MOONEY [12] and RIVLIN and SAUNDERS [13] concluded that the stress coefficienst $\hat{L}_1$, $\hat{L}_2$ are independent of the deformation invariants up to medium stretches:

$$\hat{L}_a = l_a(T; \varrho_R) \quad (a = 1, 2). \tag{6.3}$$

The Mooney-approximation for isothermal simple extension is valid up to a critical stretch $\lambda < \lambda_c(T)$, Fig. 1, [14].

For stretches $\lambda > \lambda_c(T)$, *thermal reversible crystallization* is observed in simple extension, which leads after unloading to a permanent deformation, and hence cannot be described by the thermoelastic theory.

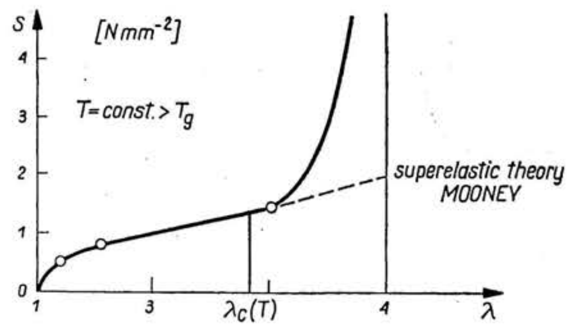

FIG. 1. Stretching force versus thermal convective stretch $\lambda = \dfrac{l}{l_0(T)}$ at constant pressure and constant temperature in simple extension.

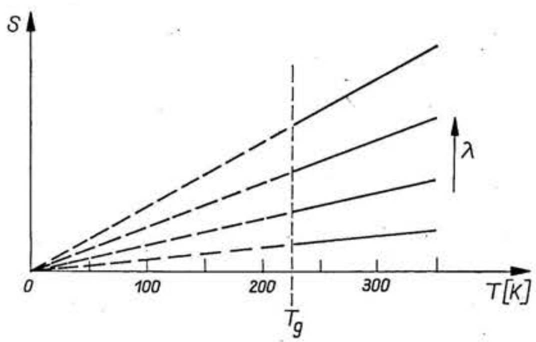

FIG. 2. Stretching force versus temperature at constant thermal convective stretch.

(v) The stretching force (in simple extension) at constant thermal convective stretch is a homogeneous linear function of the absolute temperature, [14], [15], Fig. 2:

It is easily concluded by specialization of Eq. (5.8) to simple extension cf. [16, 17], that the temperature dependence of the stress coefficients is as follows:

$$l_a(T;\varrho_R) = l_a^0 \frac{T}{T_R} \sqrt[6]{f_0(T)}\,, \quad l_a^0 = l_a(T_R;\varrho_R). \tag{6.4}$$

With the experimental results (6.1)–(6.4), we thus obtain from Eqs. (5.8) and (5.13) for the stress, the entropy and the internal energy of the high polymers in the rubberlike domain

$$t^{kl} = -pg^{kl} + \frac{1}{\sqrt[3]{f_0(T)}} \frac{T}{T_R} \left[-\frac{1}{3} (l_1^0 \cdot \hat{J}_1 + l_2^0 \cdot 2\hat{J}_2) g^{kl} + (l_1^0 + l_2^0 \cdot \hat{J}_1) \hat{B}^{kl} - l_2^0 (\hat{\mathbf{B}}^2)^{kl} \right], \tag{6.5}$$

$$\begin{aligned} \eta = \eta_R + c_p \ln \frac{T}{T_R} + \frac{p_R}{\varrho_R} \alpha_0 (T - T_R) - \frac{\alpha_0}{\varrho_R} (p - p_R) \\ - \frac{1}{2\varrho_R} \left(\frac{f_0^{1/6}}{T_R} + \frac{T}{T_R} \frac{\alpha_0}{3} f_0^{-1/3} \right) [l_1^0 \cdot (\hat{J}_1 - 3) + l_2^0 \cdot (\hat{J}_2 - 3)], \end{aligned} \tag{6.6}$$

$$\begin{aligned} \varepsilon = \varepsilon_R + \left(c_p - \frac{p_R}{\varrho_R} \alpha_0 \right) (T - T_R) - \frac{\alpha_0}{\varrho_R} T (p - p_R) \\ - \frac{T}{2\varrho_R} \frac{T}{T_R} \frac{\alpha_0}{3} f_0^{-1/3} [l_1^0 \cdot (\hat{J}_1 - 3) + l_2^0 \cdot (\hat{J}_2 - 3)]. \end{aligned} \tag{6.7}$$

These are the general results for high polymers in the rubberlike domain. If the thermal volume expansion is neglected, which amounts to setting $f_0(T) \equiv 1$, $\alpha_0 = 0$, the internal energy becomes independent of the deformations. Then, in fact, the rubberlike materials are ideal entropy elastic. But, although the thermal volume expansion is small ($\alpha_0 \approx \approx 6 \cdot 10^{-4} \mathrm{K}^{-1}$), the deformation dependent part of the internal energy is not negligible. To prove this I shall discuss the simple isothermal extension of a bar in some detail.

7. The energy elastic effect of rubber in isothermal simple extension

Solution of the boundary value problem for simple isothermal extension of a bar with free boundaries orthogonal to a uniformly distributed stress in the direction of stretch yields for the invariants

$$\hat{J}_1 = \lambda^2 + \frac{2}{\lambda}, \quad \hat{J}_2 = 2\lambda + \frac{1}{\lambda^2} \tag{7.1}$$

and for the reaction pressure

$$p = P - \frac{1}{3} \frac{T}{T_R} f_0^{-1/3} \left[l_1^0 \left(\lambda^2 - \frac{1}{\lambda} \right) + l_2 \left(\lambda - \frac{1}{\lambda^2} \right) \right], \tag{7.2}$$

where $p_R = P$ is the constant pressure with which the surroundings act on the free boundaries, and where $\lambda = \dfrac{l}{l_0(T)}$ is the thermal convective stretch in the direction of force

($l_0(T)$ = length of the bar in the traction-free state at temperature T, l = length under traction at the same temperature).

The nominal tractional stress (force per unit area of the bar in the reference configuration R) finally is given by the relation

$$\sigma(\lambda, T) = \varrho_R f_0^{-1/6}(T)\left[\left(\frac{\partial\varepsilon}{\partial\lambda}\right)_{P,T} - T\left(\frac{\partial\eta}{\partial\lambda}\right)_{P,T}\right]. \tag{7.3}$$

It follows that the supplied work W and the supplied heat Q per unit mass during isothermal simple extension are given by

$$\begin{aligned} W &= \int_1^{\lambda}\left[\left(\frac{\partial\varepsilon}{\partial\lambda'}\right)_{P,T} - T\left(\frac{\partial\eta}{\partial\lambda'}\right)_{P,T}\right]d\lambda', \\ Q &= T\int_1^{\lambda}\left(\frac{\partial\eta}{\partial\lambda'}\right)_{P,T} d\lambda', \end{aligned} \tag{7.4}$$

respectively. Insertion of Eqs. (7.1) and (7.2) into Eqs. (6.6) and (6.7) and integration of Eqs. (7.4) yields

$$\frac{Q}{W} = -1+\frac{1}{3}\frac{\alpha_0 T}{\sqrt{f_0(T)}}\frac{\left(\lambda^2-\frac{4}{\lambda}+3\right)+\frac{l_2^0}{l_1^0}3\left(1-\frac{1}{\lambda^2}\right)}{\left(\lambda^2+\frac{2}{\lambda}-3\right)+\frac{l_2^0}{l_1^0}\left(2\lambda+\frac{1}{\lambda^2}-3\right)}. \tag{7.5}$$

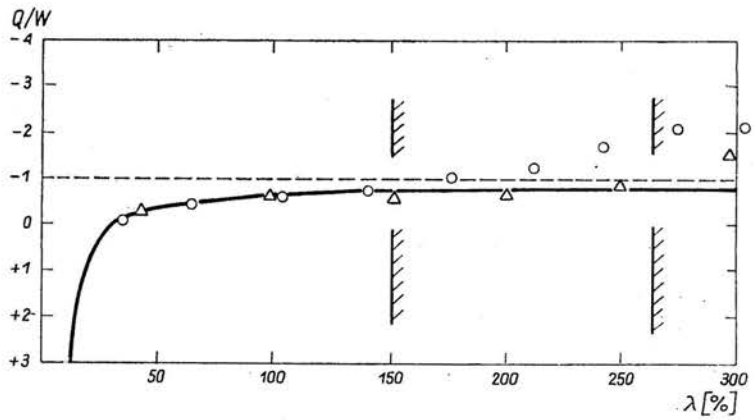

FIG. 3. Ratio of supplied heat ($Q > 0$) to supplied work ($W > 0$) in simple isothermal extension. —— theoretical curve calculated from (7.5) with $\alpha_0 = 6.36\cdot 10^{-4}$ K^{-1}, $\hat{l}_2^0/\hat{l}_1^0 = 0.2$ and $T = 294$ K, ○○○ measurements of EISELE and MORBITZER [18] at $T = 294$ K on cured polychloropren, △△△ measurements of DICK and MÜLLER [19] at $T = 304$ K on sulphur cured natural caoutchouc.

This quotient is graphically given in Fig. 3 by the solid line. It shows a very good agreement up to medium stretches with experiments of EISELE and MORBITZER [18] on cured polychloropren and of DICK and MÜLLER [19] on sulphur cured natural caoutchouc.

For ideal entropy elasticity $\frac{Q}{W} = -1$ holds. In this case the total supplied work is converted quantitatively into heat and is set free in isothermal experiments. The elastic energy contribution (proportional to α_0) reduces this amount of heat such that below 40% elongation heat must be supplied instead of being set free. This last prediction is in accordance with experimental observations, too.

I conclude: the theory is completely in accord with experimental observations up to medium deformations. Ideal entropy elasticity does not exist in rubberlike materials.

For larger deformations, however, the observed $\frac{Q}{W}$ is < -1. This means that now besides the entropy also the internal energy at constant temperature decreases with increasing stretch λ. This indicates the beginning of crystallization effects. So, measurements of work and heat in isothermal simple extension can predict a critical stretch $\lambda_c(T)$ by the condition $\frac{Q}{W} = -1$, below which the high polymers can be described by the thermoelastic theory and above which this is impossible due to the occurrence of thermal reversible crystallization.

8. Concluding remarks

The application of the theory to fiber reinforced rubberlike materials is evidently of great practical importance. It has not yet been completed due to the lack of experimental results.

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Received October 3, 1980.