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# Thermodynamic effects of linear dissipative small deformations

**Afshin Anssari-Benam · Giuseppe Viola · Theodosios Korakianitis**

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**Abstract** This paper presents a phenomenological model of dissipative losses manifested as heat transfer effects in small linear deformations of solid continua. The impetus is the need for a unified theory characterizing heat transfer effects (called "stretching calorimetry" in the literature) on the mechanics of deformations from a macroscopic point of view, overcoming the fragmentary description of these thermodynamic effects in the available literature. The model is based on derivation of mathematical expressions that quantify the contribution of the heat transfer effects and of the mechanical work in small linear deformations. The formulation has been developed by considering the Gibbs' free energy and the entropy functions of the body under deformation and applying the energy balance to the continuum. The model has been compared to available experimental data of measurements of such heat effects in linear deformations ("stretching calorimetry") of a broad range of materials. Results are presented by illustrating force-elongation values under the Hooke's law, the proposed model, and the experimental data. The calculated model results show excellent agreement with the reported experimental data, for all the different classes of materials considered.

**Keywords** Linear deformation · Deformation heating effect · Internal energy · Stretching calorimetry · Force-elongation

## Introduction

Empirical measurements of stress and strain in deformation processes have been the fundamental approach in understanding the mechanical behaviour of solid continua. The results obtained from such experiments have been the main basis of the different constitutive equations proposed to characterize the mechanics of materials, from Hooke's Law (1676–1678) up to the recent more specialized and detailed models. Although the experimental measurements of the set of these two mechanical variables (stress–strain) provide important information about the macroscopic deformation behaviour of materials, it is well established that thermodynamic parameters related to the heating effects of deformation should also be taken into consideration, for a more comprehensive constitutive description of mechanics of any solid continuum [1, 2]. The first law of thermodynamics leads to application of the energy conservation in deformation processes, thus the constitutive equations of any material must account for the mechanical work of the applied force, as well as the heat transfer effects occurring during the mechanical deformation of the body [3].

The study of interaction between deformation and heat effects has lead to development of the field of thermoelasticity. Thermoelastic models are based on the solution of the field equations, which couple the temperature and displacement fields of the continuum under deformation. In this approach, the field equations have often been flanked with the equation of heat conduction [4]. Irreversible phenomena related to thermoelastic dissipation have also

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A. Anssari-Benam · T. Korakianitis (✉)
Department of Engineering, School of Engineering
and Materials Science, Queen Mary, University of London,
Mile End Road, London E1 4NS, UK
e-mail: theodosios@alum.mit.edu

G. Viola
Department of Materials, School of Engineering and Materials
Science, Queen Mary, University of London, Mile End Road,
London E1 4NS, UK

been addressed and described using different approaches [5–7]. More recently there has been an increasing interest for thermoelastic damping phenomena in engineering practice, in particular in micromechanical resonators [8, 9], composites and hierarchical structures [10], and thermoelastic stress analysis TSA [11].

As the coupling of thermodynamic and mechanical variables is intrinsic to any deformation process, valuable information could be obtained by the simultaneous measurements of both effects. "*Stretching calorimetry*", as it is called in the literature, represents a powerful technique to study thermodynamic effects of deformation processes, as it allows measuring the heat transfer as well as the work of deformation, providing the possibility of a complete thermomechanical characterization of any solid during its stretching and/or contraction [1, 2, 12]. The deformation calorimeters commonly used in calorimetry measurements include two separate chambers, one for the deforming sample, and a second one at reference (atmospheric) temperature. In these experiments, the sample is initially elongated, typically resulting in deformation strain and a small but finite temperature change of the sample. Subsequently, the sample is kept elongated (stress is kept constant) while its temperature is gradually reduced by conduction to the surrounding air in the sample chamber, eventually returning to the initial reference temperature. The heat interaction is quantified by measuring the very small transient temperature changes during the deformation process [2, 13, 14]. The measurements are carried in very low strain rates, and in addition, each stretching step is often followed by a long time wait required for thermal relaxation [2, 13, 14]. Such conditions lead to a nearly isothermal quasi-static deformation process.

Thus during a sequence of such elongation processes there are small but finite amounts of heat transfer from the sample to its surroundings. Although the sample is kept very close to isothermal conditions, each small but finite heat transfer process results in small but finite amounts of energy dissipation to the surroundings, and entropy transfer from the sample to the surroundings via the infinitesimal heat interaction. As there is no attempt to derive any work from the temperature difference between the sample and the surroundings, this also results in small but finite amounts of entropy increase by irreversibility [15].

Although there are a considerable number of studies on calorimetric investigations, a general constitutive expression able to cover the thermomechanical behaviour of a broad range of materials based on the calorimetry findings has not yet been proposed. Göritz (1986) used a deformation calorimeter for stretching a steel alloy and polymers and used a constitutive equation based on Thompson's expression [16]. His experimental results showed a deviation from Hooke's Law, even for small strains within the linear region, since the thermodynamic variables have not been introduced in Hooke's model. Although the experimental values for the steel alloy were well described by the Göritz's equation, the results for the polymers showed evident deviations from his predictions. Privalko et al. (1999), Balta Calleja et al. (2000), Azura et al. (2003) and Karaman et al. (2005), have performed stretching calorimetry on various types of polymer networks and have proposed different constitutive expressions, in accordance to their experimental results [13, 14, 17, 18]. The variety of constitutive expressions available in the literature can also be seen for other classes of materials such as elastomers and rubbers. Reichert et al. (1987), Azura et al. (2003) and Göritz and Hafner (2003), for instance, have performed stretching calorimetry experiments on such materials and have proposed different constitutive equations [14, 19, 20]. Thus a general quantitative description of mechanical behaviour of materials still remains a challenging task in formulating constitutive models [21].

In the present paper, we propose an alternative to the current thermoelastic models, by decoupling the temperature and deformation fields using the experimental deformation calorimetry data. While each one of the processes of elongation followed by waiting for temperature equilibrium may be considered either isothermal or nearly isentropic due to the infinitesimal nature of the losses, a series of such small increments add up to small but finite energy loss via heat transfer to the surroundings, and small but finite entropy generated by irreversibility, leading to the use of the word "dissipative" in the title of the paper. This paper concentrates on the derivation of simple constitutive equations to describe this process, and a comparison with experimental data. We show that, in order to estimate the overall deformation of the body, the complexity related to the solution of the field equations of temperature and displacement can be avoided by considering the dissipative heat interaction measured by the calorimeter and by quantifying the variation of internal energy of the body during the deformation process. We then derive a new constitutive expression for elongation based on the developed internal energy function, which enables the prediction of force-elongation trends for various types of materials, overcoming the diversity of the employed approaches to couple deformation and thermal effects in the currently available calorimetry investigations. In order to verify the accuracy of the model, we compare the experimental results available in the literature with the values calculated using our model. The generality of the thermodynamic principles and the assumptions used to derive the equations, together with the simple form of the constitutive expression developed, makes the proposed model easily applicable to any type of material. The second-law implications of this process will be examined in a future paper.

## Theoretical formulation

For the purposes of this paper, we use the following definitions: a deformation is defined as linear if it obeys a linear stress-strain relationship. A specimen experiencing linear deformations may or may not return to its original length when the stress is removed. A deformation is defined as elastic if the specimen returns to its original length when the stress is removed (both stress and strain return to zero). Linear elastic deformations are those that obey both the above definitions.

For any solid continuum undergoing small linear deformations the energy balance for the closed control volume surrounding the solid is:

$$dU = dQ_{in} + dW_{in} \quad \text{or} \quad dU + dQ_{ot} = dW_{in} \tag{1}$$

where $dU$ is change in internal energy, $dQ_{ot}$ is the deformation heat transferred out of the continuum, and $dW_{in}$ is the work done on the continuum during the deformation process by an increment of applied force, $df$.

To express the linear deformation work $dW$ in (1), Hooke's Law $\sigma = E\varepsilon$, could be integrated to obtain the work of deformation per unit volume $w$ as:

$$w = \frac{1}{2}E\varepsilon^2 \tag{2}$$

By introducing the extension ratio $\lambda$ defined as the ratio $L/L_0$, with $L_0$ being the initial length of specimen and $L$ the length of the deformed specimen, it is possible to replace in (2) the deformation $\varepsilon$ by $(\lambda - 1)$ to obtain:

$$w = \frac{1}{2}E(\lambda - 1)^2. \tag{3}$$

Differentiating (3) results in

$$dw = E(\lambda - 1)d\lambda. \tag{4}$$

Since (4) gives the work per unit volume, it should be multiplied by the overall volume of the continuum, to get the total amount of work $dW$:

$$dW = ALE(\lambda - 1)d\lambda \tag{5}$$

where $A$ is the cross-sectional area of the continuum in the direction of loading.

In order to obtain the expression for the exchanged heat $dQ$ during the deformation process, we start from the definition of Gibbs' free energy of the continuum

$$G = U + P_iV - TS \tag{6}$$

where $P_i$ is the internal pressure of the solid, often referred as *hydrostatic internal pressure* (for a more detailed explanation see the references [20, 22]), $U$, $T$ and $S$ are the internal energy, the temperature and the entropy of the continuum, respectively. By differentiating both sides of the above equation one gets:

$$dG = dU + P_idV + VdP_i - TdS - SdT. \tag{7}$$

From a thermodynamic approach, for an infinitesimal uniaxial elongation with the force $f$, the deformation work $dW$ can be written as [20]:

$$dW = fdL - P_idV. \tag{8}$$

The infinitesimal term $dQ$ under the calorimetry conditions described above can be expressed as:

$$dQ = TdS. \tag{9}$$

By substituting (1), (8) and (9) into (7), we obtain:

$$dG = fdL + VdP_i - SdT. \tag{10}$$

Partial derivatives of $G$ with respect to $L$ and $T$ will subsequently be:

$$\left(\frac{\partial G}{\partial L}\right)_{T,P_i} = f, \quad \left(\frac{\partial G}{\partial T}\right)_{L,P_i} = -S. \tag{11}$$

Schwartz theorem on second mixed derivatives of the $G$ function results in

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial L}\right)_{T,P_i}\right)_{P_i,L} = \left(\frac{\partial}{\partial L}\left(\frac{\partial G}{\partial T}\right)_{P_i,L}\right)_{T,P_i}. \tag{12}$$

Thus by substituting (11) into (12) we obtain:

$$\left(\frac{\partial S}{\partial L}\right)_{T,P_i} = -\left(\frac{\partial f}{\partial T}\right)_{P_i,L}. \tag{13}$$

With respect to the state variables of Eq. 10, the entropy function can be stated as: $S = S(T,P_i,L)$, and thus the total differential of such a function would be:

$$dS = \left(\frac{\partial S}{\partial L}\right)_{T,P_i} dL + \left(\frac{\partial S}{\partial P_i}\right)_{L,T} dP_i + \left(\frac{\partial S}{\partial T}\right)_{L,P_i} dT. \tag{14}$$

By assuming an isothermal infinitesimal small deformation process, neglecting the variation of the internal pressure $P_i$ and considering (13), the above equation becomes:

$$dS = \left(\frac{\partial S}{\partial L}\right)_{P_i,T} dL = -\left(\frac{\partial f}{\partial T}\right)_{L,P_i} dL. \tag{15}$$

Substituting (15) in (9), we obtain

$$dQ = -T\left(\frac{\partial f}{\partial T}\right)_{L,P_i} dL. \tag{16}$$

Equation 16 expresses the relation between the heat exchanged between the continuum and the environment and the change in its length, during the finite straining.

As has been discussed elsewhere, the temperature dependence of the force could be considered to be given solely by the temperature dependence of the initial length, neglecting the temperature dependence of the elastic modulus [16]. The assumption is supported by the fact that the temperature variations in specimen deformation practice are relatively small that do not produce significant changes in the elastic modulus. Therefore,

$$\left(\frac{\partial f}{\partial T}\right)_{L,P_i}=\left(\frac{\partial f}{\partial L_0(T)}\right)_{L,P_i}\left(\frac{\partial L_0(T)}{\partial T}\right)_{L,P_i} \tag{17}$$

where $L_0(T)$is the length of the specimen changing with the temperature given by: $L_0(T)=L_0|_{T=0}(1+\alpha T)$, and $\alpha$ is the linear thermal expansion coefficient of the specimen [16].

Now (17) becomes:

$$\begin{aligned}\left(\frac{\partial f}{\partial T}\right)_{L,P_i}&=\left(\frac{\partial f}{\partial L_0(T)}\right)_{L,P_i}L_0\alpha\\&=\frac{\alpha}{1+\alpha T}L_0(T)\left(\frac{\partial f}{\partial L_0(T)}\right)_{L,P_i}.\end{aligned} \tag{18}$$

For simplicity we will use $L_0$ instead of $L_0$(T) from this point onward. Substitution of (18) into (16) leads to:

$$dQ=-\frac{\alpha T}{1+\alpha T}L_0\left(\frac{\partial f}{\partial L_0}\right)_{L,P_i}dL. \tag{19}$$

For linear deformations:

$$f=AE\left(\frac{L}{L_0}-1\right) \tag{20}$$

where A is the cross-section of the specimen. Thus:

$$\left(\frac{\partial f}{\partial L_0}\right)_{L,P_i}=-AE\frac{L}{L_0^2}. \tag{21}$$

By substituting (21) into (19), we will have:

$$dQ=\frac{\alpha T}{1+\alpha T}AE\frac{L}{L_0}dL. \tag{22}$$

The last term in (22) can be converted by using Hooke's law again to obtain:

$$dL=\frac{L_0}{AE}df \tag{23}$$

and thus (22) will now turn to the final form of:

$$dQ=\frac{\alpha T}{1+\alpha T}Ldf. \tag{24}$$

Equations 5 and 24 describe the total amount of work and heat, exchanged between the continuum and the environment, during the process of small linear deformations.

The total change of the internal energy of the continuum can be obtained by substituting (5) and (24) into (1), which leads to:

$$dU=\frac{\alpha T}{1+\alpha T}Ldf+AEL(\lambda-1)d\lambda. \tag{25}$$

As the extension ratio $\lambda$ is equal to $L/L_0$, d$\lambda$ would equal to $dL/L_0$, and by substituting (23) for $dL$ we obtain:

$$d\lambda=\frac{df}{AE}, \tag{26}$$

and thus (25) becomes:

$$dU=\frac{\alpha T}{1+\alpha T}Ldf+L\left(\frac{L}{L_0}-1\right)df. \tag{27}$$

Equation (27) can be rearranged as:

$$dU=\left[L\left(\frac{\alpha T}{1+\alpha T}+\left(\frac{L}{L_0}-1\right)\right)\right]df \tag{28}$$

Setting the internal energy of the continuum at its initial length of $L_0$ as the reference state of the internal energy $dU_0$, using (28) we get:

$$dU_0=\left[L_0\frac{\alpha T}{1+\alpha T}\right]df. \tag{29}$$

The absolute change of the internal energy of a continuum undergoing a finite linear deformation, $dU^*$, would be obtained as the difference, $dU^*=dU-dU_0$:

$$dU^*=dU-dU_0=\left[\Delta L\frac{\alpha T}{1+\alpha T}+L\left(\frac{L}{L_0}-1\right)\right]df \tag{30}$$

where $\Delta L=L{-}L_0$.

The term in squared brackets represents the modified form of the elongation, to that of $L-L_0=\varepsilon L_0$ given by the Hooke's law, designated by $\Delta L^*$ :

$$\Delta L^*=\Delta L\frac{\alpha T}{1+\alpha T}+L\left(\frac{L}{L_0}-1\right). \tag{31}$$

The derived model can now be summarized with the set of the following three equations:

$$dQ=\frac{\alpha T}{1+\alpha T}Ldf \tag{a}$$

$$dU=\left[L\left(\frac{\alpha T}{1+\alpha T}\right)+\left(\frac{L}{L_0}-1\right)\right]df \tag{32b}$$

$$\Delta L^*=\Delta L\frac{\alpha T}{1+\alpha T}+L\left(\frac{L}{L_0}-1\right) \tag{32c}$$

## Results

To test the validity of the model, we now compare the experimental data presented in the literature with the values calculated by the model given in (32). Stretching calorimetry data of four different classes of materials, steel; polymer; polymer composites and rubber, have been extracted from the available literature and analyzed in order to obtain the experimental values of elongation, heat, internal energy and applied force, within the linear deformation region. The elastic modulus ($E$), sample dimensions, linear thermal expansion coefficient ($\alpha$) and the ambient temperature ($T$) under which the experiments have been carried out, have all been specified in the respective cited references from which the experimental data have been extracted. For each elongation, the value of the heat was taken from the reported graphs in the cited references and by (32a), and the corresponding force was calculated. Using this force and the provided elastic modulus and sample's dimensions, the Hookean force-elongation graph was generated. Then, using Eq. 32c, the elongation predicted by the model was calculated and compared with the values given by Hooke's Law, as the commonly accepted model in small linear deformations. In all cases and for all materials considered, the proposed model is in very close agreement with the experimental data.

## Steel

Göritz investigated the deformation process of a chrome-nickel steel alloy, Chronifer 1808 (Young modulus of $E = 6.55 \times 10^{10}$ N/m$^2$), with stretching calorimetry technique and reported the experimental values of elongation and the corresponding heat and the work of the deformation [16]. Figure 1 presents the comparison of the experimental force-elongation plot in the linear small-deformation limit, with that of predicted by the model in (32), and Hooke's Law.

## Polymers

Polymers exhibit a relatively large extensibility with very complex stress-strain behaviour. To check the validity of our model for this class of materials, we compare the deformation behaviour of four different polymers obtained in experimental studies, with the predictions made by the model: Polyethylene taken from reference [16], Polycarbonate from [17], Poly($\varepsilon$-caprolactone) homopolymers PCL27 and PCL46 from [18]. The polyethylene used in the experiment was reported to have an elastic modulus of $E = 5.2 \times 10^8$ N/m$^2$ [16]. The experimental force-elongation plot against the calculated values, in the linear small deformation range, is shown in Fig. 2a. The elastic modulus of the polycarbonate has been estimated to be $E = 2.4 \times 10^9$ N/m$^2$ [17]. The comparative results for the force-elongation plot are shown in Fig. 2b. Figure 2c and d show the results for PCL27 and PCL46, respectively, with $E = 5.2 \times 10^8$ N/m$^2$ for PCL27 and $E = 5.5 \times 10^{10}$ N/m$^2$ for PCL46 [18]. The calculated values by the Hooke's law are also shown in the figure.

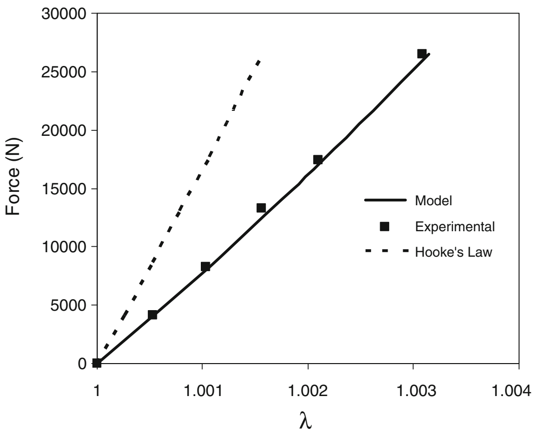

**Fig. 1** Force-extension ratio plots for Chronifer 1808

## Polymer composites

Two types of composites have been considered: Polycarbonate with multiple carbon fibres and Polycarbonate with chopped irregular carbon fibres, experimentally studied by Privalko et al. (1999) [18]. The Young's moduli are $4.4 \times 10^9$ and $5.3 \times 10^9$ N/m$^2$ for the Polycarbonate with multiple carbon fibres and Polycarbonate with chopped irregular carbon, respectively [18]. Figure 3 shows the experimental and calculated values by the model, along with those given by Hooke's Law, for the force-elongation trend of these two materials.

## Rubber

Rubber was chosen as one of the samples in order to illustrate the prediction of the model for materials exhibiting negative linear expansion coefficient. The experimental stretching calorimetry data considered are those reported in [14], for a conventional sulfur vulcanized rubber. A linear interpolation of the reported data up to

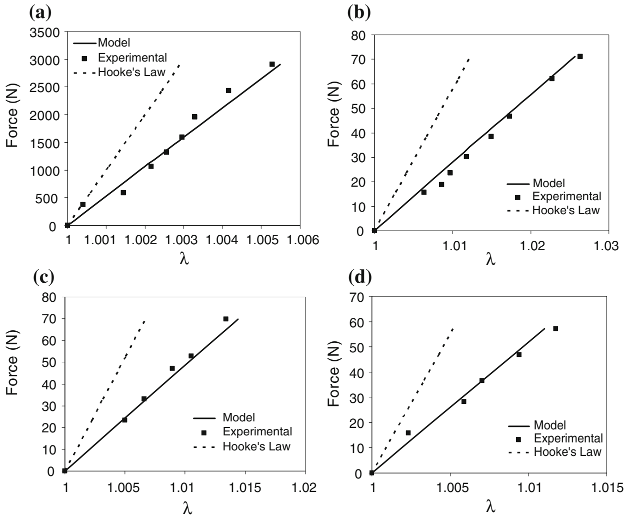

**Fig. 2** Force-elongation plots: (a) Polyethylene, (b) Polycarbonate, (c) PCL27 and (d) PCL46

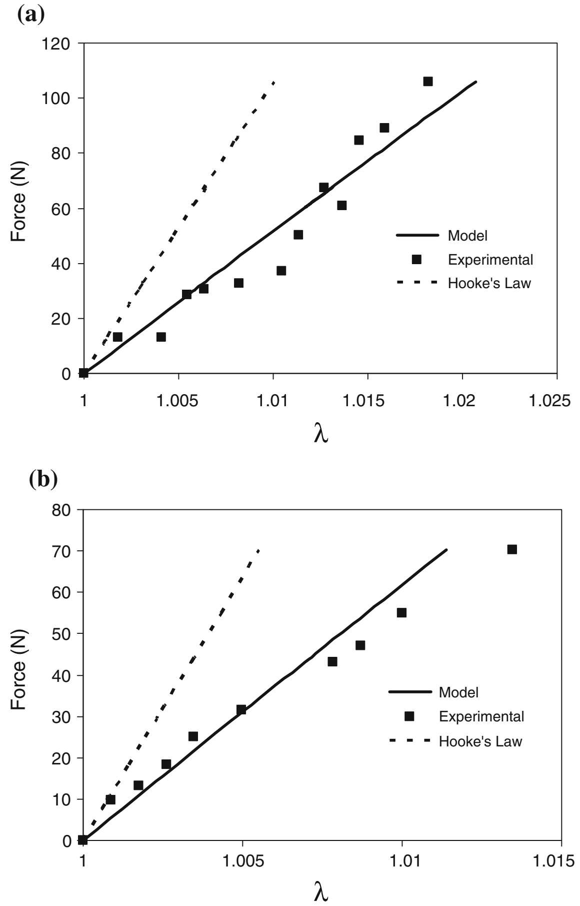

**Fig. 3** Force-elongation plots: (a) Polycarbonate with multiple carbon fibres, (b) polycarbonate with chopped irregular carbon fibres

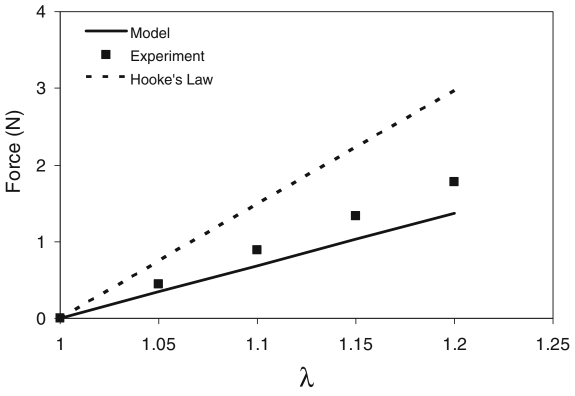

**Fig. 4** Force-elongation plot for the chosen rubber

20% of strain, within the nominal linear region for rubbers [23], gave a modulus of $E = 1.5 \times 10^6$ N/m$^2$. The comparative results of the experiment, the model and Hooke's Law are presented in Fig. 4. The effects of Poisson ratio can hardly be detected in the presented force-elongation plots. However, for the case of rubber, where transverse strain effects are much more significant, incompressibility effects together with crystallization phenomena upon deformation might cause a slightly higher deviation of the model from the experimental data, compared to the other materials considered.

## Conclusions

A phenomenological model to characterize the mechanical behaviour of solids within the linear deformation region was derived, based on a thermodynamic model that includes heat transfer effects occurring during the deformation of solid bodies. The model consists of a set of three equations as in (32), able to quantify deformation heating effects, internal energy variation and macroscopic elongation of the continuum under deformation. Furthermore, it allows the prediction of force-elongation trends based on experimental results of deformation calorimetry. Experimental data obtained from stretching calorimetry performed on different types of materials were extracted from the available literature and described with the developed model. The range of materials considered included steel alloy, different types of polymers, polymer composites and rubber. The experimental results of force-elongation within the linear deformation region of each set of materials were compared with those calculated by the model and with the ones predicted by Hooke's Law. The calculated values showed a good prediction of the experimental results, proving that by using deformation calorimetry data it is possible to decouple the temperature and deformation effects in characterizing the thermoelastic behavior of a wide range of solids in linear small deformations, and highlighting the inaccuracies that arise when the heat transfer effects involved in deformation processes are neglected.

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