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Revisiting the Chadwick and Lu & Pister models of finite thermoelasticity for isotropic materials

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Abstract

This note reviews and presents the two dominant models of thermoelasticity developed by (1) Peter Chadwick and (2) S.C.H Lu and Karl S. Pister. Both models are widely used and cited in the literature but their differences are not well delineated in a clear and accessible way. Here we briefly review the two models using a unified notation and discuss and compare their basic properties and behavior. We show that all Lu and Pister models can be written as Chadwick model. However a Chadwick model does not fully specify a Lu and Pister model. Additional (mild) assumptions must be made to convert a Chadwick model into a Lu and Pister model. A model due to L. Anand is also presented to show its conformity to both frameworks and to highlight its usefulness.

Keywords: thermoelasticity, finite deformation, isotropic materials, Lu and Pister model, Chadwick model

SG dedicates this paper to Jörg Schröder on the occasion of his 60th birthday. Jörg has been a terrific colleague for over a quarter-century, but more importantly, he and his family have demonstrated in countless ways what friendship really means.

1 Introduction

Finite thermoelastic formulations are dominated by the models of [Chadwick \(1974\)](#) and [Lu and Pister \(1975\)](#).¹ Both formulations appear to have near co-equal popularity and it is instructive to understand their similarities and differences. The model of Chadwick involves the construction of a model free energy based upon the selection of three functions: a reference temperature strain energy function, a reference temperature internal energy function, and a heat capacity function. The model of Lu and Pister also requires the selection of three functions: a thermal expansion function in terms of temperature (which is part of an assumed multiplicative split of the deformation gradient, something not present in Chadwick’s model), a one-parameter family of strain-energy functions (parameterized by temperature), and a function only dependent on temperature. In what follows we present both models using a common notation to unify ideas. To aid in the comparison, we also present an [Anand \(2023\)](#) type free energy function – a free energy function characterized by a further separation into isochoric and volumetric parts (see also [Miehe, 1995](#)).

The central question we address is, “When are the two modeling frameworks isomorphic?” Astonishingly, this fundamental question has not, to our knowledge, been addressed even though these models have been in general use for the last 50 years. We will see that Lu and Pister models are always expressible in the Chadwick framework but Chadwick models do not have unique Lu and Pister counterparts. Additionally, when the correspondence breaks down, it is related to the violation of the commonly assumed physical assumptions of stress free reference states and isotropic deformation under pure thermal loads for isotropic materials.

2 Generic thermoelasticity

The generic model for thermoelasticity (see e.g. [Miehe, 1995](#)) starts from a free-energy function per unit reference volume

$$\psi(\mathbf{C}, \theta), \tag{1}$$

where $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ is the the right Cauchy-Green deformation tensor, \mathbf{F} is the deformation gradient, and θ is the absolute temperature. The material response can be found by considering the dissipation inequality for homothermal² bodies (see e.g., [Anand and Govindjee, 2020](#), §5.3),

$$-\dot{\psi} - \eta \dot{\theta} + \mathbf{S} : \frac{1}{2} \dot{\mathbf{C}} \geq 0, \tag{2}$$

where η is the entropy density per unit reference volume and \mathbf{S} is the 2nd Piola-Kirchhoff stress. Applying the [Coleman and Noll \(1963\)](#) argument, one immediately

¹As of 2024/03/12 on Google Scholar, Chadwick’s paper has been cited 179 times and Lu and Pister’s paper has been cited 161 times. We note in passing that, quite oddly, [Lu and Pister \(1975\)](#) does not appear to be indexed on Web of Science as of this date.

²We restrict our attention to homothermal bodies simply for convenience and without any loss of generality for the purposes at hand.

finds that the material response is given as

$$\mathbf{S} = 2 \frac{\partial \psi}{\partial \mathbf{C}}; \quad \eta = -\frac{\partial \psi}{\partial \theta}. \quad (3)$$

3 The Chadwick model

The Chadwick model is found via construction of a particular form for the free-energy function (1). This is done by noting that the internal energy per unit reference volume $e = \psi + \theta\eta$ and by defining the reference temperature (θ_o) quantities

$$\psi_o(\mathbf{C}) = \psi(\mathbf{C}, \theta_o), \quad \eta_o(\mathbf{C}) = \eta(\mathbf{C}, \theta_o), \quad e_o(\mathbf{C}) = e(\mathbf{C}, \theta_o), \quad (4)$$

along with the material heat capacity (per unit reference volume and temperature) $c = \partial e / \partial \theta$. In the above, ψ_o is properly referred to as the material's strain-energy density in the reference state – likewise for η_o and e_o .

From the definition of the heat capacity and (3)₂, note that

$$c = \frac{\partial e}{\partial \theta} = \frac{\partial \psi}{\partial \theta} + \eta + \theta \frac{\partial \eta}{\partial \theta} = -\eta + \eta + \theta \frac{\partial \eta}{\partial \theta} = -\theta \frac{\partial^2 \psi}{\partial \theta^2}. \quad (5)$$

Equation (5) implies that

$$\frac{\partial \psi}{\partial \theta}(\mathbf{C}, \theta) - \frac{\partial \psi}{\partial \theta}(\mathbf{C}, \theta_o) = -\int_{\theta_o}^{\theta} \frac{c(\mathbf{C}, \theta')}{\theta'} d\theta' \quad (6)$$

and thus

$$\eta = \eta_o + \int_{\theta_o}^{\theta} \frac{c(\mathbf{C}, \theta')}{\theta'} d\theta'. \quad (7)$$

Observing that $\psi = e - \theta\eta$, allows one to write

$$\psi = e - \theta\eta_o - \theta \int_{\theta_o}^{\theta} \frac{c(\mathbf{C}, \theta')}{\theta'} d\theta' = e - \theta \frac{e_o - \psi_o}{\theta_o} - \theta \int_{\theta_o}^{\theta} \frac{c(\mathbf{C}, \theta')}{\theta'} d\theta'. \quad (8)$$

Replacing the internal energy with the expression $e = e_o + \int_{\theta_o}^{\theta} c(\mathbf{C}, \theta') d\theta'$, results, after some algebra, in Chadwick's final construction

$$\psi(\mathbf{C}, \theta) = \frac{\theta}{\theta_o} \psi_o(\mathbf{C}) - \left(\frac{\theta}{\theta_o} - 1 \right) e_o(\mathbf{C}) + \int_{\theta_o}^{\theta} \left(1 - \frac{\theta}{\theta'} \right) c(\mathbf{C}, \theta') d\theta'. \quad (9)$$

Equation (9) is the primary result of Chadwick (1974). It provides the form for the free-energy of a thermoelastic material in terms of (a) the strain energy function measured at a fixed reference temperature, (b) the internal energy function of the material at the fixed reference temperature, and (c) the heat capacity of the material as a function of deformation and temperature. It is interesting to note, that any and

all non-linear thermal effects in material response must emanate from the last term in this expression and in particular via the material's heat capacity.

As presented, the Chadwick framework applies to all thermoelastic models as it contains no assumptions beyond equilibrium thermodynamics. Put another way, all thermoelastic models must be representable in the Chadwick form (9).

4 The Lu & Pister model

The Lu and Pister model³ also starts with free-energy function (1) and stress and entropy response functions given by (3). The model however differs from the Chadwick framework in that it employs a multiplicative split of the deformation gradient into elastic and thermal parts, where only the elastic part gives rise to changes in the material's free energy. In particular [Lu and Pister \(1975\)](#) introduce the decomposition

$$\mathbf{F} = \mathbf{F}_e \mathbf{F}_\theta, \quad (10)$$

where $\mathbf{F}_\theta = \gamma(\theta)\mathbf{1}$ and $\gamma(\theta)$ dictates the material's expansion with temperature. The central assumption is then made that

$$\psi(\mathbf{C}, \theta) = W(\mathbf{C}_e, \theta) + h(\theta), \quad (11)$$

where $\mathbf{C}_e = \mathbf{F}_e^T \mathbf{F}_e = \gamma^{-2} \mathbf{C}$, $W(\cdot, \theta)$ is a one-parameter family of strain-energies indexed by temperature, and $h(\cdot)$ is an added function solely of temperature. Observe that the stress and entropy relations are more specifically given by

$$\mathbf{S} = 2 \frac{\partial W}{\partial \mathbf{C}_e} \gamma^{-2}; \quad \eta = 2\gamma^{-3} \gamma' \frac{\partial W}{\partial \mathbf{C}_e} : \mathbf{C} - \frac{\partial W}{\partial \theta} - \frac{\partial h}{\partial \theta}. \quad (12)$$

In this model the heat capacity and internal energy are implicitly defined. In particular the heat capacity is given by the modestly complex expression

$$\begin{aligned} c &= \theta \frac{\partial \eta}{\partial \theta} \\ &= -\theta \frac{\partial^2 h}{\partial \theta^2} - \theta \frac{\partial^2 W}{\partial \theta^2} + 4\gamma^{-3} \gamma' \theta \frac{\partial^2 W}{\partial \theta \partial \mathbf{C}_e} : \mathbf{C} \\ &\quad - 4\gamma^{-6} (\gamma')^2 \theta \mathbf{C} : \frac{\partial^2 W}{\partial \mathbf{C}_e \partial \mathbf{C}_e} : \mathbf{C} + 2(-3\gamma^{-4} (\gamma')^2 + \gamma^{-3} \gamma'') \theta \frac{\partial W}{\partial \mathbf{C}_e} : \mathbf{C}. \end{aligned} \quad (13)$$

The internal energy is given by

$$e = \psi + \theta \eta = W - \theta \frac{\partial W}{\partial \theta} + h - \theta \frac{\partial h}{\partial \theta} + 2\gamma^{-3} \gamma' \theta \frac{\partial W}{\partial \mathbf{C}_e} : \mathbf{C}. \quad (14)$$

³While this model is commonly attributed to [Lu and Pister \(1975\)](#), other researchers did explore aspects of it earlier; see e.g. [Stojanovitch \(1969\)](#)

It should be noted that in this model, the modeler prescribes: (a) the unconstrained thermal expansion via $\gamma(\theta)$, (b) the strain-energy indexed by temperature, and (c) the purely thermal contribution $h(\theta)$.

Note, partial derivatives with respect to θ need to be computed at constant \mathbf{C} and not constant \mathbf{C}_e ! In Lu and Pister (1975) some of the expressions appear simpler as they introduce a function $\bar{W}(\mathbf{C}, \theta) \equiv W(\mathbf{C}_e, \theta) \equiv W(\mathbf{C}\gamma^{-2}, \theta)$ and instead of derivatives of W with respect to θ at fixed \mathbf{C} , they give expressions in terms of \bar{W} . This has the effect of hiding the γ terms in (12)₂ and (13).

5 Reconciliation of Models

For both the Lu and Pister and Chadwick models, there are three functional parameters required to fully define the free energy function and, consequently, the material response. In order for the models to be consistent with one another, it would have to be the case that the functions γ , W , and h can be determined (perhaps non-uniquely) if c , ψ_o and e_o are known, or vice-versa. Furthermore, it must be the case that any derived functions agree with the physical reality the models purport to reflect.

5.1 All Lu and Pister models are Chadwick models

Since the Chadwick framework does not involve assumptions (beyond the standard ones), all Lu and Pister models must be representable as Chadwick models. In fact given a Lu and Pister model, it is easy to determine the Chadwick functions ψ_o , e_o , and $c(\mathbf{C}, \theta)$. These are given by

$$\psi_o(\mathbf{C}) = W(\mathbf{C}_{e,o}, \theta_o) + h(\theta_o) \quad (15)$$

$$e_o(\mathbf{C}) = \psi_o(\mathbf{C}) + \theta_o \eta(\mathbf{C}_{e,o}, \theta_o), \quad (16)$$

where $\mathbf{C}_{e,o} = \gamma^{-2}(\theta_o)\mathbf{C}$, the entropy function in (16) is given in (12)₂, and the heat capacity is as given in (13). Note $\gamma(\theta_o)$ is generally unity, so $\mathbf{C}_{e,o} = \mathbf{C}$ in most situations. Thus if one knows W , h , and γ , then there are explicit expressions to compute ψ_o , e_o , and $c(\mathbf{C}, \theta)$ in the Chadwick formulation.

5.2 Are all Chadwick models Lu and Pister models?

Suppose one is given the Chadwick functions c, ψ_o, e_o . By examining the forms of (9) and (11), one can gain insight on potential forms of h and W . For instance, since ψ_o and e_o are functions of only \mathbf{C} , the only potential contribution to h from the terms in (9) containing these would come from any constants in the expressions. Here, the notation ψ_1, e_1, k_ψ, k_e , are introduced to denote the functions without any constant terms and the constant terms from the functions, respectively. One can also write $c(\mathbf{C}, \theta) = c^*(\mathbf{C}, \theta) + \bar{c}(\theta)$, where \bar{c} denotes the largest function of only θ contained in c . For example, if I_1 and I_2 are the first and second invariants of \mathbf{C} and $c = I_1\theta + I_2\theta^2 + \theta + 1$, then $\bar{c} = \theta + 1$ and $c^* = I_1\theta + I_2\theta^2$. From this, it is immediate that h is, at most

$$h(\theta) = \frac{\theta}{\theta_o} k_\psi - \left(\frac{\theta}{\theta_o} - 1 \right) k_e + \int_{\theta_o}^{\theta} \left(\frac{\theta}{\theta'} - 1 \right) \bar{c}(\theta') d\theta'. \quad (17)$$

It follows that W is at least

$$\begin{aligned} W(\mathbf{C}_e, \theta) &= \frac{\theta}{\theta_o} \psi_1(\mathbf{C}_e \gamma^2(\theta)) - \left(\frac{\theta}{\theta_o} - 1 \right) e_1(\gamma^2(\theta) \mathbf{C}_e) \\ &\quad + \int_{\theta_o}^{\theta} \left(\frac{\theta}{\theta'} - 1 \right) c^*(\mathbf{C}_e \gamma^2(\theta'), \theta') d\theta'. \end{aligned} \quad (18)$$

In (18), the fact that there are \mathbf{C}_e and γ such that $\mathbf{C} = \gamma^2 \mathbf{C}_e$ is implicitly assumed, however below this assertion is proved explicitly. Note also that one could add any function of only θ , say $z(\theta)$, to W , and still have a consistent free energy definition, so long as one also adds $-z(\theta)$ to h .

The above demonstrates that a Chadwick model can possibly be converted to a Lu and Pister model, but it does not uniquely define W or h ; nor do the forms provide the $\gamma(\theta)$ function in the Lu and Pister framework.

Claim 1 For any Chadwick functions ψ_o , e_o , and c such that

$$\psi = \frac{\theta}{\theta_o} \psi_o(\mathbf{C}) - \left(\frac{\theta}{\theta_o} - 1 \right) e_o(\mathbf{C}) + \int_{\theta_o}^{\theta} \left(\frac{\theta}{\theta'} - 1 \right) c(\mathbf{C}, \theta') d\theta',$$

and for any choice of $\gamma(\theta)$ such that $\gamma > 0$, there exists a curve \mathbf{C}_e in Lin^+ such that $\mathbf{C} = \mathbf{C}_e \gamma^2$ and $\psi(\mathbf{C}, \theta) = W(\mathbf{C}_e, \theta) + h(\theta)$ for functions W and h as in (17) and (18).

Proof The main point to prove here is that $\mathbf{C}_e \in Lin^+$ and this follows trivially from the assumptions $\gamma > 0$ and $\mathbf{C} \in Lin^+$. It does however remain to show that any arbitrary choice of positive function γ is compatible with the given heat capacity function, c . First note, $c = -\theta \partial^2 \psi / \partial \theta^2$, where the partial derivative is taken with respect to a fixed value of \mathbf{C} . A quick examination of (17) and (18) indicates that the computation of $-\theta \partial^2 (W + h) / \partial \theta^2$ at fixed \mathbf{C} will recover $c^* + \bar{c}$ as desired. Thus, compatible Lu and Pister functions can be (non-uniquely) determined from any set of Chadwick functions, with γ being an *arbitrary*, positive function. \square

Remark 1 To determine γ explicitly, one needs to take into account physical restrictions on the free energy function that both models must respect: for example, the fact that unrestrained heating should be stress free. If no gamma satisfies the condition, then this would constitute a counter example to a modified version of Claim 1 with this physical restriction imposed. Given that the Lu and Pister formulation assumes the validity of the fact that unrestrained heating is stress free, this would also constitute a counter-example to the Lu and Pister formulation assuming this is the only restriction imposed.

5.2.1 Determining γ

As noted, the question of how to define γ cannot be answered by the provided ψ_o , e_o , and c functions alone. A physical argument is needed to derive this function. It is well established that unrestrained heating should be a stress free process. Furthermore, all deformation in this process is due to thermal effects, and hence it should be the case that $\mathbf{C}_e = \mathbf{1}$, and hence $\mathbf{C} = \gamma^2 \mathbf{1}$. Setting the derivative of (9) with respect to \mathbf{C} equal to zero and substituting $\gamma^2 \mathbf{1}$ for \mathbf{C} , we arrive at

$$\frac{\theta}{\theta_o} \frac{\partial \psi_o}{\partial \mathbf{C}}(\gamma^2 \mathbf{1}) - \left(\frac{\theta}{\theta_o} - 1 \right) \frac{\partial e_o}{\partial \mathbf{C}}(\gamma^2 \mathbf{1}) + \int_{\theta_o}^{\theta} \left(\frac{\theta}{\theta'} - 1 \right) \frac{\partial c}{\partial \mathbf{C}}(\gamma^2 \mathbf{1}, \theta') d\theta' = 0. \quad (19)$$

Positive solutions to (19) for γ , if they exist, would constitute acceptable choices for the needed third Lu and Pister function. However, if multiple such solutions exist, then the implication of the choice of γ is that it also determines the curve \mathbf{C}_e for given \mathbf{C} . The curve \mathbf{C}_e is physically significant in that it represents the elastic portion of the deformation at a given temperature and deformation \mathbf{C} .

5.2.2 Implication of shifting W or h by a function of θ

As stated, W and h are only uniquely determined up to a function of θ assuming that γ exists. The question of what happens when these functions are shifted by a function of only θ naturally arises. It should be clear that there is no effect on any quantity that is derived from ψ alone, as the sum of W and h must always agree with the ψ given by the Chadwick functions, by construction. Hence, only quantities derived from only W or h are affected by a shift in either.

Given that W represents the strain energy function for the material under an isothermal process at a given temperature θ , a shift in W by a function of only θ constitutes a constant shift in the strain energy function for any fixed temperature. That is, if at a given temperature there is some restriction on the strain energy at a certain value of \mathbf{C}_e , this can be accommodated by a shift in W by a function of theta (and a corresponding shift in h by the negative of the function added to W). For instance, if $\overline{W}(\mathbf{1}, \theta)$ is to be zero at each temperature, where \overline{W} is W as a function of \mathbf{C} , then W can be adjusted accordingly by adding some function $z(\theta)$ while simultaneously adjusting h by $-z(\theta)$ without compromising agreement with the Chadwick free energy or consistency of the overarching thermoelastic theory.

Assuming that a shift in h is met with a corresponding shift in W as described, then shifting h has no physical consequences. Indeed, the purpose of h in this context is as a sort of adjustment to W , as a means of aligning the family of isothermal strain energy functions with the thermoelastic Helmholtz free energy, as described by Chadwick. It is important to note that choice of γ does not affect the definitions of W and h as functions of \mathbf{C} , as γ only appears as an argument of ψ_1 , e_1 , and c^* along with \mathbf{C}_e , and it is necessarily the case that $\mathbf{C} = \gamma^2 \mathbf{C}_e$. By the definitions of these functions, W and h have no dependency on the choice of γ .

5.2.3 Example: Finding γ for a particular model

Suppose a neo-hookean type Chadwick formulation, where

$$\psi_o(\mathbf{C}) = \frac{\mu_o}{2}(\text{tr}(\mathbf{C}) - 3 - 2\ln(J)) + \left(\kappa_o - \frac{2}{3}\mu_o\right) \frac{1}{4}(J^2 - 1 - 2\ln(J)), \quad (20)$$

$$e_o(\mathbf{C}) = 3\kappa_o\alpha_o\theta_o \ln(J), \quad (21)$$

$$c(\mathbf{C}, \theta) = c_o, \quad (22)$$

where $J = \det[\mathbf{F}]$, (μ_o, κ_o) are the small-strain shear and bulk moduli of the material in the reference state, α_o is the material's linear coefficient of thermal expansion, and c_o is the material's (constant) heat capacity. Such a choice is a not unimaginable form as each term has an easy physical justification.

Taking partial derivatives, one obtains:

$$\frac{\partial\psi_o}{\partial\mathbf{C}} = \frac{\mu_o}{2}(\mathbf{1} - \mathbf{C}^{-1}) + \left(\kappa_o - \frac{2}{3}\mu_o\right) \frac{1}{4}(J^2\mathbf{C}^{-1} - \mathbf{C}^{-1}), \quad (23)$$

$$\frac{\partial e_o}{\partial\mathbf{C}} = \frac{3}{2}\kappa_o\alpha_o\theta_o\mathbf{C}^{-1}, \quad (24)$$

$$\frac{\partial c}{\partial\mathbf{C}} = 0. \quad (25)$$

Substituting (23)-(25) into (19), noting that in this case $J = \gamma^6$, one obtains

$$\frac{\mu_o\theta}{2\theta_o}(1 - \gamma^{-2})\mathbf{1} + \left(\kappa_o - \frac{2}{3}\mu_o\right) \frac{\theta}{4\theta_o}(\gamma^4 - \gamma^{-2})\mathbf{1} + \left(1 - \frac{\theta}{\theta_o}\right) \left(\frac{3}{2}\kappa_o\alpha_o\theta_o\gamma^{-2}\right) \mathbf{1} = 0, \quad (26)$$

and after multiplying through by γ^2 one gets

$$\frac{\mu_o\theta}{2\theta_o}(\gamma^2 - 1)\mathbf{1} + \left(\kappa_o - \frac{2}{3}\mu_o\right) \frac{\theta}{4\theta_o}(\gamma^6 - 1)\mathbf{1} + \left(1 - \frac{\theta}{\theta_o}\right) \left(\frac{3}{2}\kappa_o\alpha_o\theta_o\right) \mathbf{1} = 0. \quad (27)$$

Solving (27) for γ amounts to solving the equation $A\gamma^6 + B\gamma^2 + C = 0$, with $A = (\kappa_o - \frac{2}{3}\mu_o) \frac{\theta}{4\theta_o}$, $B = \frac{\mu_o\theta}{2\theta_o}$, and $C = -\frac{\mu_o\theta}{2\theta_o} - (\kappa_o - \frac{2}{3}\mu_o) \frac{\theta}{4\theta_o} + \left(1 - \frac{\theta}{\theta_o}\right) \left(\frac{3}{2}\kappa_o\alpha_o\theta_o\right)$. Clearly, this polynomial is analytically solvable with the transformation $x = \gamma^2$. Notice that B and A are necessarily positive for materials with positive Lamé constants ($\kappa_o - \frac{2}{3}\mu_o > 0, \mu_o > 0$). For such materials, Descartes' rule of signs (see, e.g. [Conte and de Boor, 1980](#), §3.6) states there will always be a positive solution for γ for any θ such that C is negative. However, in the regime where $\theta \approx 0$, it must be the case that C is positive, and by Descartes' rule of signs, there will be no positive, real solutions for γ . Given that most materials have a positive first Lamé constant, this constitutes an example where there is no consistent Lu and Pister formulation for a given Chadwick model (at least for all admissible temperatures).

When there are to be temperatures where γ cannot be defined, one could argue that the starting free energy function is not admissible within that range of temperatures, as the deformation of an isotropic material under unconstrained heating (cooling) should be a uniform expansion (contraction). Put another way, if one requires that the deformation of an isotropic material under isothermal heating should be of the form $\mathbf{F} = \zeta \mathbf{1}$ for some positive scalar ζ for all θ , it follows that, for such materials, any Chadwick model is only admissible in the range of temperatures for which a positive solution to (19) exists. That is, a Chadwick model is admissible in a given temperature range if and only if a Lu and Pister function γ can be defined for the that range.

These examples motivate the following claim, the proof of which should be obvious at this point.

Claim 2 Given a Chadwick free energy and assuming

1. unconstrained thermal expansion is stress free, and
2. unconstrained thermal expansion has a deformation gradient of the form $\mathbf{F} = \gamma(\theta)\mathbf{1}$, where γ is positive, then

the Chadwick free energy function is admissible for all θ if and only if it is reconcilable with a Lu and Pister free energy function.

5.2.4 Example: A free energy function with a $\gamma > 0$, $\forall \theta \geq 0$

Consider the following form of the Neo-hookean strain energy presented by [Anand \(2023\)](#), based on the findings of [Treloar \(1975\)](#):

$$\begin{aligned} \psi(\mathbf{C}, \theta) = & \frac{3}{2}\mu(\bar{\lambda}^2 - 1) + \frac{1}{2}\kappa_o(\ln J)^2 - 3\kappa_o\alpha_o(\ln J)(\theta - \theta_o) \\ & + c_o(\theta - \theta_o) - \theta c_o(\ln \theta - \ln \theta_o), \end{aligned} \quad (28)$$

where $\bar{\lambda}^2 = \frac{1}{3} \text{tr}(J^{-2/3}\mathbf{C})$ and κ_o , α_o , and c_o are the (linear) bulk modulus, coefficient of thermal expansion, and specific heat (respectively). This free energy function is applicable for small to moderate values of $\bar{\lambda}$. In general, the material properties in this model would be functions of temperature and deformation, but here they are taken to be positive constants. $\mu = Nk_B\theta$ is taken to be the temperature dependent shear modulus, where N is the number of polymer chains per unit reference volume (taken to be independent of temperature and deformation here) and k_B is Boltzmann's constant. Here, we define $\mu_o = Nk_B\theta_o$ to be the reference linear shear modulus for the material. Indeed, linearization of this free energy function yields the typical stress strain relationship in linear isotropic thermal elasticity. It is important to note that the basis of this model is the idea that the free energy can be decomposed into a part depending only on the isochoric part of the deformation, $J^{-1/3}\mathbf{F}$, and a part depending only on the volumetric part, J . It is easy to see that the Chadwick functions for this free energy are

$$\psi_o = \frac{3}{2}\mu_o(\bar{\lambda}^2 - 1) + \frac{1}{2}\kappa_o(\ln J)^2, \quad (29)$$

$$e_o = 3\kappa_o\alpha_o\theta_o(\ln J) + \frac{1}{2}\kappa_o(\ln J)^2, \quad (30)$$

$$c = c_o. \quad (31)$$

Following the procedure of section 5.2.1, we take partial derivatives to achieve

$$\frac{\partial\psi_o}{\partial\mathbf{C}} = \frac{1}{2}\kappa_o(\ln J)\mathbf{C}^{-1} + \frac{1}{2}\mu_o J^{-2/3} \left(\mathbb{I}^{(4s)} - \frac{1}{3}\mathbf{C}^{-1} \otimes \mathbf{C} \right) : \mathbf{1}, \quad (32)$$

$$\frac{\partial e_o}{\partial\mathbf{C}} = \frac{3}{2}\kappa_o\theta_o\alpha_o\mathbf{C}^{-1} + \frac{1}{2}\kappa_o(\ln J)\mathbf{C}^{-1}, \quad (33)$$

$$\frac{\partial c}{\partial\mathbf{C}} = 0, \quad (34)$$

where $\mathbb{I}^{(4s)}$ is the symmetric 4th order identity tensor. Letting $\mathbf{C} = \gamma^2\mathbf{1}$, $J = \gamma^3$, it can be seen after plugging (32)-(34) into (19) that

$$\frac{1}{2}\mu\gamma^{-2}(\mathbf{1} - \frac{1}{3}(3\gamma^2)\gamma^{-2}\mathbf{1}) - \frac{3}{2}\kappa_o\alpha_o(\theta - \theta_o)\gamma^{-2}\mathbf{1} + \frac{1}{2}\kappa_o \ln \gamma^3 \gamma^{-2}\mathbf{1} = 0. \quad (35)$$

Simple algebra then yields

$$\gamma(\theta) = \exp[\alpha_o(\theta - \theta_o)], \quad (36)$$

which is the unique, positive, solution to gamma for this free energy function. Note that this is exactly the form of gamma proposed in Lu and Pister (1975). Although the functions W and h that can be constructed in this case are non-unique, natural choices arise following the procedure at the beginning of section 5.2 if one desires that W be zero when $\mathbf{F} = \mathbf{1}$ for all temperatures θ :

$$W(\mathbf{C}_e, \theta) = \frac{3}{2}G_o(\bar{\lambda}^2 - 1) + \frac{1}{2}\kappa_o(\ln J)^2 - 3\kappa_o\alpha_o(\ln J)(\theta - \theta_o), \quad (37)$$

$$h(\theta) = c_o(\theta - \theta_o) - \theta c_o(\ln \theta - \ln \theta_o), \quad (38)$$

where $\mathbf{F} = \gamma(\theta)\mathbf{F}_e$ and γ is as defined in (36). Here, (36)-(38) are fully consistent with (29)-(31).

5.2.5 Criterion to guarantee existence of admissible solutions

The above example motivates the following claim regarding a subset of Chadwick free energy functions that will always yield an admissible γ function.

Claim 3 Isotropic materials with free energy functions of the form

$$\psi(\mathbf{C}, \theta) = \psi_I(\bar{\mathbf{C}}) + (\theta - \theta_o)P_n + Q_m + h(\theta) \quad (39)$$

where ψ_I is an isotropic function of the isochoric part of \mathbf{C} , viz. invariants of $\bar{\mathbf{C}} = J^{-2/3}\mathbf{C}$, and P and Q are polynomials of $\ln J$ of order n and m , respectively, will yield positive solutions to (33), provided that the polynomial $(\theta - \theta_o)P'_n(x) + Q'_m(x) = 0$ has a solution that is real for all values of θ .

Proof First, notice that for isotropic materials, $\partial\psi_I/\partial\mathbf{C}$ evaluated at $\mathbf{C} = \gamma^2\mathbf{1}$ will be zero. This follows from the chain rule and the observation that for such \mathbf{C} the derivative $\partial\bar{\mathbf{C}}/\partial\mathbf{C}$ will be a scalar multiple of the standard deviatoric projector, which ends up being double contracted with a scalar multiple of the identity. What remains of (19) is $(\theta - \theta_o)P'_n(x) + Q'_m(x) = 0$. Then, if $x_o(\theta)$ is a solution to this equation that is real for all values of θ , we have

$$\gamma = \exp\left[\frac{1}{3}x_o(\theta)\right] \quad (40)$$

is an admissible solution (after noting that $J = \gamma^3$ for the assumed deformation). \square

Here the polynomials P_n and Q_m are not necessarily arbitrary; they must be admissible, such that $e_o(\mathbf{C}) \rightarrow \infty$ as $J \rightarrow 0$ and $e_o(\mathbf{C}) \rightarrow \infty$ as $J \rightarrow \infty$. While for higher orders it may not be trivial or even possible to determine if there is an explicit solution for x that is real for all values of $\theta \geq 0$, it is readily apparent per the example given in (28) that if $n = 1$ and $m = 2$, there will always exist a unique solution. Furthermore, this claim demonstrates that, for Anand type free energy functions, the existence of a solution to (19) depends only on the form of the volumetric part of the free energy.

6 Closing comments

The thermoelasticity models of Lu and Pister (1975) and Chadwick (1974) are seen to be specified in different manners. The framework of Chadwick requires the measurement/specification of the strain energy function at a chosen reference temperature, the determination of the internal energy at the reference temperature as a function of deformation, and the determination of the material's heat capacity as a function of temperature and deformation. The best means to accomplish these latter two points is somewhat unclear but can certainly be accomplished via regression against a variety of thermomechanical processes – for example the ones illustrated in Appendix C. The specification of the Lu and Pister model requires the measurement of the strain energy of the material indexed by temperature. Additionally one must specify the unconstrained thermal expansion of the material as a function of temperature. Once this has been done, the remaining “ $h(\cdot)$ ” function can be found once the heat capacity of the material is known as a function of temperature and deformation – a nontrivial exercise and one also needed in the Chadwick model.

The physical response of the three models using the forms most cited in the literature results in quite similar behavior for constrained pressure changes during heating, isothermal stress-strain response, and adiabatic heating during deformation. Only the linear expansion during unconstrained heating differs for the common specifications of the models when looking at large temperature excursions, but with appropriate choices this could be changed. Evidence to this effect can be found in Appendix C.

It should be observed that in the commonly used forms the Lu and Pister model has a heat capacity that is dependent on temperature and deformation, whereas the Chadwick model is often used with a constant heat capacity (though the model itself is not restricted at all to this case). The constant heat capacity assumption appears largely as a consequence of the difficulty of measuring the heat capacity simultaneously as a function of deformation and temperature.

Overall, it seems that since stress-strain measurements are relatively common, and doing so at a variety of temperatures is not too burdensome, that the Lu and Pister model may be slightly easier to specify, once the free thermal expansion response has been determined. Notwithstanding the Chadwick framework has the advantage of only requiring the stress-strain response at a fixed temperature. This is compensated for by requiring the determination of the internal energy at the fixed temperature as a function of deformation – a step which has a classically known (but somewhat involved) experimental protocol (see, e.g. [Treloar, 1975](#), Chap. 2). Both models require the complicated step of determining the material’s heat capacity as a function of both deformation and temperature – a task whose difficulty should not be underestimated.

Lastly we note that given any Lu and Pister model, its Chadwick counterpart is easily specified via algebraic operations. The reverse is not as straightforward, as Lu and Pister functions cannot be uniquely determined. In fact, if the condition that unrestrained heating be stress free is rightfully enforced, then some seemingly reasonable free energy functions that can be described with the Chadwick model cannot be described by the Lu and Pister model for all temperatures. However, if the further restriction is to be imposed that unconstrained heating of an isotropic material must yield a deformation of the form $\mathbf{F} = \zeta \mathbf{1}$ for some positive scalar ζ , then the fact that the model cannot be described by a Lu and Pister model within, say, a given temperature range implies that the Chadwick free energy is actually inadmissible within that temperature range. Thus, the two models must be reconcilable analytically for a free energy function to be deemed admissible. Noting this, extra care must be taken when specifying a Chadwick model to ensure that it is admissible over a desired range of temperatures. This is not an issue for a Lu and Pister and Anand constructions satisfying Claim 3. Of the free energy functions given here, Anand’s free energy function (or generalizations of it) would then be preferable in most circumstances given that it has the added benefit of being easier to specify.

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Appendix A Concrete Chadwick example

As a concrete example of a Chadwick-style model let us consider a compressible neo-hookean material whose reference temperature strain-energy density is given by

$$\psi_o(\mathbf{C}) = \frac{\mu_o}{2}(\text{tr } \mathbf{C} - 3 - 2 \ln J) + \left(\kappa_o - \frac{2}{3}\mu_o \right) \frac{1}{4}(J^2 - 1 - 2 \ln J), \quad (\text{A1})$$

where $J = \det \mathbf{F}$ and (μ_o, κ_o) are the small-strain shear and bulk moduli of the material in the reference state.⁴ We will further assume that the reference internal

⁴This latter point can be seen by considering the expression for the Cauchy stress along with the two deformations $\mathbf{F} = \mathbf{1} + \gamma \mathbf{e}_1 \otimes \mathbf{e}_2$ and $\mathbf{F} = (1 + \epsilon_v/3)\mathbf{1}$, $(\gamma, \epsilon_v) \ll 1$, which results in $\boldsymbol{\sigma} \approx \gamma \mu_o (\mathbf{e}_1 \otimes \mathbf{e}_2 + \mathbf{e}_2 \otimes \mathbf{e}_1)$ and $\boldsymbol{\sigma} \approx \kappa_o \epsilon_v \mathbf{1}$, respectively.

energy only depends on the Jacobian determinant

$$e_o(\mathbf{C}) = 3\kappa_o\alpha_o\theta_o \ln J, \quad (\text{A2})$$

where α_o is the material's *linear* coefficient of thermal expansion. Lastly we will assume that the material's heat capacity is a constant, c_o , so that the third term in (9) is given as

$$\int_{\theta_o}^{\theta} \left(1 - \frac{\theta}{\theta'}\right) \underbrace{c(\mathbf{C}, \theta')}_{=c_o} d\theta' = c_o \left(\theta - \theta_o - \theta \ln \left(\frac{\theta}{\theta_o}\right)\right). \quad (\text{A3})$$

This assumption is not physically correct for temperatures which are low with respect to the material's Debye temperature where one expects a non-linear decrease to zero with temperature (see e.g., Reif, 2009, §10.2).

A.1 Stress and entropy expressions

With the assumed functions the material response functions are easily at hand. The entropy is given as

$$\eta(\mathbf{C}, \theta) = -\frac{\partial \psi}{\partial \theta} = -\frac{\psi_o(\mathbf{C}) - e_o(\mathbf{C})}{\theta_o} + c_o \ln \left(\frac{\theta}{\theta_o}\right). \quad (\text{A4})$$

The Cauchy stress $\boldsymbol{\sigma} = \mathbf{F}\mathbf{S}\mathbf{F}^T/J$ is given as

$$\boldsymbol{\sigma} = \frac{\theta}{\theta_o} \frac{\mu_o}{J} (\mathbf{b} - \mathbf{1}) + \left(\frac{\theta}{\theta_o} \left(\kappa_o - \frac{2}{3}\mu_o\right) \frac{1}{2} \left(J - \frac{1}{J}\right) - 3\frac{\kappa_o\alpha_o}{J}(\theta - \theta_o)\right) \mathbf{1}. \quad (\text{A5})$$

A.2 Constrained heating

For this model during constrained heating, where $\mathbf{b} = \mathbf{1}$ and $J = 1$, one sees that

$$\boldsymbol{\sigma} = -3\kappa_o\alpha_o(\theta - \theta_o)\mathbf{1}, \quad (\text{A6})$$

which corresponds to the simplest thermoelastic response of a material.

A.3 Unconstrained heating

At the other limit, when $\boldsymbol{\sigma} = \mathbf{0}$ during heating, one finds that the deformation is given by

$$\mathbf{F} = J^{\frac{1}{3}}\mathbf{1}, \quad (\text{A7})$$

where J is found by solving the non-linear relation

$$0 = \frac{\theta}{\theta_o} \frac{\mu_o}{J} (J^{\frac{2}{3}} - 1) + \left(\frac{\theta}{\theta_o} \left(\kappa_o - \frac{2}{3}\mu_o\right) \frac{1}{2} \left(J - \frac{1}{J}\right) - 3\frac{\kappa_o\alpha_o}{J}(\theta - \theta_o)\right). \quad (\text{A8})$$

Observe that the *linear* expansion is not simply given by $J^{\frac{1}{3}} - 1 = \alpha_o(\theta - \theta_o)$.

Appendix B Concrete Lu & Pister model

As a concrete example of a Lu and Pister model let us consider again a compressible neo-hookean material, where

$$W(\mathbf{C}_e, \theta) = \frac{\theta}{\theta_o} \frac{\mu_o}{2} (\text{tr } \mathbf{C}_e - 3 - 2 \ln J_e) + \left(\kappa_o - \frac{2}{3} \frac{\theta}{\theta_o} \mu_o \right) \frac{1}{4} (J_e^2 - 1 - 2 \ln J_e). \quad (\text{B9})$$

We will assume that

$$\gamma(\theta) = 1 + \alpha(\theta - \theta_o). \quad (\text{B10})$$

We also assume $h(\theta) = c_o \left(\theta - \theta_o - \theta \ln \left(\frac{\theta}{\theta_o} \right) \right)$. Note that the meaning of μ_o and κ_o are that they are the small-strain shear and bulk modulus in the reference state. However c_o is not the material's complete heat capacity due to a deformational coupling.

B.1 Stress and entropy expressions

For our assumed model, the Cauchy stress is given by

$$\boldsymbol{\sigma} = \frac{\theta}{\theta_o} \frac{\mu_o}{J} (\mathbf{b} \gamma^{-2} - \mathbf{1}) + \left(\kappa_o - \frac{2}{3} \frac{\theta}{\theta_o} \mu_o \right) \frac{1}{2} \left(J \gamma^{-3} - \frac{1}{J \gamma^{-3}} \right) \mathbf{1}. \quad (\text{B11})$$

The entropy relation is given as

$$\begin{aligned} \eta &= c_o \ln \left(\frac{\theta}{\theta_o} \right) \\ &- \frac{1}{\theta_o} \frac{\mu_o}{2} (\text{tr } \mathbf{C} \gamma^{-2} - 3 - 2 \ln(J \gamma^{-3})) + \frac{\mu_o}{6 \theta_o} (J^2 \gamma^{-6} - 1 - 2 \ln(J \gamma^{-3})) \\ &+ \gamma' \gamma^{-3} \left(\frac{\theta \mu_o}{\theta_o} (\text{tr } \mathbf{C} - 3 \frac{1}{J} \gamma^2) + \left(\kappa_o - \frac{2}{3} \frac{\theta}{\theta_o} \mu_o \right) \frac{3}{2} \left(J^2 \gamma^{-4} - \frac{1}{J} \gamma^2 \right) \right). \end{aligned} \quad (\text{B12})$$

B.2 Constrained heating

Under constrained heating $\mathbf{b} = \mathbf{1}$ and $J = 1$, one sees for this model that

$$\boldsymbol{\sigma} = \left(\frac{\theta}{\theta_o} \mu_o (\gamma^{-2} - 1) + \left(\kappa_o - \frac{2}{3} \frac{\theta}{\theta_o} \mu_o \right) \frac{1}{2} \left(\gamma^{-3} - \frac{1}{\gamma^{-3}} \right) \right) \mathbf{1}. \quad (\text{B13})$$

This expression looks a fair bit different from the Chadwick expression (A6) but for relevant material properties can be numerically quite similar.

B.3 Unconstrained heating

At the other limit, when $\boldsymbol{\sigma} = \mathbf{0}$ during heating, one finds that the deformation is given by

$$\mathbf{F} = J^{\frac{1}{3}} \mathbf{1} = \gamma \mathbf{1} = (1 + \alpha_o(\theta - \theta_o)) \mathbf{1}, \quad (\text{B14})$$

The *linear* expansion is simply given by $\alpha_o(\theta - \theta_o)$. Thus in the [Lu and Pister \(1975\)](#) framework it is much easier to impose the free expansion behavior in comparison to the [Chadwick \(1974\)](#) framework, cf. [\(A8\)](#).

Appendix C Comparing the models

In this section we detail numerical examples to give a sense of the numerical and functional behavior of the two specific models presented in [Appendices A and B](#), as well as the Anand model. They have a great deal of similarity to each other even though they differ in the details of their expressions and it is instructive to understand how they behave over a wide range of inputs. Assuming the statements in [Claim 2](#) are enforced, the Chadwick model presented is inadmissible at low temperatures. However, given that the model is admissible for temperatures one would reasonably encounter for many real materials, it would still be a reasonable model to use. By looking at numerical examples we can gain an appreciation for the similarity or lack thereof between the models when they are utilized in their common forms as outlined above.

For material properties we will use $\alpha_o = 3.4 \times 10^{-4} \text{ K}^{-1}$, $\mu_o = 1 \text{ MPa}$, $\kappa_o = 1 \text{ GPa}$, and $\theta_o = 300 \text{ K}$. These do not correspond to any particular material but are reasonable for various silicone rubbers. Note that for these values, the Chadwick model proposed is valid only for temperatures greater than 36 K, since there are no positive solutions to γ below this temperature. Additionally, for the Anand model, we assume that the temperature dependent shear modulus at the reference temperature is equal to the linear shear modulus. For a heat capacity model we will consider $c_o = 1000 \text{ J K}^{-1} \text{ kg}^{-1}$.

As examples we will consider the following 6 processes:

1. The pressure during fully constrained heating.
2. The (linear) thermal expansion $J^{1/3} - 1$ during heating.
3. Temperature changes during adiabatic uniaxial and pure shear deformation.
4. The stress-stretch behavior at various temperatures for uniaxial and pure shear deformations.
5. The entropy-stretch behavior at various temperatures for uniaxial and pure shear deformations.
6. The heat capacity-stretch behavior at various temperatures for uniaxial and pure shear deformations.

C.1 Functional expressions

As noted, given a Lu and Pister model specification, it is possible to compute the Chadwick base functions ψ_o, e_o, c . For our concrete example, we see that

$$\begin{aligned} W(\mathbf{C}_{e,o}, \theta_o) &= \frac{\theta_o \mu_o}{\theta_o} (\text{tr } \mathbf{C}_{e,o} - 3 - 2 \ln J_{e,o}) + \left(\kappa_o - \frac{2 \theta_o}{3 \theta_o} \mu_o \right) \frac{1}{4} (J_{e,o}^2 - 1 - 2 \ln J_{e,o}) \\ &= \frac{\mu_o}{2} (\text{tr } \mathbf{C} - 3 - 2 \ln J) + \left(\kappa_o - \frac{2}{3} \mu_o \right) \frac{1}{4} (J^2 - 1 - 2 \ln J), \end{aligned} \tag{C15}$$

which exactly matches the usual Chadwick reference density, i.e. [\(A1\)](#).

For the reference internal energy implied by the usual Lu and Pister model we see that

$$\begin{aligned}
e_o &= \psi_o + \theta_o \eta_o \\
&= \frac{\mu_o}{2} (\text{tr } \mathbf{C} - 3 - 2 \ln J) + \left(\kappa_o - \frac{2}{3} \mu_o \right) \frac{1}{4} (J^2 - 1 - 2 \ln J) \\
&+ \theta_o \left[-\frac{1}{\theta_o} \frac{\mu_o}{2} (\text{tr } \mathbf{C} - 3 - 2 \ln J) + \frac{\mu_o}{6\theta_o} (J^2 - 1 - 2 \ln J) \right. \\
&\left. + \alpha \left(\mu_o (\text{tr } \mathbf{C} - 3 \frac{1}{J}) + \left(\kappa_o - \frac{2}{3} \mu_o \right) \frac{3}{2} \left(J^2 - \frac{1}{J} \right) \right) \right] \\
&= \kappa_o \frac{1}{4} (J^2 - 1 - 2 \ln J) + \theta_o \alpha \left[\mu_o (\text{tr } \mathbf{C} - 3 \frac{1}{J}) + \left(\kappa_o - \frac{2}{3} \mu_o \right) \frac{3}{2} \left(J^2 - \frac{1}{J} \right) \right], \tag{C16}
\end{aligned}$$

a relation that is a fair bit more complex than the usual Chadwick expression (A2).

A similar situation holds for the heat capacity which is built into the Lu and Pister model. In particular, it is certainly not a constant.

For the Anand (2023) free energy (28), the Cauchy stress is given as

$$\boldsymbol{\sigma} = \frac{G_o}{J} \left[\left(J^{-2/3} \right) \left(\mathbf{B} - \frac{1}{3} \text{tr}(\mathbf{B}) \mathbf{1} \right) \right] + \frac{\kappa_o}{J} (\ln J - 3\alpha_o(\theta - \theta_o)) \mathbf{1}. \tag{C17}$$

Here, the reference free energy is given in (30), and the entropy is

$$\eta(\mathbf{C}, \theta) = 3\kappa_o \alpha_o (\ln J) + c_o (\ln \theta - \ln \theta_o) - \frac{3}{2} N k_b (\bar{\lambda}^2 - 1). \tag{C18}$$

Similar to the Chadwick material, the heat capacity for the Anand model is assumed constant.

C.2 Constrained and free heating

In both the Chadwick and Anand models, the pressure during constrained heating is given by (A6) – a linear relation. For the Lu and Pister model, it is given by (B13) – a nonlinear expression. For our concrete models, however, the differences are seen to be relatively minor as seen in Fig. C1(left)

For unconstrained temperature changes, the linear thermal strain is given by $J^{1/3} - 1$. For the Chadwick model, one needs to solve the nonlinear relation (A8) for J for given temperatures. This can be effectively accomplished using Newton's method; though care needs to be taken that the initial iterate is large enough to ensure convergence. For the reconcilable Anand model, γ has already been calculated analytically as an exponential in (36). In the Lu and Pister model, the specification of $\gamma(\theta)$ directly gives this information. For our concrete models, Fig. C1(right), one sees rather different model responses once one considers large thermal changes. For small thermal changes, the models are quite similar.

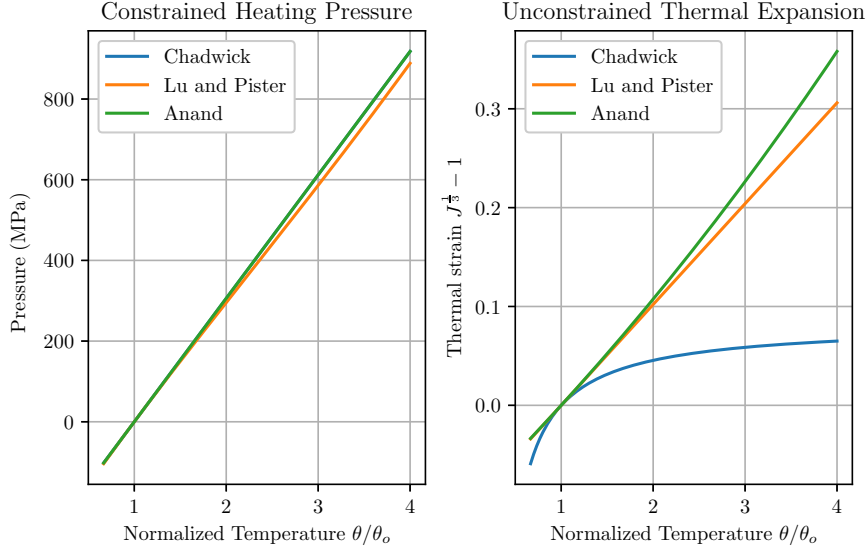


Fig. C1 Fully constrained pressure changes during thermal changes (left). Linear thermal expansion during unconstrained thermal changes (right).

Of course different functional choices in the models would allow the two models to match in this response. But we only consider the choices commonly cited in the literature, as this is how these models would be naïvely applied in practice.

C.3 Adiabatic temperature changes during uniaxial and pure shear deformations

During adiabatic deformation, the entropy is considered to be constant (isentropic deformation). For the Chadwick model, one can solve (A4) for the temperature given the deformation. Note that in uniaxial deformation $\mathbf{C} = \text{diag}(\lambda_1, \lambda_2, \lambda_2)$. The transverse stretch λ_2 is determined from (A5) by enforcing the transverse stresses to be zero. For convenience, we specify the axial stress value and solve for λ_1 from (A5). Thus in total three nonlinear equations in three unknowns need to be solved. This is accomplished again using Newton's method. During pure shear, it is noted that $\mathbf{C} = \text{diag}(\lambda_1, \lambda_2, 1)$ and the 2-direction stress is zero. For the Lu and Pister model we employ the same procedure, now using (B11) and (B12). The solution procedure is the exact same for the Anand free energy using (C17) and (C18).

The results are shown in Fig. C2. It is seen that all models return very similar results for both modes of deformation.

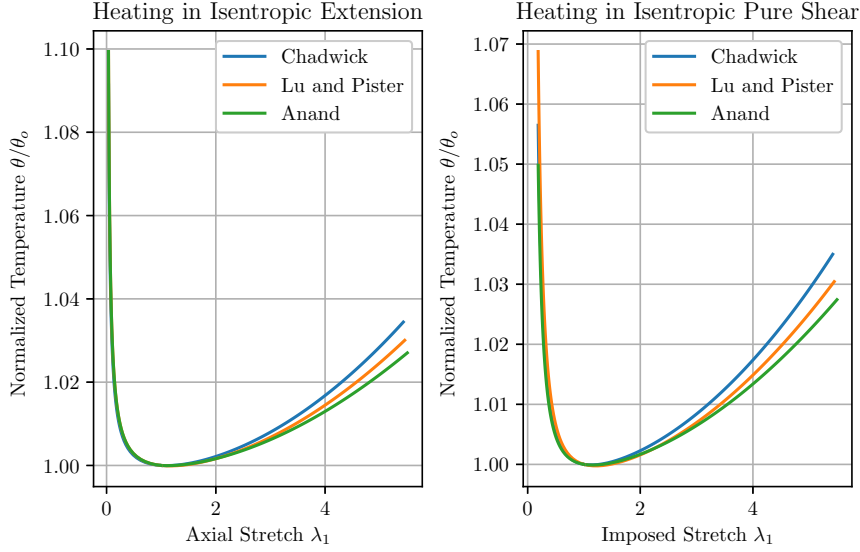


Fig. C2 Adiabatic temperature changes during deformation. Uniaxial deformation (left). Pure shear deformation (right).

C.4 Isothermal stress-stretch response during uniaxial and pure shear deformations

To compute isothermal stress-stretch response for the Chadwick model one needs to evaluate (A5) where the transverse stress is taken as zero. This is efficiently done using Newton’s method as described above for both uniaxial and pure shear deformations. For the Lu and Pister model, the exact same procedure is used with (B11). Again, the procedure is the same for the Anand free energy with (C17).

The results are shown in Fig. C3. It is seen that all models produce very similar results for both modes of deformation.

C.5 Isothermal entropy-stretch response during uniaxial and pure shear deformations

To compute isothermal entropy-stretch response for the Chadwick model one follows the procedure as outlined for computing stresses and utilizes the computed deformation state to evaluate (A4). For the Lu and Pister model, the exact same procedure is used but with (B12). Again, the procedure is the same for the Anand free energy with (C18).

The results are shown in Fig. C4. It is seen that all models produce very similar variations with respect to deformation for both modes of deformation. However at lower temperatures, numerical differences occur. Notwithstanding, qualitatively the models are quite similar with respect to their entropy response as a function of deformation.

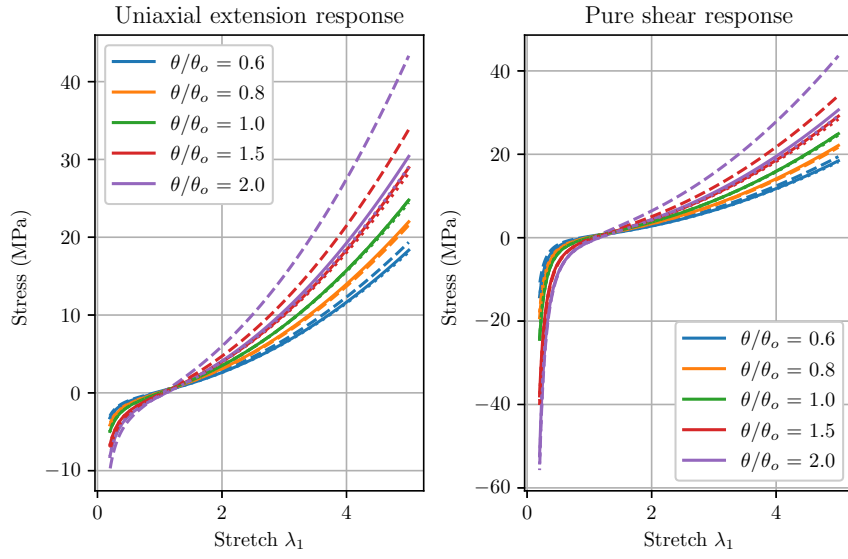


Fig. C3 Stress-stretch response at various temperatures. Solid lines = Lu and Pister. Dashed lines = Chadwick. Dotted lines = Anand. Uniaxial deformation (left). Pure shear deformation (right).

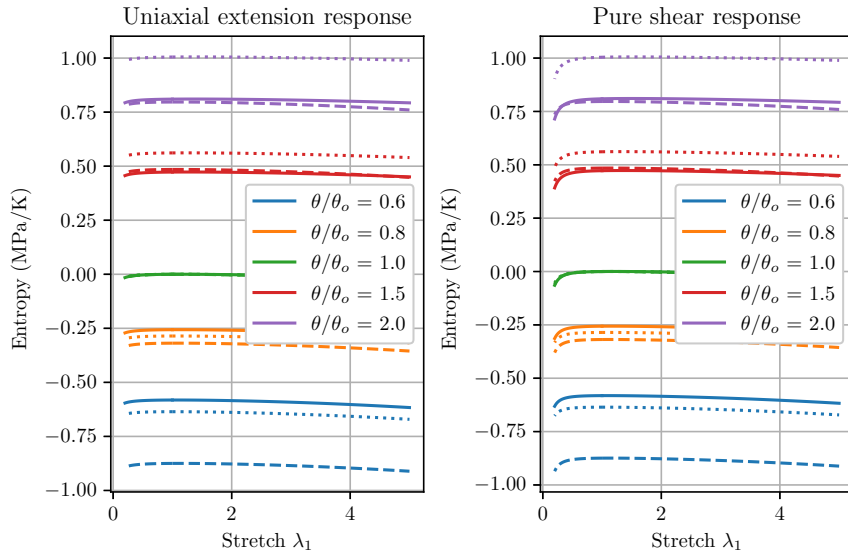


Fig. C4 Entropy-stretch response at various temperatures. Solid lines = Lu and Pister. Dashed lines = Chadwick. Dotted lines = Anand. Uniaxial deformation (left). Pure shear deformation (right).

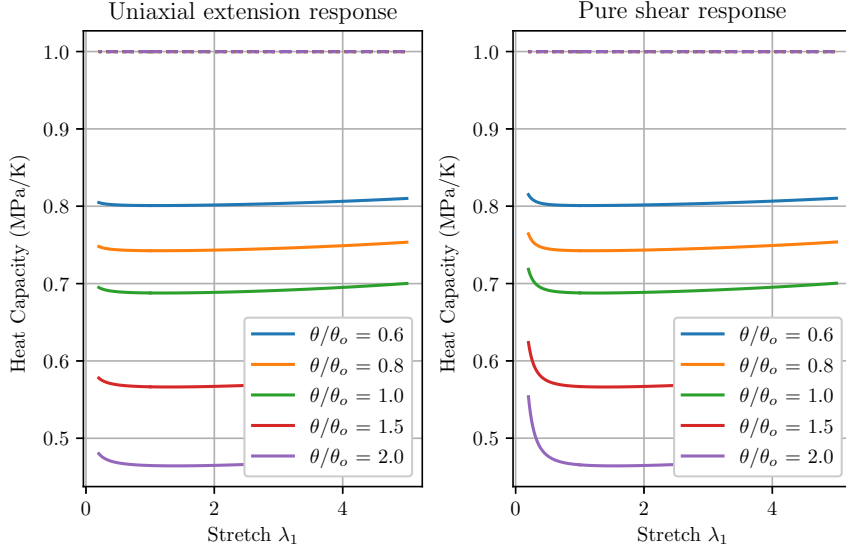


Fig. C5 Heat capacity-stretch response at various temperatures. Solid lines = Lu and Pister. Dashed lines = Chadwick. Dotted lines = Anand. Uniaxial deformation (left). Pure shear deformation (right).

C.6 Isothermal heat capacity-stretch response during uniaxial and pure shear deformations

To compute heat capacity along isothermal deformation paths one can use the results of the preceding section and compute the derivative with respect to temperature, followed by a multiplication by temperature.

The results are shown in Fig. C5. In the Chadwick and Anand models, the heat capacity we assumed was constant, and the computation bears that out. Independent of temperature or deformation state the heat capacity does not change.

For the Lu and Pister model, one sees a response that indicates that under extension, the heat capacity is largely constant but that there are strong variations in compression and with respect to temperature. It is also noted that the built-in couplings to deformation are providing negative contributions to the heat capacity. The other oddity of the Lu and Pister model is that the simple heat capacity formulation we are using is decreasing with an increase in temperature in contradiction to expectations from statistical physics. Thus the $h(\theta)$ expression should be adjusted to compensate for this. Note, however, that doing so will come at the expense of the numerical matching seen in many of the prior comparison tests.

C.7 Reference internal energy-stretch response during uniaxial and pure shear deformations

To compute the reference internal energy for the given deformation paths we only need evaluate (A2), (30), and (C16).

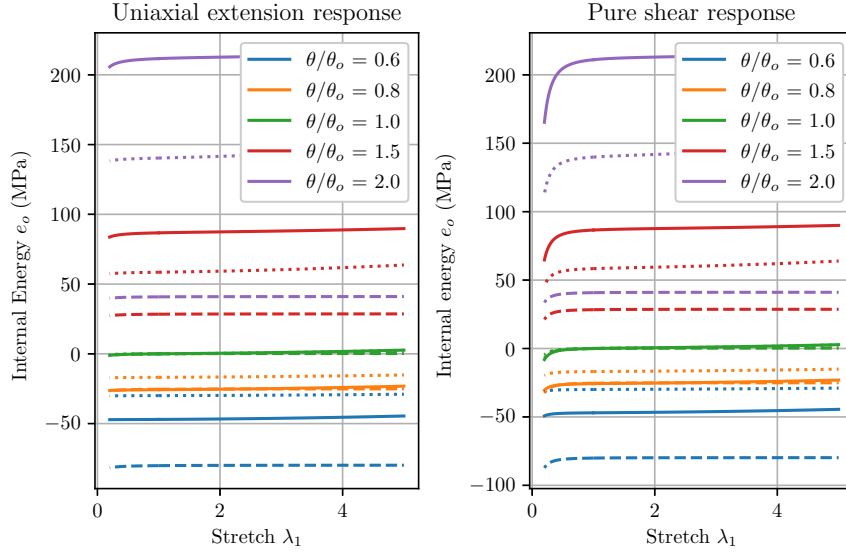


Fig. C6 Reference internal energy-stretch response at various temperatures. Solid lines = Lu and Pister. Dashed lines = Chadwick. Dotted lines = Anand. Uniaxial deformation (left). Pure shear deformation (right).

The results are shown in Fig. C6. For all models with these deformation paths, the internal energy is largely constant at each temperature, though in compression some non-linear variations are apparent. Each model shows similar qualitative behavior with respect to temperature, though numerical values do differ.