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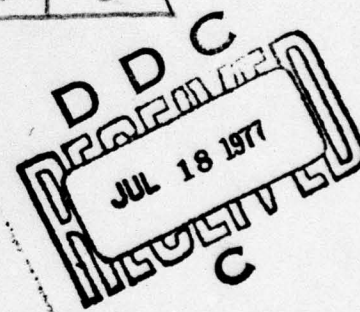
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10 M. J. Crochet and P. M. Naghdi

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On Thermomechanics of Polymers in the
Transition and Rubber Regions

by

M. J. Crochet[†] and P. M. Naghdi[‡]

Abstract. A nonisothermal theory of viscoelastic media, motivated by thermomechanical behavior of polymeric materials in the transition zone between the rubber and glassy states, was developed previously by Crochet and Naghdi and this included as a special case a theory with small deformation suitable for thermorheologically simple materials. The object of the present paper is to modify the form of the previous constitutive equations slightly in order to extend the validity of the theory to the rubber region in which the medium behaves elastically.

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1. Introduction. General background.

This paper elaborates on some aspects of a non-isothermal theory of viscoelasticity, which was developed previously by Crochet and Naghdi [4-8] for application to polymeric materials in the so-called transition zone between the rubber and the glassy states, and its slight modification in order to extend the validity of the theory also to the rubber region. Before describing the contents of the paper, by way of background, we recall that an appropriate phenomenological description of polymeric materials is given by the elastic model when they may be classified as rubbers and glasses (or resins). After a cycle of application and removal of external load, both rubbers and glasses return without delay to a reference stress-free configuration. Although the rubber and glassy states are both characterized by a disordered and amorphous structure, their mechanical properties are essentially different: rubbers are soft and highly deformable, while glasses are hard and brittle. Moreover, they exhibit an essential difference in the temperature dependence of their elastic properties: the thermal behavior of glasses is similar to that usually encountered in metals, while rubbers exhibit peculiar properties, such as the thermoelastic inversion, which have been the object of extensive studies (see, for example, Treloar [1, Ch. 2]).

When a polymeric material in the rubber state is cooled over a large temperature range, eventually it becomes a glass. Of course, the transition from a rubber to a glass is not discontinuous. To elaborate, consider the behavior of polymers which, under small deformations, can be characterized by constitutive equations of linear isotropic viscoelasticity. The nature of transition from a rubber to a glass may then be described in terms of the variation with frequency of the real part of the dynamic relaxation modulus, say $G'(\omega)$. Although the material response in both the rubber and glassy states may be characterized, respectively, by a low and a high constant value of $G'(\omega)$, the complex modulus is not a constant in the intermediate temperature

ranges. Moreover, $G'(w)$ at low frequencies has a value close to that in the rubber region, while its value at high frequencies tends to that of the glassy state. The domain of temperature in which the real part of the complex modulus exhibits a continuous change from the rubber state to the glassy state is called the transition zone between rubberlike and glasslike behavior, and a rough estimate of the location of the transition zone on the temperature scale is given by the glass transition temperature.^{*}

The variation of the complex moduli with frequency is a clear indication of the viscoelastic behavior of polymeric materials in the transition zone. It may be noted that the transition zone in which the viscoelastic character dominates extends generally over a wide temperature range, and the dependence of the thermoviscoelastic response on temperature is inherently nonlinear. The difficulties associated with the nonlinear dependence of the viscoelastic response on temperature are somewhat lessened in view of an interesting observation made on a class of polymeric materials, known as 'thermorheologically simple,' hereafter abbreviated as T.M.S. Consider, for example, the relaxation functions at various fixed temperatures, plotted against a logarithmic time-scale: it is found that the various isothermal curves plotted in this manner superimpose fairly well upon each other by a horizontal shift. Essentially, on the basis of data obtained at different fixed temperatures, one can construct a shift function which together with any one of these curves[†] determine the physical properties of polymers in the transition zone.

It should be pointed out that most often the "master" curves mentioned above are limited to the transition zone and do not extend to the plateau zones in the rubber and glassy states. These "master" curves are constructed on the

^{*} For a discussion of the glass transition temperature, the reader is referred to Ferry [2, p. 307] or Christensen [3, p. 92].

[†] Such curves in polymeric literature are usually referred to as a "composite" or "master" curve.

basis of isothermal curves and, in general, they give no indication of the transient character of the moduli when the temperature varies with time.

It should be recalled that a transition zone may also be defined with reference to the mechanical behavior of uncrosslinked polymers, polymeric solutions, and inorganic glasses at various constant temperatures. For these, the transition occurs between a glassy state at low temperature, and the liquid state at high temperature.

In a series of papers published over the last few years, Crochet and Naghdi [4-8] have shown how the material behavior in the transition zone between the rubber and glassy states, or between the glass and the liquid states, may be described by a special or restricted theory of simple materials. Essentially, after defining what is meant by thermal dilatation, they postulate a special form for the specific free energy based on the material behavior at a reference temperature. More specifically, their restricted theory of simple materials with fading memory, apart from the heat flux and the modified time scale, requires the knowledge of three functionals. One of these represents the history of the thermal stretch under vanishing stress, while the sum of the remaining two functionals represents the free energy. Of the latter two functionals again one of them depends on the temperature history only and the other is determined from the knowledge of the isothermal free energy functional. The modified time scale, utilized in the development of the theory, is prescribed by a functional which depends on the past history of temperature only.

In section 2, we show how the special class of materials considered previously may be also characterized on the basis of its stress-strain relations in the transition region; the form of the free energy is then deduced by integration of the constitutive relation for stress. This leads us to consider a modification of our previous constitutive relations, in order to extend the validity of the theory also to the rubber region in which region the material

behaves elastically. This is discussed in more detail in section 3, where we derive the form of the internal energy in the rubber region, and calculate also an example based on the data of Wood and Martin [9]. In this connection, it should be noted that thermomechanics of rubberlike materials has been dealt with to some extent by Besseling and Voetman [10] and more generally by Chadwick [11]. As indicated in the latter part of section 3, our results for the rubber region agree with those obtained by Chadwick [11] whose development is based on an entirely different model.

2. Constitutive equations in the transition zone.

Let X denote a material point of a body and designate a neighborhood of X by η . It is convenient to introduce several configurations for the neighborhood η . Thus, let κ_0 be the configuration occupied by η in a fixed reference state, $\kappa(t)$ the corresponding configuration at the present time t and $\kappa(\tau)$ the configuration occupied by η at time $\tau \leq t$. Also, in what follows, for simplicity we consistently use the notation $\kappa = \kappa(t)$. Suppose that now the body is subjected to a thermal history specified by a uniform temperature field $\theta(\tau)$, $-\infty < \tau \leq t$. Under such thermal histories, we denote by $\kappa^*(\tau)$ the configuration of η at time τ when the stress history vanishes identically and also use the notation $\kappa^* = \kappa^*(t)$. It may be noted here that our reason for considering a neighborhood of a material point is due to the fact that, in general, it is not possible to determine a global configuration corresponding to κ^* when the temperature field is not spatially homogeneous. Alternatively, since we are concerned with constitutive equations which are valid at every material point, we may establish our main results by employing spatially homogeneous strain and temperature fields. The various configurations of the neighborhood η introduced above, along with corresponding deformation gradients, are schematically depicted in Fig. 1.

The stretch tensor of the material point X in the configuration κ^* relative to the reference configuration κ_0 , called the thermal stretch, will be denoted by[†]

$$\bar{U} = \bar{U}(t) = \underset{0 < s < \infty}{u} (\theta_r(t-s); \theta) , \quad (2.1)$$

where the subscript r is used to indicate the restriction on the domain of the history of the temperature $\theta(t-s)$ to positive values of s , thus excluding the present value $\theta = \theta(t)$. We also recall the equation

[†]The use of an overbar is for later convenience and in order to conform with the notation used previously [8].

$$\frac{\rho_0}{\rho^*} = \det \bar{U}, \quad (2.2)$$

which relates the mass density $\rho^* = \rho^*(t)$ at X in the configuration κ^* to its value ρ_0 in the reference configuration κ_0 . In our previous developments [4-8], guided by experimental observations (see, e.g., Ferry [2, Ch. 11]) on polymeric materials, the constitutive equation for the stress in the transition region was constructed on the assumption that at the reference temperature θ_0 the Cauchy stress $\tilde{T}$ is given by a known isothermal functional $\mathcal{S}^*$ of the history of the deformation gradient $\tilde{F}(\tau)$, $-\infty < \tau \leq t$, relative to κ_0 :

$$\tilde{T}(t) = \mathcal{S}^*_{0 < s < \infty} (\tilde{F}_x(t-s); \tilde{T}). \quad (2.3)$$

Suppose now that the body is maintained at the uniform temperature θ_1 different from θ_0 , while it is subjected to a deformation history specified by the deformation gradient $\tilde{F}^*(\tau)$ of the configuration $\kappa(\tau)$ relative to $\kappa^*(\tau)$. For a class of materials exhibiting T.M.S. characteristics, the stress constitutive equation in terms of a stress functional whose arguments are the deformation gradients and their history relative to κ^* may then be expressed as

$$\tilde{T}(t) = \frac{\rho_1^*}{\rho_0} \mathcal{S}^*_{0 < s < \infty} (\tilde{F}_x^*(t-\xi_s); \tilde{T}^*), \quad (2.4)$$

where ρ_1^* is the mass density of κ^* , ξ_s is a modified time scale defined by

$$\xi_s = \frac{s}{\phi(\theta_1)} \quad (2.5)$$

and $\phi(\theta_1)$ is called a shift function. A constitutive equation of the form (2.4) provides a good agreement with experimental results in the transition zone. In this connection, it may be emphasized that the constitutive equation (2.4) holds

[§] Here, instead of $\kappa^*(\tau)$, we can write $\kappa^* = \kappa^*(t)$ since the temperature field is also uniform in time and hence $\kappa^*(\tau)$ is always the same for all $\tau \leq t$.

at constant temperatures and, as yet, constitutive equations which would account for the effect of variable temperature fields have not been introduced. Thus, the time scale ξ_s which occurs in (2.4) is only a function (rather than a functional) of temperature; and it is, in fact, the basis of the theory of T.M.S. materials, which prior to the developments in [4], was confined to only infinitesimal deformation.*

We now turn to the consideration of a modified form of our previous constitutive relations (2.4). The modification is motivated by the definition of the so-called "ideal rubber" in the literature on polymer chemistry. Let ϵ, η and ψ denote the specific internal energy, the specific entropy and the specific Helmholtz free energy, respectively. Then, briefly, an "ideal rubber" is one (Flory [13, Ch. 11]) whose configurational changes do not affect the value of the internal energy. It follows that the strain affects the specific Helmholtz free energy only through its contribution to the specific entropy; and, with the use of the classical relation $\psi = \epsilon - \theta\eta$, one concludes that the expression for the stress tensor for an "ideal rubber" is proportional to the temperature θ . The same argument is used in the work of Rouse [14], where the factor θ arises from the assumption that every configuration of the coiled molecules in a dilute solution has the same internal energy. Experimental results reported by Treloar [1], however, show that the volumetric changes only slightly affect the internal energy, and we arrive at essentially the same conclusion in the present paper.

Keeping the above background in mind, it seems to be sufficient to introduce a slight modification of the stress constitutive equation (2.4) and write

* A paper by Lianis [12] on the subject, in the presence of finite deformation, appeared about the same time when [4] was completed. However, his development is too special and does not account for the past history of thermal dilatation.

$$\tilde{T}(t) = \frac{\rho_1^*}{\rho_0} \frac{\theta_1}{\theta_0} \sum_{0 < s < \infty}^* (F_x^*(t - \xi_s); \tilde{F}^*(t)) \quad (2.6)$$

The above constitutive equation differs from (2.4) by only the factor θ_1/θ_0 , i.e., the ratio of a constant uniform temperature θ_1 to the reference temperature θ_0 . Moreover, the shift function associated with ξ_s in (2.6) is not the same as that in (2.5). A further justification for writing (2.6) will be discussed in Sec. 3. Here, however, we note certain implications of an assumption of the form (2.6). In a theory valid for the transition zone, say that of the ordinary T.M.S. materials, the shift function serves as a basis for constructing the so-called "master curve" for T.M.S. materials. The presence of a factor of the type θ_1/θ_0 requires a different shift function, but as noted by Ferry [2,p.299] the difference between the two expressions for the stress is of no consequence in the transition zone. Here, it may be worth recalling that the extension of Rouse's theory [14] for dilute polymer solutions to undiluted polymers evidently requires also the presence of a factor $\rho_1^*\theta_1/\rho_0\theta_0$ preceding an isothermal functional; in this connection, see also Ferry [2, pp. 206-213].

Most of the experimental investigations on the behavior of polymeric materials have been limited to uniform (time-independent) temperature fields which are different from a reference temperature. When the temperature field is regarded to vary with time, the constitutive equations (2.4) and (2.6) may be generalized in the form

$$\tilde{T}(t) = \frac{\rho^*}{\rho_0} \sum_{0 < s < \infty}^* (F_x^*(t - \xi_s); \tilde{F}^*) \quad (2.7)$$

and

$$\tilde{T}(t) = \frac{\rho^*}{\rho_0} \frac{\theta}{\theta_0} \sum_{0 < s < \infty}^* (F_x^*(t - \xi_s); \tilde{F}^*) \quad (2.8)$$

respectively, where ρ^* refers to the mass density in the configuration κ^* at time t introduced earlier in this section, while $\tilde{F}^*(\tau)$ stands for the deformation gradient relative to $\kappa^*(\tau)$. Also, in (2.7) and (2.8), the modified time scale ξ_s is now a functional of the past history of temperature. A simple form of such a functional, namely

$$s = \int_0^{\xi} \phi[\theta(t-u)] du ,$$

was first introduced by Hopkins [15] and adopted subsequently by Morland and Lee [16] in the context of the theory of T.M.S. materials with infinitesimal deformation. For a discussion of a more general functional of this kind, see [4].

In a number of papers (see, e.g., [8], which contains additional references), limited to the transition zone of polymers, Crochet and Naghdi started their developments by examining the stress constitutive equations and motivated an appropriate assumed form for the free energy functional from which (2.7) could be derived. For the purpose of extending the previous work to the rubber region, here we begin by introducing first the form (2.7) or (2.8) as an assumption for the stress constitutive equation and then ask the following question: if the medium is a simple material with fading memory, what is the most general form of the free energy functional which will lead to the forms (2.7) or (2.8) under the conditions of fading memory? As will become evident presently, even in the case of (2.7) the resulting free energy functional will be slightly different from those discussed in [4,5,6,7,8]. To elaborate, we recall that for the nonisothermal theory of simple materials with fading memory, the specific free energy ψ may be specified by

$$\psi = \tilde{\mathcal{F}}_{-\infty < s < 0} [C(t-s), \theta(t-s); \tilde{C}, \theta] , \quad (2.9)$$

where $\tilde{C}$ is the right Cauchy-Green strain tensor. In terms of the free energy

response functional $\tilde{\mathcal{F}}$, the Cauchy stress $\tilde{T}$ is given by[†]

$$\tilde{T}(t) = \frac{\rho}{\rho_0} \tilde{F} \left\{ \left(\frac{\partial}{\partial \tilde{C}} + \frac{\partial}{\partial \tilde{C}^T} \right) (\rho_0 \tilde{\mathcal{F}}) \right\} \tilde{F}^T. \quad (2.10)$$

In view of the definition (2.1) and the decomposition

$$\tilde{F}(\tau) = \tilde{F}^*(\tau) \tilde{U}(\tau) \quad (2.11)$$

employed previously [6,8], without loss in generality, the free energy (2.9) may be expressed in the alternative form

$$\psi(t) = \mathcal{F} \left[\tilde{C}^*(t-\xi_s), \theta(t-s); \tilde{C}^*, \theta \right], \quad (2.12)$$

$-\infty < s < 0$

where

$$\tilde{C}^*(\tau) = [\tilde{F}^*(\tau)]^T \tilde{F}^*(\tau) \quad (2.13)$$

and $\mathcal{F}$ in (2.12) is now a different functional from that in (2.9). By direct calculation, instead of (2.10), the stress constitutive equation in terms of the functional $\mathcal{F}$ in (2.12) is easily found to be

$$\tilde{T}(t) = \frac{\rho}{\rho_0} \tilde{F}^* \left(\frac{\partial}{\partial \tilde{C}^*} + \frac{\partial}{\partial \tilde{C}^{*T}} \right) (\rho_0 \mathcal{F}) \tilde{F}^{*T} \quad (2.14)$$

or

$$\tilde{T}(t) = \frac{\rho}{\rho_0} \frac{1}{\det \tilde{F}^*} \tilde{F}^* \left\{ \left(\frac{\partial}{\partial \tilde{C}^*} + \frac{\partial}{\partial \tilde{C}^{*T}} \right) (\rho_0 \mathcal{F}) \right\} \tilde{F}^{*T}, \quad (2.15)$$

where we have also used the identity

$$\rho = \rho^* [\det \tilde{F}^*]^{-1}, \quad (2.16)$$

which follows from (2.2) and (2.11). It may be emphasized that at this stage the expression (2.15) is fully general within the scope of the theory of simple materials with fading memory.

We now restrict ourselves to a special class of simple materials with fading memory corresponding to the behavior of polymers in the transition zone. This

[†]The expression (2.10) along with one for the specific entropy, in terms of the partial derivatives of the free energy response functional, are a form of the generalized stress derived by Coleman [17] with the use of the Clausius-Duhem inequality. However, it should be noted that the same expressions follow from the results which have been obtained in a recent paper by Green and Naghdi [18] on the basis of an entirely new approach to continuum thermodynamics. The latter paper contains also a discussion of some shortcomings of the Clausius-Duhem inequality.

can be accomplished by identifying the right-hand side of (2.15) either with (2.7) or (2.8). In the former case, we have the identity

$$\begin{aligned} \left(\frac{\partial}{\partial \tilde{C}^*} + \frac{\partial}{\partial \tilde{C}^{*T}} \right) (\rho_0 \int_{0 < s < \infty} \mathcal{F}) [\tilde{C}^*(t - \xi_s), \theta(t-s); \tilde{C}^*, \theta] \\ = \det \tilde{F}^* (\tilde{F}^*)^{-1} \int_{0 < s < \infty} \tilde{S}^* [\tilde{F}^*(t - \xi_s); \tilde{F}^*] (\tilde{F}^{*T})^{-1} , \end{aligned} \quad (2.17)$$

which relates the isothermal stress functional $\tilde{S}^*$ to the free energy functional $\mathcal{F}$. It then follows that corresponding to the stress (2.7) the free energy must be of the form

$$\psi(t) = \int_{0 < s < \infty} \mathcal{F}^* [\tilde{C}^*(t - \xi_s); \tilde{C}^*] + \mathcal{B} \int_{0 < s < \infty} \tilde{C}^*(t - \xi_s), \theta(t-s); \theta] . \quad (2.18)$$

It should be noted that the functional $\mathcal{B}$ does not depend on the present value $\tilde{C}^*$ and hence makes no contribution to the stress response. The essential difference between (2.18) and our earlier developments (e.g., [8]) is that previously the part of the free energy which corresponds to $\mathcal{B}$ above was assumed to be independent of the past history of strain altogether; here, we have started with (2.7) as an assumption and then derived (2.18).

If we use (2.8) as a starting assumption, then in an entirely similar manner we find

$$\psi(t) = \frac{\theta}{\theta_0} \int_{0 < s < \infty} \mathcal{F}^* [\tilde{C}^*(t - \xi_s); \tilde{C}^*] + \mathcal{B} \int_{0 < s < \infty} \tilde{C}^*(t - \xi_s), \theta(t-s); \theta] . \quad (2.19)$$

3. Extension to the rubber zone.

The relationship between the time variables s and ξ_s at a fixed uniform temperature θ_1 is indicated in (2.5). With reference to this expression, a study of polymeric materials and inorganic glasses reveals that in the rubber region the shift function $\phi(\theta_1)$ becomes large for increasing values of θ_1 , while in the glassy region the function $\phi(\theta_1)$ becomes small for decreasing values of θ_1 . To gain a better understanding of the nature of the constitutive relations under discussion in the rubber zone, it is instructive to examine the limiting behavior of the modified history of a given strain history when the temperature reaches that in the rubber region. In the rubber region $\phi(\theta_1) \gg 1$ and, by virtue of (2.5), $\xi_s \ll s$ for all values of s . It follows that the effect of a temperature increase is equivalent to a retardation of the strain history, and when θ becomes large we obtain for all s

$$\lim[\underline{C}(t-\xi_s) - \underline{C}1^+(s)] = 0 ,$$

where $1^+(s)$ denotes the constant function with value 1.

The above discussion suggests that the functional $\mathfrak{F}^*$ in (2.18) and (2.19) becomes a function of the present value $\underline{C}^*$ in the rubber region. If we make the further assumption that the functional $\mathfrak{B}$ is independent of the past history of the temperature in the rubber region, then it follows that $\mathfrak{B}$ is independent of the past history of strain $\underline{C}_r^*(t-\xi_s)$ since the variable ξ_s itself is dependent upon the temperature history. Hence, the functional $\mathfrak{B}$ reduces to a function of temperature only. Thus, the above assumptions require that in the rubber zone the expressions for the specific Helmholtz free energy corresponding to (2.18) and (2.19) assume the forms:

$$\psi(t) = \psi^*(\underline{C}^*) + B(\theta) \quad (3.1)$$

and

$$\psi(t) = \frac{\theta}{\theta_0} \psi^*(\tilde{c}^*) + B(\theta) \quad , \quad (3.2)$$

respectively. The corresponding expressions for the Cauchy stress calculated from (3.1) and (3.2) are given, respectively, by

$$\tilde{T}(t) = \frac{\rho}{\rho_0} \tilde{T}^*(F^*) \quad (3.3)$$

and

$$\tilde{T}(t) = \frac{\rho}{\rho_0} \frac{\theta}{\theta_0} \tilde{T}^*(F^*) \quad . \quad (3.4)$$

While the inclusion of the factor θ/θ_0 in (2.8) is not essential in the transition zone, as remarked previously in section 2 the situation is quite different in the rubber state. Rubber elasticity has certain distinctive features and characteristics when compared to other elastic materials or the elastic range of other materials such as metals; for details see Treloar [1, Ch. 2] and Flory [13, Ch. 11]. Apart from being able to sustain very large deformations and to recover their initial states upon unloading, rubbers exhibit a peculiar behavior with respect to temperature changes. In early experiments in which a simple tension test was utilized, to within an experimental error not exceeding a few per cent, it was found that the stress plotted against the extension ratio is proportional to the absolute temperature for values of the extension ratio up to 2. This extension ratio is obtained by comparing the length of the specimen under tension at temperature θ with the length of the stress-free specimen at the same temperature. Thus, the extension ratio may be regarded as the relative elongation from a configuration such as κ^* (defined in Section 2) and the present configuration κ and corresponds to that which can be calculated from (2.13) in terms of the definition of $\tilde{F}^*$. The same type of results were also found in the corresponding simple shear experiments. Inasmuch as the ratio ρ^*/ρ_0 differs from one by only a few per cent and that this is of the same order as the experimental error mentioned above, we may conclude that the stress constitutive equation (3.4) could possibly provide an adequate description of the rubber

behavior while (3.3) does not.[‡]

Another distinctive feature of rubber behavior is the thermoelastic inversion phenomenon.[†] Briefly, in a simple traction experiment, a plot of tensile force versus temperature for fixed values of the elongation (from κ_0 to κ) shows that a value of the strain exists below which the tensile force decreases with temperature, while it increases above that same limit. In this connection, we note that it can be readily demonstrated (although the calculations are lengthy but routine) that (3.4) exhibits thermoelastic inversion, while (3.3) does not. Moreover, the detailed calculations (not included here) also show that for isometric, isotonic and isentropic simple tension tests,^{*} thermoelastic inversion occurs at the strain

$$e \cong \frac{1}{3} \alpha \theta_0, \quad (3.5)$$

where α is the coefficient of thermal expansion at the reference temperature θ_0 . For the first order estimate of the thermoelastic inversion, the strain given by (3.5) coincides with the values found by Chadwick [11] on the basis of a different expression for the free energy. Qualitatively, the appearance of the thermoelastic inversion may be explained as follows: Consider a cylindrical tensile specimen and choose the X_1 -axis along its longitudinal axis in the

^{*}The same argument holds when the stress is calculated per unit area of the configuration κ_0 or the configuration κ^* , in view of the fact that the ratio ρ^*/ρ_0 is very nearly equal to one and that the rubber is very nearly incompressible under isothermal conditions.

[†]We wish to acknowledge a written discussion received from Professor P. Chadwick which, in turn, called our attention to this point while the investigation was in progress.

^{*}The distinguishing features of these tests are as follows: in an isometric test the length of the cylindrical specimen is held fixed; in an isotonic test the longitudinal stress and the lateral pressure are held fixed; and in an isentropic test the specimen is extended without change in entropy.

undeformed reference state. Further, let the x_1 -axis be in the direction of elongated specimen resulting from a one-dimensional homogeneous extensional deformation. Then, the position of a point on the longitudinal axis in the deformed state is $x_1 = X_1 + u_1(X_1)$, where u_1 is the relative longitudinal displacement, and the component of the deformation gradient $F_{11} = 1 + \partial u_1 / \partial X_1$. Also, we denote the corresponding component of the Cauchy stress by t_{11} . We observe that for a fixed value of F_{11} , the component F_{11}^* will decrease when θ increases in view of the thermal dilatation. Moreover, since the stress t_{11} is an increasing function of F_{11} (or equivalently the strain) at the reference temperature, the stress $^\dagger t_{11}^*$ will decrease when θ increases for fixed F_{11} . However, if we consider (3.4), an opposite effect will occur when t_{11}^* is sufficiently large, in view of the factor

$$\frac{\theta}{\theta_0} = 1 + \frac{\theta - \theta_0}{\theta_0} \quad (3.6)$$

preceding T^* . Thus, above a given value of strain, the effect of the factor θ/θ_0 will dominate and give rise to thermoelastic inversion. It is essentially due to the absence of θ/θ_0 that the relation (3.3) does not include the feature associated with thermoelastic inversion.

In order to gain a better understanding of the decomposition (3.2) of the specific free energy, we first calculate the expression for the specific internal energy in the case of an isotropic rubber for which the thermal stretch is

$$\bar{U}(\theta) = u(\theta) \underline{1} \quad (3.7)$$

where $\underline{1}$ is the unit tensor. For an elastic material, the constitutive relations for the specific entropy η and the specific internal energy ϵ in terms of the

[†] The stress t_{11}^* , associated with the one-dimensional homogeneous extensional deformation, is the component of the stress T^* which occurs on the right-hand sides of (3.3) and (3.4). Recall that the dependence of T^* upon F^* is obtained from isothermal experiments at the temperature θ_0 .

free energy response function $\hat{\psi} = \hat{\psi}(\underline{C}, \theta)$ are given by

$$\begin{aligned} \eta &= - \left. \frac{\partial \hat{\psi}}{\partial \theta} \right|_{\underline{F}} , \quad \psi = \hat{\psi}(\underline{C}, \theta) , \\ \epsilon &= \psi + \theta \eta = \psi - \theta \left. \frac{\partial \hat{\psi}}{\partial \theta} \right|_{\underline{F}} = - \theta^2 \left. \frac{\partial}{\partial \theta} \left(\frac{\hat{\psi}}{\theta} \right) \right|_{\underline{F}} . \end{aligned} \quad (3.8)$$

After identifying the right-hand sides of (3.8)₂ and (3.2), we obtain

$$\epsilon = [\partial u / \partial \theta / (u / \theta)] \frac{\theta}{\theta_0} \text{tr} \left\{ 2 \frac{\partial \hat{\psi}^*}{\partial \underline{C}^*} \underline{C}^* \right\} - \theta^2 \frac{\partial}{\partial \theta} \left(\frac{B}{\theta} \right) . \quad (3.9)$$

Next, we define a function $\bar{B}$ by

$$\bar{B}(\theta) = - \theta^2 \frac{\partial}{\partial \theta} \left(\frac{B}{\theta} \right) \quad (3.10)$$

and after recalling the expression for the stress in terms of the free energy response we have

$$\text{tr } \underline{T} = \rho \frac{\theta}{\theta_0} \text{tr} \left\{ 2 \frac{\partial \hat{\psi}^*}{\partial \underline{C}^*} \underline{C}^* \right\} \quad (3.11)$$

and then (3.9) can be expressed as

$$\rho \epsilon = \frac{\partial u / \partial \theta}{(u / \theta)} \text{tr } \underline{T} + \rho \bar{B}(\theta) . \quad (3.12)$$

According to (3.12), $\bar{B}(\theta)$ represents the specific internal energy of the rubber at zero stress, and (3.10) provides a way of calculating $B(\theta)$ in terms of the specific heat. Also, the form of (3.12), permits us to decide (by direct calculations) on the relative importance of the two terms on its right-hand side. The calculations that follow are based on the data of Wood and Martin [9] which were also adopted by Chadwick [11]. Thus, at a reference temperature $\theta_0 = 298^\circ \text{K}$, we have

$$\left\{ \begin{array}{l} \text{density } \rho_0 = 906.5 \text{ Kg m}^{-3} \\ \text{volume coefficient of thermal expansion } \alpha_0 = 6.36 \times 10^{-4} (^\circ \text{K})^{-1} \\ \text{specific heat at constant deformation } c_0 = 1662 \text{ J Kg}^{-1} (^\circ \text{K})^{-1} . \end{array} \right.$$

In terms of the above data, in the neighborhood of $\theta_0 = 298^\circ\text{K}$ we have

$$u = 1 + \frac{1}{3} \alpha(\theta - \theta_0) \quad , \quad \frac{\partial u}{\partial \theta} = \frac{1}{3} \alpha \quad ,$$

$$\frac{\partial u / \partial \theta}{u / \theta} = \frac{1}{3} \alpha \left\{ \left[1 + \frac{1}{3} \alpha(\theta - \theta_0) \right] \frac{1}{\theta_0} \left[1 + \frac{\theta - \theta_0}{\theta_0} \right]^{-1} \right\}^{-1}$$

$$\cong \frac{\alpha \theta_0}{3} \left[1 + \left(\frac{1}{\theta_0} - \frac{\alpha}{3} \right) (\theta - \theta_0) \right] \cong 298 \left(\frac{\alpha}{3} \right) \quad .$$

Then, with the use of (3.12), we can readily obtain for ϵ the estimate

$$\begin{aligned} p\epsilon &\cong \frac{1}{3} \frac{\alpha_0}{(1/298)} \text{tr } \underline{T} + \rho_0 c_0 (\theta - \theta_0) \\ &= \left\{ \left(\frac{1}{3} 6.36 \times 10^{-4} \times 298 \times 1.013 \times 10^5 \right) \text{tr } \underline{T} + 906.5 \times 1662 (\theta - \theta_0) \right\} \\ &\cong 6.4 \times 10^3 \text{tr } \underline{T} + 1.5 \times 10^6 (\theta - \theta_0) \end{aligned} \quad (3.13)$$

where $\underline{T}$ is expressed in atm., $(\theta - \theta_0)$ in $^\circ\text{K}$ and $p\epsilon$ in $^\dagger \text{Nm}^{-2}$.

Since the second term on the right-hand side of (3.13) dominates the value of $p\epsilon$, it is clear that the internal energy depends chiefly on the temperature and is only slightly affected by the deformation (or the corresponding stress). Moreover, in an isotropic and compressible material and for small strains, the value of $\text{tr } \underline{T}$ and hence $p\epsilon$ depend only on dilatation or volumetric deformation. These observations are in agreement with those arrived at by Chadwick [11]. In fact, an estimate of the various terms in Chadwick's expression for the specific internal energy (Eq. (10), p. 376 of [11]) give precisely the same result as above if one also assumes that $\text{tr } \underline{T}$ in (3.13) depends only upon volumetric changes.

We close the present paper with an illustration, which shows how the preceding development can be used to predict the behavior of natural rubber in compressibility tests at various temperatures and compare the results with

[†]The abbreviation Nm^{-2} stands for Newton/(meter)².

experimental values obtained by Wood and Martin [9]. Let the reference state be specified by the reference temperature θ_0 and zero pressure. Then, in a configuration corresponding to κ_0 maintained at the temperature θ_0 , the pressure-specific density (or the pressure-specific volume) relation takes the form

$$p = p^* \left(\frac{\rho}{\rho_0} \right) = p^* \left(\frac{1}{\det \underline{F}} \right), \quad (3.14)$$

where ρ_0 is the reference mass density at zero pressure and at temperature θ_0 . With the help of (3.4) and at an arbitrary temperature $\theta \neq \theta_0$, we find

$$p = \frac{\rho}{\rho_0} \frac{\theta}{\theta_0} p^* \left(\frac{1}{\det \underline{F}^*} \right) = \frac{\rho}{\rho_0} \frac{\theta}{\theta_0} p^* \left(\frac{\rho}{\rho^*} \right), \quad (3.15)$$

where ρ^* is the value of the specific mass density of the rubber at temperature θ and at zero pressure. Various forms of the function p^* in (3.15) are discussed by Chadwick [11, pp. 386-387]. As in [11], we may specify p^* by

$$p^*(x) = \kappa \frac{1}{m} (x^m - 1), \quad (3.16)$$

where the isothermal bulk modulus κ is given by[§]

$$\kappa = 1.95 \times 10^6 \text{ KPa}$$

and m is a fixed parameter. Selecting the value $m=15$ and $\theta_0 = 10^\circ\text{C}$, the values of the specific volumes at various pressures and temperatures (see Table 1) are calculated from (3.16). The corresponding experimental values of Wood and Martin [9] are listed in Table 2. Comparison of the two tables indicates that the maximum deviation occurs when the pressure is ^{*} 500 Kg/cm² and the temperature is 25°C, with a relative error of 1.9×10^{-3} . It is of interest to note that for Chadwick's more complicated model which does not have its starting point in an isothermal law at a reference temperature, the maximum relative error for the specific volume is 0.5×10^{-3} .

[§]The abbreviation KPa stands for Kilo Pascal = 1000 Pascal = 1000 Newton/m²
= (1000/9.81) Kg/m².

^{*}The physical dimension of pressure is indicated here in Kg/cm² in order to conform with the data of Wood and Martin [9].

<u>p(kg/cm²)</u>	<u>v(25°C)</u>	<u>v(20°C)</u>	<u>v(10°C)</u>	<u>v(0°C)</u>
0	1.1032	1.0998	1.0927	1.0857
100	1.0981	1.0946	1.0874	1.0803
200	1.0933	1.0898	1.0825	1.0753
300	1.0888	1.0853	1.0779	1.0706
400	1.0847	1.0811	1.0736	1.0663
500	1.0807	1.0771	1.0696	1.0622

Table 1: Calculated specific volumes $v = \frac{1}{\rho}$ in $10^{-3} \text{ m}^3/\text{Kg}$.

The experiments performed by Wood and Martin [9] give the following data (Table 2).

<u>p(kg/cm²)</u>	<u>v(25°C)</u>	<u>v(20°C)</u>	<u>v(10°C)</u>	<u>v(0°C)</u>
0	1.1032	1.0998	1.0927	1.0857
100	1.0977	1.0944	1.0876	1.0807
200	1.0926	1.0894	1.0828	1.0763
300	1.0877	1.0846	1.0782	1.0719
400	1.0830	1.0801	1.0739	1.0678
500	1.0786	1.0756	1.0697	1.0637

Table 2: Specific volumes $v = \frac{1}{\rho}$ in $10^{-3} \text{ m}^3/\text{Kg}$ obtained by Wood and Martin [9].

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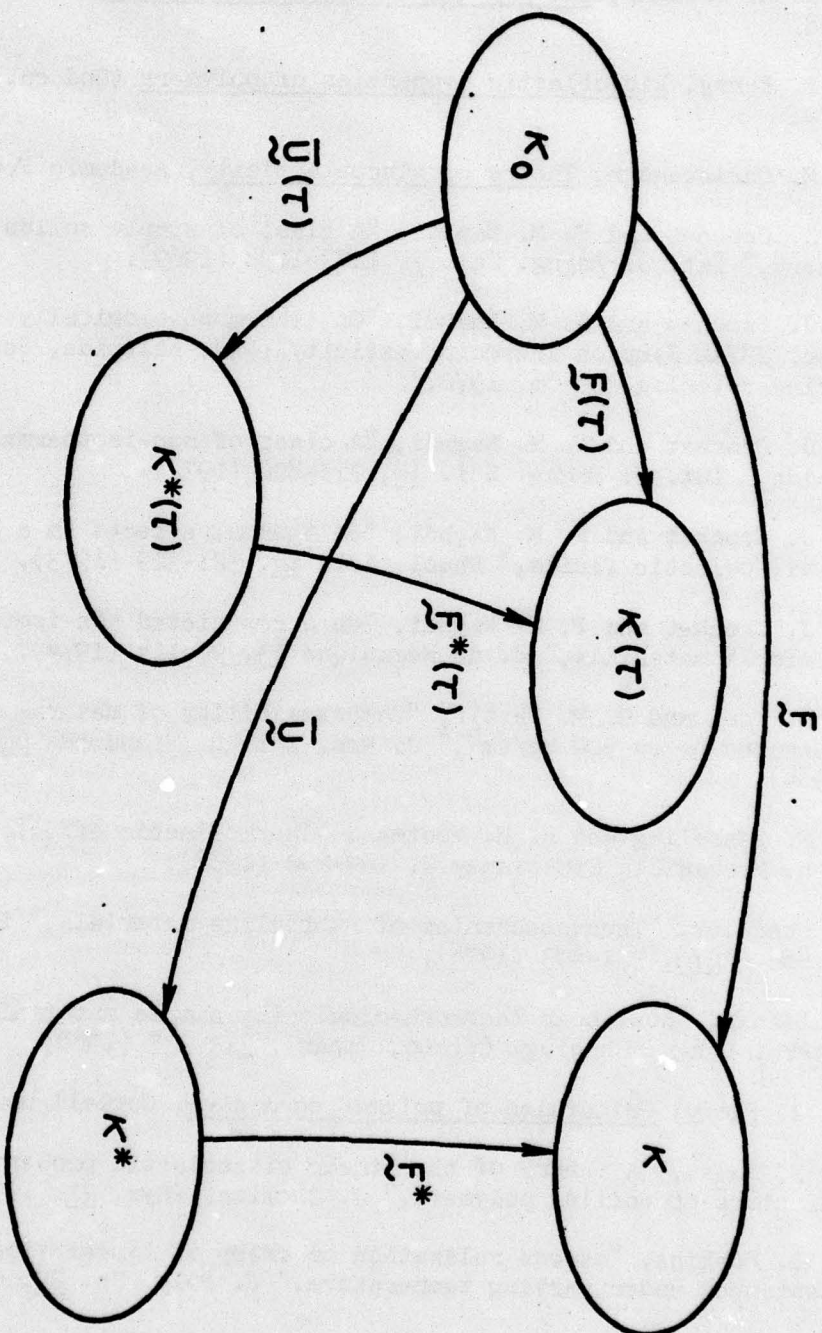


Fig. 1: A schematic diagram depicting various configurations of a neighborhood of particles, along with corresponding deformation gradient.

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