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Thermodynamics of Thermo-deformable Solids

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Overview

Thermal deformation is an aspect very important from the application standpoint. On this behalf, most general and widely applicable model has for many years been pursued. Modern approaches in mathematical description of the phenomena occurring in thermo-deformable solids incorporate thermodynamics as a restrictive condition for governing and constitutive equations. This however, due to numerous simplifications, on many occasions leads to special cases of modeled materials, and thus the search for generalized approach is far from coming to an end. Herein, the concepts of thermo-deformable solid models are presented along with special cases and the benefits and drawbacks of using them.

The Object of Science

Solid bodies, in contradiction to fluids, are endowed with constant shape and an internal susceptibility for transmitting compression, tractions, and shear. Depending on its elastic response to mechanical load, solid bodies may be divided into two categories: deformable and rigid. However, "mechanically rigid" body may undergo change in volume, if subjected to thermal load, and thus may be qualified as thermo-deformable. This distinction is fundamental in the course of our science, since one of the basic laws, expressed by the Duhamel-Neumann equation, assumes possibility of an additive decomposition into two phenomena, namely, an isothermal deformation and a rigid body thermal strain.

Both, in nature and in technology, induction of thermal strain, and the resulting thermal stresses, is easily distinguished and has repeatedly been observed with the naked eye [1–5]. In nature, thermal loads are mostly elicited by the Sun (radiation heat), cyclic season changes in a year cycle, and daily temperature differences. The most severe thermal loads however are witnessed in eruption of liquid magma to the surface of the Earth and during its solidification. Cyclic effect of these loads in nature concludes in heat fatigue of the rock material and its thermal crack.

Most of the effects related to thermal deformations find application in technology [6, 7]. Fortunately, they also occur in man-made materials, like alloys, steels, plastics, concretes, and ceramics. The importance of heat loads becomes particularly significant for laminates, fibers, etc. Mostly meaningful are also processes involving durability and failure of thin thermal barriers applied to surfaces of elements operating in elevated temperatures [8]. One of the most complex phenomena, however, is the heat-induced phase transition. It results in a mechanical effect with release of a latent phase transition work, particularly observed in the martensite-austenite transition. For exceptionally large thermal loads, melting of solid bodies occurs (e.g., ice into water) or solidification of a melted body under cooling conditions [9].

Usually, research in thermo-deformability is conducted under specified mechanical load – very often, if possible, in absence of any forces. This paradigm of research has developed suitable tools for calculation and measurement; it later allows for thinking separation of the joint effects to purely mechanical and purely thermal. This approach allowed also for dividing mathematical description into two stages [5, 9]. In the first stage, solid body $\mathcal{B}$, treated to be a mechanically rigid heat conductor, would have determined temperature and entropy fields, by solving equation of "heat motion" for the specific boundary conditions, where heating or cooling takes place. In the second stage, thermal effects would "initiate" equations of motion, and the state of deformation along with the thermal stresses would be adjusted through a self-balanced mechanical stresses and thermal strains related to them. At this stage, the problem of mechanical strain resulting from the mechanical load is solved separately, taking into account, however, changes in mechanical properties of the material accordingly to the temperature fields, acquired in the first stage [3, 10].

This means that the two stages are not interchangeable – the result of mechanical load applied to previously heated body is not identical to the result of heating a previously mechanically loaded body. In many cases, for example, determination of residual stresses at an interface between two layers after passage of moving heat source should be approached simultaneously. It is rendered possible, since in most cases the two regions, for mechanical problem and for thermal problem, do coincide; there are however problems with region of heat transfer larger than the volume of a solid body.

Another minor stream of research is also embraced by the thermodynamics of thermo-deformable bodies, somewhat less often addressed from the technological standpoint. It is an observation of thermal phenomena initiated with a mechanical load applied to a solid body in the absence of thermal loads [11, 12]. That is, the heating or cooling at external surfaces is omitted. One of the most important phenomena in this case is generation of heat during internal and external friction; another is heat emission during plastic flow of metals, and a high-rate viscoelastic deformation. Very significant is also heat emitted during the cracking or tearing of steel and other phenomena related to mechanical loading [13].

While the mentioned emission of heat is bound with irreversible mechanical deformation, heat generation in acoustics is related to a reversible elastic conversion of vibration into heat and vice versa – in thermo-acoustic engines, heat is converted into work [14]. A very important case of mechanical load is an appearance of stress-induced phase transition that leads to a release of latent phase transition heat and, in consequence, to significant heating or cooling of the neighboring region.

Mechanically induced thermal deformations and thermal stresses, found in the second stream, are inferior, so to speak, and often not taken into account during study and modeling. In this entry, due to spatial restrictions, we will follow this trend and limit our considerations to the mainstream research for thermo-deformation, which is the most proper.

Tasks of Thermodynamics

As yet no agreement has been reached concerning the views on the tasks of thermodynamics. Some claim mischievously that there are as many thermodynamics as there are thermodynamicists. Beside doubtless differences in approaches and content, there is a problem of thermodynamic language, which leads, in Kestin's opinion, to thermodynamic Tower of Babel [15].

However, in the context of thermoelasticity, little authors have ever questioned correctness of the basics, comprised of the laws of conservation of mass, momentum, moment of momentum, law of half-conservation of entropy, and the balance of energy, which are often used interchangeably with postulated equation of heat. Sometimes the principle of relative motions accompanies the mentioned group of equations, which is a sort of extended Galilean principle of relativity to continuum physics and classical field theory. In other approaches, principle of ubiquity is postulated, otherwise known as the principle of equipartition [15, 16]. Both principles are meaningful during the setup of mathematical model of the phenomenon – while the principle of relative motions serves to check for model correctness, equipartition principle, having its relative in the principle of energy conversion, serves as a necessary condition for correct models.

In this entry, we shall define the science of thermodynamics as follows: Thermodynamics is a science that covers all other natural and technical sciences that verifies their correctness, conclusions, knowledge, and tools in an aspect of violation, or non-violation, of the laws of thermodynamics. There is a common agreement that these laws are first and second law of thermodynamics. In an everyday language, both of the laws have its colloquial representatives and are called *perpetuum mobilae*, of the first and the second kind, respectively. Thus the task that lies ahead of us is to prove that thermodynamics of thermo-deformable bodies is not perpetuum mobile of the first kind – that is, it does not generate energy in the way of heat or work ex nihilo and that there does not exist any eternal thermal motion (perpetuum mobile of the second kind). Unfortunately, in both cases – even if restricted solely to the thermoelasticity – there is no agreement provided in literature for the ultimate form of these laws. That is why thermodynamics is the science of infinite simplifications, assumptions, hidden hypotheses, etc. It is mostly advisable to warn the reader honestly of numerous snares and traps that await him during its cognition.

In this entry, we focus on reversible properties of material models that allow for complete and reversible conversion of thermal energy into mechanical energy and vice versa. Any material, after undergoing any closed cycle of changes, that meets the condition of returning to its initial internal energy and state parameters would be called the Carnot thermoelastic material.

Simple Thermoelastic Material in the Carnot Sense

Usually materials are called simple, if an entire energy conversion follows from the parameters of state, which means that spatial and temporal gradients do not play any role in interactions. Thermoelastic material in a Carnot sense is a material, whose equations of state satisfy the rule of agreement with the primal energy balance, which in turn states that a total work of a cycle performed by internal forces is compensated by a total internal heat. Let us emphasize the fact that the cycle does not only undergo processes considered in a hypothetical Carnot engine (constant internal energy and constant entropy) but any process involving all four parameters of state: extensive (thermodynamic stress $\overleftrightarrow{\sigma} = \sigma_{ij}\vec{e}_i \otimes \vec{e}_j,\ i,j = (x.y.z)$ and thermodynamic temperature θ) and intensive (elastic strain $\overleftrightarrow{\varepsilon} = \varepsilon_{ij}\vec{e}_i \otimes \vec{e}_j$ and specific entropy η). For the clarity of notation, we will omit indices "rev" and "e," which denote sole reversible part of these objects – it is justified, since we consider thermoelasticity, so that the viscous stress tensor, the plastic strain tensor, or the irreversible entropy do not occur per se.

The fundamental quantity that is silently implied by the energy balance is an existence of a potential (reserve) of energy, known as the specific internal energy which is a function of intensive parameters: $\epsilon = \epsilon(\varepsilon_{ij}, \eta)$. Internal energy proposed by Carnot, Rankine, and Clausius is a primal potential, which means that the energy balance does not concern other potentials, for example, Helmholtz free energy ψ. Moreover, a material which is not required to possess a potential, for example, thermoelastic Duhamel-Neumann or Cauchy elastic material, cannot be proven directly not to be a *perpetuum mobile of the first kind*.

First, let us consider the primal energy balance in the form of a global equality:

$$\frac{d}{dt}(U + K + \Phi) = \oiint_{\partial V} \left(\vec{\mathcal{F}}_{\text{work}} + \vec{\mathcal{F}}_{\text{heat}}\right) \cdot \vec{n} dA \tag{1}$$

Here for a body $\mathcal{B}$, with a total volume V and a boundary ∂V, oriented with a normal vector $\vec{n}$, we have denoted the internal energy by $\mathcal{U} = \iiint_V \rho\epsilon \, dV$, the kinetic energy by

$\mathcal{K} = \iiint_V \rho\kappa \, dV$, and the potential energy of body forces by $\Phi = \iiint_V \rho\phi \, dV$. Equation (1) reads that the total change of stored energy of the body $\mathcal{B}$ is compensated by an energy being supplied (or extracted) with the mechanical energy flux of Umov-Volterra type $\vec{\mathcal{F}}_{\text{work}} = \overleftrightarrow{\sigma}\vec{v}$ and the heat energy flux of Rankine-Stokes type $\vec{\mathcal{F}}_{\text{heat}} = \vec{h}\theta$. Definitions for these fluxes are fundamental for the primal form of the energy balance in the Carnot sense – they contain the total, and not only reversible, momentum flux $\overleftrightarrow{\sigma}$ and the diffusive flux of entropy $\vec{h}$.

Even though the mechanical and heat energy fluxes are applied on disjoint side surfaces $\partial V = A_{heat} \cup A_{work}$, there is no mathematical obstacle whatsoever to employ the theorem for divergence. Assuming that $\frac{d}{dt}\rho = \frac{d}{dt}\rho_0 = \dot{\rho} = 0$ or, in other words, there is satisfaction of the mass balance, (1) may be rewritten:

$$\iiint_V \left[\rho(\dot{\epsilon} + \dot{\kappa} + \dot{\phi}) - \operatorname{div}(\overleftrightarrow{\sigma}\vec{v} + \vec{h}\theta)\right] \, dV = 0 \tag{2}$$

This equation is always true, regardless if the set of the governing equations (i.e., equations for mass, momentum, and entropy balances) is satisfied or not. It will now be shown that if the fields and parameters of state satisfy conditions laid on by governing equations, the equation of energy receives a very important form allowing for further restrictions to describing fields – it means that even though the solutions may satisfy the conservation equations for mass, momentum, and entropy, they need not satisfy the balance equation for energy and in consequence lead to generating energy ex nihilo. Material derivatives of the kinetic and potential energies are $\dot{\kappa} = \dot{v} \cdot \vec{v}$ and $\dot{\phi} = -\frac{\partial\phi}{\partial\vec{x}} \cdot \dot{\vec{x}} = -\vec{b} \cdot \vec{v}$, respectively. The following identities also occur: $\operatorname{div}(\overleftrightarrow{\sigma}\vec{v}) = \operatorname{div} \overleftrightarrow{\sigma} \cdot \vec{v} + \overleftrightarrow{\sigma} \cdot \operatorname{grad} \vec{v}$ and $\operatorname{div}(\vec{h}\theta) = \theta \operatorname{div} \vec{h} + \vec{h} \cdot \operatorname{grad}\theta$. According to the tradition, velocity gradient will be denoted by $\overleftrightarrow{l}$ and decomposed into symmetric and antisymmetric part $\overleftrightarrow{l} = \overleftrightarrow{d} + \overleftrightarrow{w}$. Temperature gradient will be denoted by $\vec{g} = \operatorname{grad}\theta$. Through addition and subtraction of $\pm\,\theta(\rho\,\dot{\eta} - \rho s_\eta)$ in (2), the integral of (2) becomes:

$$\iiint_V \Big\{\rho\dot{\epsilon} - \left(\operatorname{div}\overleftrightarrow{\sigma} + \rho\vec{b} - \rho\dot{\vec{v}}\right) \cdot \vec{v} - (\operatorname{div}\vec{h} + \rho s_\eta - \rho\dot{\eta})\,\theta$$
$$- \theta(\rho\dot{\eta} - \rho s_\eta) - \vec{h} \cdot \vec{g} - \overleftrightarrow{\sigma} \cdot \overleftrightarrow{l}\Big\} dV = 0 \tag{3}$$

Once the fields $\rho, \overleftrightarrow{\sigma}, \vec{v}, \vec{h}, \eta, \theta$ satisfy balance equations of mass, momentum, moment of momentum $\overleftrightarrow{\sigma} = \overleftrightarrow{\sigma}^{\mathrm{T}}$, and entropy, including that $\overleftrightarrow{\sigma} \cdot \overleftrightarrow{l} = \overleftrightarrow{\sigma} \cdot \overleftrightarrow{d} \cong \overleftrightarrow{\sigma} \cdot \dot{\overleftrightarrow{\varepsilon}}$, energy (3) transforms to:

$$\iiint_V \left\{\rho\dot{\epsilon} - \theta(\rho\dot{\eta} - \rho s_\eta) - \vec{h} \cdot \vec{g} - \overleftrightarrow{\sigma} \cdot \dot{\overleftrightarrow{\varepsilon}}\right\} \, dV = 0 \tag{4}$$

It should be noted that the scalar quantity $\overleftrightarrow{\sigma} \cdot \dot{\overleftrightarrow{\varepsilon}}$ in this case has a generalized form for it is a product of total momentum flux and total rate of deformation, for example, $(\overleftrightarrow{\sigma}^{e} + \overleftrightarrow{\sigma}^{vis}) \cdot (\dot{\overleftrightarrow{\varepsilon}}^{e} + \dot{\overleftrightarrow{\varepsilon}}^{pl} + \dot{\overleftrightarrow{\varepsilon}}^{cr} + \cdots)$. Similarly, the temperature field and the entropy flux may be decomposed into reversible and irreversible components: $\theta\vec{h} = (\theta^{rev} + \theta^{ir})(\vec{h}^{rev} + \vec{h}^{ir})$ – it is so because they originate from the total fluxes of other balanced quantities.

By taking material time derivative of the internal energy (here, we do not make use of the so-called Gibbs equation), we have:

$$\iiint_V \left\{\left(\rho\frac{\partial\epsilon}{\partial\varepsilon_{ij}}|\eta - \sigma_{ij}\right)\dot{\varepsilon}_{ij} + \rho\left(\frac{\partial\epsilon}{\partial\eta}|\overleftrightarrow{\varepsilon} - \theta\right)\dot{\eta}\right.$$
$$\left. + \rho\theta s_\eta - \vec{h} \cdot \vec{g}\right\}, dV = 0 \tag{5}$$

Material will be thermoelastic in the Carnot sense if, and only if, the total flux of momentum and the total temperature are connected with the internal energy by the equations of state:

$$\sigma_{ij} = \rho\frac{\partial\epsilon}{\partial\varepsilon_{ij}}|\eta; \quad \theta = \frac{\partial\epsilon}{\partial\eta}|\overleftrightarrow{\varepsilon}. \tag{6}$$

while the entropy source s_η is agreed with the diffusive entropy flux:

$$\rho\theta s_\eta = \vec{h}\cdot\vec{g} \tag{7}$$

Carnot material used for modeling endo-reversible cycles [17] satisfies an additional condition of zeroing the entropy source. It follows that in endo-reversible Carnot material any temperature gradients may not exist: $\vec{g} \equiv 0$. Additionally, internal energy may not be an arbitrary function of intensive parameters of state. In accordance with principle of energy conversion, it has to satisfy a supplementary condition: It is required that the actual state is acquirable with interchangeable cycle combinations; this may be expressed mathematically with the first equation of the Clapeyron-Clausius thermodynamics:

$$\frac{\partial}{\partial\overleftrightarrow{\varepsilon}}\left(\frac{\partial\epsilon}{\partial\eta}\right) = \frac{\partial}{\partial\eta}\left(\frac{\partial\epsilon}{\partial\overleftrightarrow{\varepsilon}}\right) \tag{8}$$

The above compatibility condition is easily fulfilled in case of a quadratic approximation for ϵ expressing additive properties of the parameters of state [10]:

$$\rho\ \epsilon = \frac{1}{2}C^a_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - \upsilon_{ij}\varepsilon_{ij}(\tilde{\eta} - \tilde{\eta}_0) + \frac{1}{2}C^\varepsilon(\tilde{\eta} - \tilde{\eta}_0)^2 \tag{9}$$

Satisfying (8) and leading to the following equations of state:

$$\begin{aligned} \sigma_{ij} &= C^a_{ijkl}\varepsilon_{kl} - \upsilon_{ij}(\tilde{\eta} - \tilde{\eta}_0) \\ \theta &= -\upsilon_{ij}\varepsilon_{ij} + C^\varepsilon(\tilde{\eta} - \tilde{\eta}_0) \end{aligned} \tag{10}$$

For a technical reason, we use here entropy related to the volume $\tilde{\eta} = \rho\eta$, and C^a_{ijkl} is a fourth-order tensor of adiabatic mechanical capacitance, C^ε is a heat capacitance under constant deformation, and υ_{ij} is a caloric tension dyadic - Equation (10) reads as follows: Any increase in entropy results in a decrease of stresses and an increase of temperature, while any increase in strain (tension) results in an increase of stresses and decrease of temperature. The latter effect of decreasing temperature with tension has an analogue in lowering gas temperature during its expansion, also to negative temperatures (e.g., −150° C in de Laval nozzle). In the case of solid bodies, the change in temperature is utterly small (0.1–0.2° C); for this reason the effect has been discovered very late by Joule. Contemporarily, reversible transverse effect became the basis for TSA (thermoelastic stress analysis) measuring technique. In this method, temperature is measured by infrared detector [18]. Needless to say, material is no longer Carnotian, when the dyadic of caloric tension, responsible for energy conversion, equals zero: $\upsilon_{ij} = 0$.

First Gradient Carnot Material

It is well known that nano-materials, including nano-metals, require models accounting for their very rich internal nano-structure. Classical simple materials do not reflect all the energy conversions therein; therefore, it is reasonable to develop higher order models. In the Carnot material of the first gradient, it is assumed that the internal energy is composed not only of the extensive parameters of state, η, ε_{ij}, but also of their spatial gradients: $\vec{\eta} = \mathrm{grad}\eta$ and grad $\overleftrightarrow{\varepsilon}$. Diffusive equation describing an enhanced transport of heat should also be extended with an extra flux $\overleftrightarrow{H}$, which depends on the second temperature gradient.

Therefore, we postulate an enriched external exchange (heating and working) through extra fluxes of mechanical energy and thermal energy, called "interstitial working," $\vec{\mathcal{F}}^{int}_{work} = \Sigma\mathrm{grad}\,\vec{v} = \Sigma_{ijk}v_{j,k}\vec{e}_i$, and "interstitial heating," $\vec{\mathcal{F}}^{int}_{heat} = \vec{h}_\eta\dot{\eta} + \overleftrightarrow{H}\,\vec{g} = (h_{(\eta)i}\dot{\eta} + H_{ij}g_j)\vec{e}_i$. Hence we have:

$$\begin{aligned} \oiint \vec{\mathcal{F}}_{work}\cdot\vec{n}\,dA &= \iiint [\mathrm{div}\overleftrightarrow{\sigma}\cdot\vec{v} + \overleftrightarrow{\sigma}\cdot\overleftrightarrow{l} \\ &\quad + \mathrm{div}\Sigma\cdot\overleftrightarrow{l} + \Sigma\cdot\mathrm{grad}\,\overleftrightarrow{l}]\ \mathrm{dV} \\ \oiint \vec{\mathcal{F}}_{heat}\cdot\vec{n}\,dA &= \iiint \Big[\theta\mathrm{div}\,\vec{h} + \vec{h}\cdot\vec{g} \\ &\quad + \dot{\eta}\mathrm{div}\vec{h}_\eta + \vec{h}_\eta\cdot\mathrm{grad}\dot{\eta} \\ &\quad + \mathrm{div}\overleftrightarrow{H}\cdot\vec{g} + \overleftrightarrow{H}\cdot\mathrm{grad}\vec{g}\Big]\,dV \end{aligned} \tag{11}$$

Derivatives of kinetic and potential energies in (1) remain identical with those for a simple material, and material increase of internal energy is:

$$\frac{d}{dt}U = \iiint \rho \left[\frac{\partial \epsilon}{\partial \varepsilon_{ij}} \dot{\varepsilon}_{ij} + \frac{\partial \epsilon}{\partial \varepsilon_{ij.k}} \dot{\overline{\varepsilon_{ij,k}}} + \frac{\partial \epsilon}{\partial \eta} \dot{\eta} + \frac{\partial \epsilon}{\partial \eta_{,i}} \dot{\overline{\eta_{,\imath}}} \right] dV \tag{12}$$

Let it be assumed that within the adopted geometric simplifications, material time derivative and spatial gradient commute with each other: $\dot{\overline{\varepsilon_{ij,k}}} = (\dot{\varepsilon}_{ij})_{,k}$, while for entropy gradient $\vec{\eta}$ there occurs:

$$\frac{d}{dt}\vec{\eta} = \text{grad}\left(\dot{\vec{\eta}}\right) + [\text{grad}^{\mathrm{T}}\vec{\eta} - \text{grad}\vec{\eta}]\vec{v} - \vec{\eta}(\text{grad}\vec{v}) \tag{13}$$

Substituting (11), (12), and (13) into (1) ultimately yields:

$$\begin{aligned}
&\iiint_V \{(\dot{\rho} + \rho\,\text{div}\vec{v})\epsilon \\
&- \left(\text{div}\overset{\leftrightarrow}{\sigma} + \rho\vec{b} - \rho\dot{\vec{v}}\right) \cdot \vec{v} - (\text{div}\vec{h} + \rho s_\eta - \rho\dot{\eta})\theta \\
&+ \left[\rho\frac{\partial \epsilon}{\partial \varepsilon_{ij}} - \Sigma_{ijk,k} - \frac{1}{2}\rho\left(\frac{\partial \epsilon}{\partial \eta_i}\eta_j + \eta_i\frac{\partial \epsilon}{\partial \eta_j}\right) - \sigma_{ij}\right]\dot{\varepsilon}_{ij} \\
&+ \left[\Sigma_{ijk} - \rho\frac{\partial \epsilon}{\partial \varepsilon_{ij,k}}\right](\dot{\varepsilon}_{ij})_{,k} + \rho\left[\frac{\partial \epsilon}{\partial \eta} - \rho^{-1}h_{(\eta)i,i} - \theta\right]\dot{\eta} \\
&+ \left[\rho\frac{\partial \epsilon}{\partial \eta_k} - h_{(\eta)k}\right](\dot{\eta})_{,k} - (h_i + H_{ij,j})g_i \\
&\quad H_{ij}g_{i,j} + \rho\theta s_\eta\}\, dV = 0
\end{aligned}$$

Since gradient Carnot material will not create energy ex nihilo, provided that at the same time the following are satisfied – balance conditions for mass, momentum, and entropy along with the following constitutive equations:

Total flux of momentum

$$\overset{\leftrightarrow}{\sigma} = \rho\frac{\partial \epsilon}{\partial \overset{\leftrightarrow}{\varepsilon}} - \text{div}\Sigma - \frac{1}{2}\rho\left(\frac{\partial \epsilon}{\partial \vec{\eta}} \otimes \vec{\eta} + \vec{\eta} \otimes \frac{\partial \epsilon}{\partial \vec{\eta}}\right) \tag{14}$$

Total temperature $\theta = \frac{\partial \epsilon}{\partial \eta} - \rho^{-1}\text{div}\vec{h}_\eta$ (15)

Thermodynamic hyper-stress

$$\Sigma = \rho\frac{\partial \epsilon}{\partial(\text{grad}\,\overset{\leftrightarrow}{\varepsilon})} \tag{16}$$

Entropy hyper-vector $\vec{h}_\eta = \rho\frac{\partial \epsilon}{\partial \vec{\eta}}$ (17)

Equation for the source of entropy

$$\rho\theta s_\eta = (\vec{h} + \text{div}\overset{\leftrightarrow}{H}) \cdot \vec{g} + \overset{\leftrightarrow}{H} \cdot \text{grad}\,\vec{g} \tag{18}$$

In the case of linearized equation of state, internal energy (9) may be complemented with contributions of stored energy, through proper gradients:

$$\rho\epsilon = \rho\epsilon(\varepsilon_{ij}, \eta) + \frac{1}{2}l_\Sigma^2 C^a_{ijkl}\varepsilon_{ij,m}\varepsilon_{kl,m} + \frac{1}{2}l_\eta^2 C^\varepsilon \tilde{\eta}_m\tilde{\eta}_m \tag{19}$$

Employing definitions given above, instead of algebraic, we receive differential equations of state:

$$\sigma_{ij} = C^a_{ijkl}(1 - l_\Sigma^2\text{lap})\varepsilon_{kl} - \upsilon_{ij}(\tilde{\eta} - \tilde{\eta}_0) - l_\eta^2\tilde{\eta}_{,i}\tilde{\eta}_{,j} \tag{20}$$

$$\theta = -\upsilon_{ij}\varepsilon_{ij} + C^\varepsilon\left(1 - l_\eta^2\text{lap}\right)(\tilde{\eta} - \tilde{\eta}_0) \tag{21}$$

where l_Σ and l_η are the two coupling lengths associated with the material nano-structure, while the Laplacian is denoted lap = div(grad). The determination and eventual calibration of the two constants l_Σ and l_η requires separate study [19]. In the equation for stress tensor, along with mechanical stresses, there exist two additional contributions of thermal character. The latter has a similar interpretation to Korteweg extra-stresses in fluid with nano-structure [20]. It should not, however, be misidentified with Maxwell's thermal transpiration stress [21].

An Enhanced Heat Equation

According to the restrictions introduced by the energy balance (14)–(18), the gradient Carnot material possesses the following nonlinear equation of motion of heat:

$$\rho\dot{\eta} = \mathrm{div}\vec{h} + (\vec{h} + \mathrm{div}_{\leftrightarrow}H) \cdot \vec{g} + \overleftrightarrow{H} \cdot \mathrm{grad}\,\vec{g} \tag{22}$$

where diffusive entropy fluxes remain undefined: $\vec{h}$ and $\overleftrightarrow{H}$. They may be described with dissipative functional $\varpi(\vec{g},\ \mathrm{grad}\vec{g}) = \frac{1}{2}k_\eta\vec{g}^2 + \frac{1}{2}k_\eta l_k^2(\mathrm{grad}\,\vec{g})$ $\cdot(\mathrm{grad}\vec{g})$, where k_η is the heat conduction coefficient related to the Fourier heat conduction coefficient k, while l_k is the length of enhanced nano-transport. Thus:

$$\vec{h} = \frac{\partial\varpi}{\partial\vec{g}} = \mathrm{k}_\eta\vec{g}; \quad \overleftrightarrow{H} = l_k^2\mathrm{k}_\eta\mathrm{grad}\vec{g} \tag{23}$$

In case of a rigid heat-conducting material, $\theta = C^\epsilon\left(1 - l_\eta^2\mathrm{lap}\right)\tilde{\eta};\ \tilde{\eta}_0 \cong 0$ and from (22) we get nonlinear fourth-order differential equation with respect to entropy:

$$\begin{aligned}\dot{\tilde{\eta}} = {} & k_\eta\mathrm{lap}(1 + l_k^2\mathrm{lap})\tilde{\eta} + k_\eta\left[(\theta_{,x})^2 + (\theta_{,x})^2 + (\theta_{,x})^2\right] \\ & + \{k_\eta l_k^2[\theta_{,x}\mathrm{lap}(\theta_{,x}) + \theta_{,y}\mathrm{lap}(\theta_{,y}) + \theta_{,z}\mathrm{lap}(\theta_{,z})] \\ & + k_\eta l_k^2\theta_{,ij}\theta_{,ij}\}\end{aligned} \tag{24}$$

where terms in braces {.} are entirely dependent on the contribution of $\mathrm{grad}\vec{g}$ in the dissipative potential ϖ and may be omitted, if the heat exchange length l_k is small compared to a characteristic domain dimension. Due to the fourth-order derivative heat equation, (24) takes form analogous to the Cahn-Hilliard type equation referring to scalar parameter of regularity/arrangement [22].

Thermoelastic Duhamel-Neumann Material

The basic practically and one of the first concepts of thermoelasticity is the "thermal stress." It appears in the Duhamel-Neumann phenomenological equations of state [3, 4, 6, 7]:

$$\begin{aligned}\sigma_{ij} &= C_{ijkl}^\theta\varepsilon_{kl} - \beta_{ij}(\theta - \theta_0) \\ \tilde{\eta} &= \beta_{ij}\varepsilon_{ij} + C^\theta(\theta - \theta_0)\end{aligned} \tag{25}$$

where thermal capacitances occur: elastic C_{ijkl}^θ and heat C^θ, whose connection with adiabatic Carnot material constants (10) is proven [4, 23]. The base for conversion here is the symmetric dyadic of thermal tension β_{ij}. Its symmetry and transverse contribution in both equations indicate that there may exist a potential satisfying the conditions of the first equation for thermodynamics (8) – the role of this potential has Reech-Helmholtz free energy $\psi(\varepsilon_{ij}, \theta)$, which is related to the internal energy through contact transformation [1] $\psi = \epsilon - \theta\eta$. This leads to a conclusion that the Duhamel-Neumann material is a simple material in the Carnot sense. Unfortunately, the literature does not indicate how could the contact transformation between ψ and ϵ be defined in case of the first order material; hence a gradient Duhamel-Neumann material expression requires further study. For example, in work [24], analogously to (14), extratension exists originating from internal parameter related to temperature.

Thermo-Rheological Material

Thermal damping discovered by Zeuner may be modeled imitating Kelvin mechanical damping, where total stress becomes a sum of elastic and viscous stresses, with viscous stresses being a function of velocity mechanical parameter of state. Substituting in this rheological approach mechanical parameter with heat parameter, we acquire additional terms describing thermal damping:

$$\begin{aligned}\sigma_{ij} &= C_{ijkl}^\theta\varepsilon_{kl} - \beta_{ij}(\theta - \theta_0 + \tau_\theta\dot{\theta}) \\ \tilde{\eta} &= \beta_{ij}\varepsilon_{ij} + C^\theta(\theta - \theta_0 + \tau_\eta\dot{\theta})\end{aligned} \tag{26}$$

Here, τ_θ and τ_η are thermal damping time constant and entropy relaxation, respectively. Let it be noted that introduction of an irreversible term in the equation for reversible thermoelasticity has also ultimate importance in describing finite heat wave propagation velocity [2, 25].

Heat Superconductive Material

If the essence of thermo-rheological material is a supplementation of reversible relations with minuscule irreversible contributions – thermal damping – then quite contrary situation takes place when concerning fully dissipative equation constituting diffusive Fourier heat transport. Here, with use of Natanson expressions, in opposition, to a fully irreversible phenomenon, we add a minuscule elastic memory. When this memory increases, along with the decrease of diffusive contribution, at a limit we receive heat superconductivity, known as ballistic mode [17, 20]. According to this concept, we may acquire diffusion equations extension (23) in form [2, 13]:

$$\vec{h} + \tau_{rel}\dot{\vec{h}} = k_\eta\left(\vec{g} + \tau_{ret}\dot{\vec{g}}\right) \tag{27}$$

that has its analogue in Jeffers rheological material, which on the other hand is a composition of Kelvin and Maxwell modes. Here, τ_{rel} is a relaxation time of a flux, and τ_{rel} is a retardation time of the stimulus [2]. In the literature, particularly concerning extended nonequilibrium thermodynamics, many extensions to this equation exist [26], with respect to heat energy flux $\vec{q} = \theta\vec{h}$; one of the very important ideas is substitution of a "total" material derivatives with a certain "fractional" counterpart [27].

Hetnarski-Ignaczak Material

The authors' idea of this material type was an introduction of an internal vector parameter $\vec{\beta}$, interpreted to be a reversible heat flux. This parameter's rate of change is described with a following evolution equation [28]:

$$\dot{\beta}_i = -\frac{A}{\theta}\theta_{,i} \tag{28}$$

where $A > 0$ is a new constitutive parameter. This way, vector $\vec{\beta}$ is independent, along with θ and ε_{ij}, parameter of state, and hence may appear in the free energy $\psi(\theta, \vec{\varepsilon}, \vec{\beta})$; this should lead to a modified form of Duhamel-Neumann equations. One of the Hetnarski-Ignaczak model's postulates is that the vector $\vec{\beta}$ may be included in a constitutive equation for heat flux, to result in the following modified Fourier equation [8, 28]:

$$\vec{q} = -k\,\mathrm{grad}\,\theta + \overrightarrow{\beta} \tag{29}$$

As it turns out, this new heat transport mode is important for describing waveform heat transport at low temperatures [8]. The advantages of this model over other approaches are discussed in work [29].

Green-Lindsay Material

This model is based on the concept proposed by Ingo Müller [25] of discarding thermal energy flux of the Rankine-Stokes type $\theta\vec{h}$ and replacing it with a generalized $\phi\vec{h}$ relation. This means that the temperature is now replaced with a more general function, called "the coldness": $\phi = \phi(\theta, \theta_{,i}, \theta_{,ij}, \dot{\theta}, \ddot{\theta}, (\dot{\theta})_{,i})$. From the thermodynamic standpoint, this operation is correct – it is crucial to find a relation between the heat energy flux vector and the entropy vector. However, the transferring "the coldness" to a contact transformation and replacing $\psi = \epsilon - \theta\eta$ with $\psi = \epsilon - \phi\eta$ is no longer justified [30]. The constitutive equations received by the authors from the Clausius-Duhem inequality have a form [30]:

$$\begin{aligned} \sigma_{ij} &= C^{\theta}_{ijkl}\varepsilon_{kl} - \beta_{ij}(\theta + \tau_\theta\dot{\theta}) \\ \rho\eta &= \beta_{ij}\varepsilon_{ij} + C^{\theta}(\theta + \tau_\eta\dot{\theta}) - b_i\theta_{,i} \\ q_i &= -\theta_0(b_i\dot{\theta} + k_{ij}\theta_{,j}) \end{aligned} \tag{30}$$

where a constant vector, depending on anisotropy direction b_i, is equal to zero for isotropic material. The Green-Lindsay equations then reduce to the thermo-rheological ones [8].

Green-Naghdi Material

Reformulation of set of governing equations in a way that at least some of them are satisfied identically is achieved in the classical field theory with help of potentials. One of these potentials would be the Biot potential vector admitting of replacing entropy with a vector field: $\eta = -\mathrm{div}\vec{B}$ [3]. Another such potential would be φ, called thermoelastic dislocation and defined to be a volume integral of temperature [7]. For this reason Green and Naghdi [14] introduce thermal dislocation β, which is a temperature integral, but over time: $\beta = \int_0^t \theta(s)ds$. This way, introduction of the new parameter, having status of "internal parameter" [15], allows for completely discarding of diffusive heat transport and replacing it with superconductivity mode, relating rate of heat flux with temperature gradient.

Let us recall that a generalized possibility of employing internal parameter for formulation of heat transport was given by Kosiński and Perzyna [24] – heat flux was defined there to be $\vec{q} = -\alpha\,\mathrm{grad}\beta$, where β parameter has a more general definition and is interpreted as "history of the temperature." Its relation to temperature is also more general and has a form: $\tau_q\,\dot{\beta} = \theta - \beta$, where τ_q is some relaxation. After taking a gradient of both sides of equation, it leads to relaxation transfer equation (Maxwell, Natanson, Cattaneo, Kaliski, Vernotte, Madejski, etc.) $\tau_q\vec{q} + \vec{q} = -\alpha(k)\vec{g}$. In other words, internal parameter of Kosiński-Perzyna allows for introduction of both heat transport forms into play: diffusive and superconductive; Green-Naghdi solution discards diffusive mode and accounts only for the superconductive – reversible – mode. Such limitation results in reversibility and hence is correctly described by authors as "thermoelasticity without energy dissipation" [14].

Strictly speaking, Green and Naghdi [14] examine three types of equations derived by the standard Coleman-Noll procedure:

$$\begin{aligned} \text{Type I} :&\psi = \psi(\varepsilon_{ij}, \dot{\beta}, \mathrm{grad}\dot{\beta}) \\ \text{Type II} :&\psi = \psi(\varepsilon_{ij}, \beta, \dot{\beta}, \mathrm{grad}\dot{\beta}) \\ \text{Type III} :&\psi = \psi(\varepsilon_{ij}, \beta, \dot{\beta}, \mathrm{grad}\beta, \mathrm{grad}\dot{\beta}) \end{aligned} \tag{31}$$

The structure of the Green-Naghdi model (of all three types) is additionally limited, frankly speaking unnecessarily, with a fixed relation between the thermal energy flux and the entropy flux, restricting the applicability range of the model, ex cathedra. Since, in the model, ab initio there is no Fourier-wise conduction constant, the Green-Naghdi model may be applied only to a special class of materials, whereas for steels and alloys the diffusive Fourier-wise transport is dominant and must not be neglected.

Summary

Thermoelastic material science is the oldest of sciences concerning reversible conversion of heat into work and, vice versa, of work into heat. Hence it is, so to speak, the source of classical thermodynamics, which sets the condition of fulfilling the first and second law of thermodynamics crucial. In the literature devoted to the bases of thermoelasticity, impact is laid mostly on conditions resulting from the second law of thermodynamics. In a slight contrast to this tendency, in this entry, we bring up, rather underestimated in the literature, the primal form of the first law of thermodynamics. It is understood as a requisite of inability to create energy ex nihilo, during the closed process of thermoelastic transformations. The procedure of "elevating" the first law of thermodynamics we've designed concludes with the definition of a simple thermoelastic material in the Carnot sense and in the definition for the gradient Carnot material. On their basis, the leading models of classical and generalized thermoelasticity were discussed.

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Thermodynamics: The Nineteenth-Century History

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Overview

Thermodynamics may be considered as the doctrine of energy and entropy, two quantities that are engaged in a universal competition trying to dictate the thermomechanical behavior of bodies: Energy may be called *deterministic* in that it pulls a body into potential minima offered by the body itself or by its environment. Entropy on the other hand tends to grow by making a body tend to spread out *probabilistically* over all possible configurations. Temperature determines which one of these often opposing tendencies prevails. Low temperature keeps a body frozen in its energetic wells, and high temperature makes it ignore those wells. As a result of that competition, it is usually neither the energy that becomes minimal, nor the entropy which becomes maximal; the opposing tendencies compromise and make the available free energy a minimum. In actual practice, this means that – as equilibrium is approached – a body tends to a state of homogeneous fields of