High-temperature effect on the material constants and elastic moduli for solid rocks

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Abstract
Thermally coupled constitutive relations are generally used to determine material constants and elastic moduli (Young’s modulus and shear modulus) of solid media. Conventional studies on this issue are mainly based on the linear temperature dependence of elastic moduli, whereas analytical difficulties are often encountered in theoretical studies on nonlinear temperature dependence, particularly at high temperatures. This study investigates the thermally coupled constitutive relations for elastic moduli and material constants using the assumption of axisymmetric fields, with applications to geologic materials (marble, limestone and granite). The Taylor power series of the Helmholtz free energy function within dimensionless temperatures could be used to develop the thermally coupled constitutive relations. The thermoelastic equivalent constitutive equations were formulated under the generalized Hooke’s law. The material constants of solid rocks were determined by fitting experimental data using axisymmetric stress and strain fields at different temperatures, based on their thermomechanical properties. For these geologic materials, the resultant equivalent elastic moduli and deformations were in good agreement with those from the experimental measurements. Thermal stresses, internal moisture evaporation and internal rock compositions significantly affected the experimental results. This study provides a profound understanding of the thermally coupled constitutive relations that are associated with the thermomechanical properties of solid rocks exposed to high temperatures.

Keywords: material constants, thermally coupled constitutive relations, equivalent elastic moduli, Helmholtz free energy, high temperatures

1. Introduction

Research into the temperature dependence of the thermomechanical properties of rocks is rapidly increasing due to its widespread application in pressure pipes and vessels, nuclear reactors and high-speed cosmic flights (Wang et al. 2015). It can also be used in numerous rock engineering applications, such as stability analysis of constructions (Lai et al. 2014), rock drilling (Alm et al. 1985), geothermal resource development (Pearson et al. 1983) and underground coal gasification (Roddy & Younger 2010). Thermomechanical parameters (e.g. Young’s modulus, shear modulus, peak compressive strength, tensile strength and Poisson’s ratio) are known to change as temperature increases (Lomakin 1976). Conventional studies on this issue are mainly based on
linearly temperature-related elastic moduli (e.g. Young's modulus and shear modulus). However, very few studies have focused on the nonlinear temperature dependence of elastic moduli and material constants. Currently, we do not have a convincing explanation for the influence of high temperatures on material constants. In this article, we proceed with thermally constitutive relations and include experimental observations of geologic materials (marble, limestone and granite) subjected to high-temperature thermal treatments to provide more quantitative evaluations of the effect of high temperature on material constants and elastic moduli of solid rocks.

Thermally constitutive relations have been derived based on the assumption of the Helmholtz free energy, such as the second-order for Mooney–Rivlin materials (Mooney 1940), as well as three-term (Yeoh 1933) and four-term (Biderman 1958) experiential strain energy models for rubber elastomers, with an attempt to fit the laboratory data. However, the previously mentioned method may be limited by a paucity of theoretical basis. For large elastic deformation of incompressible rubberlike solids, Ogden (1972) presented a Taylor power series of the Helmholtz free energy function, which could be explained by the classical elasticity theory. However, the constitutive relations are formulated without considering the effect of temperature fields.

Various thermoelastic problems with variable thermal material properties have been extensively investigated based on the generalized theories of thermoelasticity and thermally constitutive relations (Aouadi 2006), but most of them are based on the linear temperature dependence of the material properties (Allam et al. 2010; Sherief & El-Latif 2013). Few studies have examined the thermally coupled constitutive relations of solid rocks using the Taylor power series of the Helmholtz free energy function. However, the key is to establish how to obtain the equivalent elastic moduli for nonlinear behaviors at high temperatures.

Many researchers have studied the thermomechanical properties of rocks, including acoustic emissions (AE) (Chen et al. 2017), tensile strength (Zhao et al. 2016), microcrack development (Batzle et al. 1980) and peak compressive strength (Yang et al. 2019b). However, material constants could not be tested directly because of experimental instruments and analytical difficulties. Wang (1989) introduced a method for determining the material constants based on thermally coupled constitutive relations derived from the Taylor power series of the Helmholtz free energy function without considering the effect of Poisson’s ratios. Hu et al. (2018) used the Helmholtz free energy function at high temperatures to formulate the thermally coupled constitutive relations for metal (magnesium alloy) under the assumption of planar stress and strain fields. Thereafter, they considered the influence of Poisson’s ratio and Young’s modulus and determined the material constants by fitting experimental data, even though material constants are inappropriate for determining equivalent elastic moduli. The scheme for determining material constants associated with thermally coupled constitutive relations for metals could be extended to solid rocks using the assumption of the axisymmetric stress and strain fields, as addressed in this paper.

In this study, we investigate material constants and thermomechanical properties in terms of dimensionless temperature, with applications to geologic materials (marble, limestone and granite). First, we briefly introduce the thermally coupled constitutive relations based on the Taylor power series of the Helmholtz free energy function. Thereafter, we formulate the thermoelastic equivalent constitutive equations according to the generalized Hooke’s law. Next, we use marble, granite and limestone samples to investigate the thermomechanical properties and material constants of rock materials subjected to high-temperature heating. The material constants with the influence of Poisson’s ratio and Young’s modulus can be obtained by fitting the experimental data using the axisymmetric stress and strain fields for these rock materials subjected to high-temperature heating. The resulting equivalent elastic moduli, which are represented by a quadratic equation, show a quadratic temperature dependence and are in good agreement with the experimental measurements. Finally, the influence of thermal stresses, internal moisture and internal rock composition on the experimental result is discussed in detail. This study is expected to improve the thermally coupled constitutive relations related to the thermomechanical properties of solid media, particularly for geologic materials that are exposed to high temperatures.

2. Theoretical background

2.1. Strain energy function and thermally coupled constitutive relations

In terms of the Helmholtz free energy function, the stress tensor, \( \sigma_{ij} \), is expressed as

\[
\sigma_{ij} = \frac{\partial \Psi}{\partial \varepsilon_{ij}},
\]

where \( \Psi = \Psi(\varepsilon_{ij}, \theta^*) \) represents the free energy function and \( \varepsilon_{ij} \) stands for the corresponding strain tensor. The dimensionless temperature variation, \( \theta^* \), can be calculated from functions of \( \theta^* = \frac{T - T_0}{\theta_0} \), where \( T_0 \) represents the reference temperature and \( T \) represents the absolute temperature. The free energy function for isotropic materials is calculated using functions of the Taylor power series in terms of \( \varepsilon_{ij} \) and \( \theta^* \), as shown (Dillon 1962)

\[
\Psi(\varepsilon_{ij}, \theta^*) = a_0 + a_1 \varepsilon_1 + a_2 \varepsilon_2 + a_3 \varepsilon_3 + a_4 \theta^* + a_5 \theta^{*2} + a_7 \varepsilon_1 \theta^* + a_8 \varepsilon_1 \theta^* + a_9 \varepsilon_1 \varepsilon_2 + \cdots,
\]

where \( \varepsilon_1, \varepsilon_2, \varepsilon_3 \) are the principal strains, \( \theta^* \) is the dimensionless temperature variation, and \( a_0, a_1, a_2, a_3, a_4, a_5, a_6, a_7, a_8, a_9 \) are the material constants.
where \( a_{ij}, a_{ij}, \ldots \) denote the material constants of the medium and \( I_1, I_2, I_3 \) denote invariants of the strain tensor in the following form

\[
\begin{align*}
I_1 &= e_{ij}^2, \\
I_2 &= \frac{1}{2} (e_{ij} e_{ij} - e_{ij} e_{ji}), \\
I_3 &= \det e_{ij}.
\end{align*}
\] (3)

It is important to note that the influences of \( e_{ij} \) over the third order and \( \theta \) over the fourth order on the free energy function can be ignored by Equation (2) (Gatewood 1957). Subsequently, the free energy function in equation (1) could be rewritten as

\[
\Psi(e_{ij}, \theta) = a_1 + a_2 \theta \epsilon + a_3 \theta^2 + a_4 \theta^3 + a_5 \theta^4 + a_6 I_1 + a_7 I_2 \epsilon + a_8 I_3 \theta + a_9 I_2 \theta^2 + a_{10} I_3 \theta^3 + a_{11} I_2 \theta^4 + a_{12} I_1 \theta^5 + a_{13} I_1 \theta^6 + a_{14} I_1 \theta^7 + a_{15} I_1 \theta^8 + a_{16} I_2 \theta^9 + a_{17} I_2 \theta^{10} + a_{18} I_2 \theta^{11} + a_{19} I_1 I_2 \theta^{12} + a_{20} I_3 \theta^{13} + a_{21} I_1 \theta^{14}.
\] (4)

Equation (1) can be expressed using the chain rule of equation (3) as follows (Kostek et al. 1993)

\[
\sigma_{ij} = \frac{\partial \Psi}{\partial e_{ij}} = \frac{\partial \Psi}{\partial I_1} \frac{\partial I_1}{\partial e_{ij}} + \frac{\partial \Psi}{\partial I_2} \frac{\partial I_2}{\partial e_{ij}} + \frac{\partial \Psi}{\partial I_3} \frac{\partial I_3}{\partial e_{ij}}.
\] (5)

Combined with equations (4) and (5), the following is obtained

\[
\sigma_{ij} = \delta_{ij} \left( a_1 \theta + a_2 \theta^2 + a_3 \theta^3 \right) + I_1 \delta_{ij} \left( 2(a_{10} + a_{11} \theta + a_{12} \theta^2) \right) + \left( a_{15} + a_{16} \theta + a_{17} \theta^2 \right) - e_{ij} \left( a_{15} + a_{16} \theta + a_{17} \theta^2 \right),
\] (6)

where \( \delta_{ij} \) is the Kronecker delta.

The generalized elastic modulus, \( E_{gmn} \), is calculated as follows

\[
E_{gmn} = \frac{\partial \sigma_{ij}}{\partial \epsilon_{mn}} = \left[ 2(a_{10} + a_{11} \theta + a_{12} \theta^2) \right] + \left( a_{15} + a_{16} \theta + a_{17} \theta^2 \right) \delta_{mn} \delta_{il} - \left( a_{15} + a_{16} \theta + a_{17} \theta^2 \right) \delta_{mi} \delta_{nl}.
\] (7)

For the case of uniaxial tension or compression, Young’s modulus becomes

\[
E = E_{1111} = E_{2222} = E_{3333} = 2(a_{10} + a_{11} \theta + a_{12} \theta^2).
\] (8)

The shear modulus is calculated as follows

\[
\mu = \frac{1}{2} E_{1212} = \frac{1}{2} E_{2323} = \frac{1}{2} E_{3131} = \frac{1}{2} \left( a_{15} + a_{16} \theta + a_{17} \theta^2 \right).
\] (9)

Based on the relationship between elastic coefficients, we have

\[
E = 2\mu(1 + \nu),
\] (10)

where \( \nu \) denotes Poisson’s ratio.

For an axisymmetric problem, the thermally coupled constitutive relations can be simplified from equation (6) as

\[
\begin{align*}
\sigma_r &= l \theta^* + m \epsilon_r + (m + n) (\epsilon_r^* + \epsilon_z^*), \\
\sigma_\theta &= l \theta^* + m \epsilon_\theta + (m + n) (\epsilon_r^* + \epsilon_\theta^*), \\
\sigma_z &= l \theta^* + m \epsilon_z + (m + n) (\epsilon_r^* + \epsilon_\theta^*), \\
\sigma_{rz} &= -ne_{rz}.
\end{align*}
\] (11)

where the subscripts \( r, \theta \) and \( z \) are the radial, circumferential and axial tensors, respectively. The \( l, m \) and \( n \) parameters are determined from a function of the dimensionless temperature

\[
\begin{align*}
l(\theta^*) &= a_7 + a_8 \theta^* + a_9 \theta^2, \\
m(\theta^*) &= 2(a_{10} + a_{11} \theta + a_{12} \theta^2), \\
n(\theta^*) &= a_{15} + a_{16} \theta^* + a_{17} \theta^2.
\end{align*}
\] (12)

The thermomechanical properties of the materials exhibit a strong nonlinearity in terms of the dimensionless temperature, as illustrated by the thermally coupled constitutive relations in equations (6) and (11).

### 2.2. Determination of material constants

The material constants that are associated with the thermally coupled constitutive relations were investigated using the assumption of the axisymmetric stress and strain fields. By introducing the static Young’s modulus, \( E \), the thermal expansion coefficient, \( \alpha \), and the static Poisson’s ratio, \( \nu \), the equivalent constitutive equations based on the generalized Hooke’s law could be written as

\[
\begin{align*}
\sigma_r &= \frac{E(1 + \nu)}{(1 + \nu)(1 - 2\nu)} \epsilon_r + \frac{E\alpha}{(1 + \nu)(1 - 2\nu)} \epsilon_r^* + \frac{E}{1 - 2\nu} \alpha T_0 \theta^*, \\
\sigma_\theta &= \frac{E(1 + \nu)}{(1 + \nu)(1 - 2\nu)} \epsilon_\theta + \frac{E\alpha}{(1 + \nu)(1 - 2\nu)} \epsilon_\theta^* + \frac{E}{1 - 2\nu} \alpha T_0 \theta^*, \\
\sigma_z &= \frac{E(1 + \nu)}{(1 + \nu)(1 - 2\nu)} \epsilon_z + \frac{E\alpha}{(1 + \nu)(1 - 2\nu)} \epsilon_z^* + \frac{E}{1 - 2\nu} \alpha T_0 \theta^*, \\
\sigma_{rz} &= \frac{E}{(1 + \nu)} \tau_{rz}.
\end{align*}
\] (13)

Generally, material constants are obtained by fitting the experimental data using the axisymmetric stress and strain fields from equation (12). By comparing the thermally coupled constitutive relations (equations (11) and (12)) with the equivalent constitutive relations (equation (13)), we can relate the material constants to the equivalent elastic moduli.
as follows

\[
\begin{align*}
\ell(\theta^*) &= a_7 + a_8 \theta^* + a_9 \theta^{*2} = -\frac{E}{1-\nu} \alpha T_0 \\
m(\theta^*) &= 2(a_{10} + a_{11} \theta^* + a_{12} \theta^{*2}) = \frac{E(1-\nu)}{(1+(1-2\nu))(1+\nu)} \\
n(\theta^*) &= a_{15} + a_{16} \theta^* + a_{17} \theta^{*2} = -\frac{E}{(1+\nu)}.
\end{align*}
\]

(14)

It should be noted that determining the material constants, \(a_i (i = 7 \sim 9)\), is difficult because there are insufficient data on thermal expansion coefficients. Equations (8) and (9) can be used to calculate the equivalent Young’s modulus and shear modulus, respectively, as functions of temperatures. The thermomechanical properties of rocks have been demonstrated to have a linear temperature dependence of elastic moduli (Wang 1988) and a cubic or quadratic function with thermal expansion coefficients (Morse & Lawson 1967; Yang et al. 2019a). However, by ignoring the effect of temperature, Poisson’s ratio is usually recognized as a constant (Wang 1988). The temperature has a significant effect on Poisson’s ratio (Du et al. 2004).

3. Experimental data

We used published experimental data to study the equivalent elastic moduli and material constants of rock materials. Experimental measurements (Xia et al. 2004; Yang et al. 2017; Zhang et al. 2017) were conducted for geological materials (marble, granite and limestone) that were subjected to high-temperature heating. These samples, which were collected from different regions in China, were cored from the same blocks to a length of approximately 100 mm and a diameter of about 50 mm. A uniaxial compression test was conducted using the recommended method of the International Society for Rock Mechanics (Fairhurst & Hudson 1999). Table 1 lists the experimental instruments and their corresponding materials. The average linear deformation stage of the complete stress–strain curve in the uniaxial compressive test can be used to obtain the static Young’s modulus, whereas an absolute value of the lateral to vertical deformation ratio can be used to calculate the static Poisson’s ratio.

The experimental procedure (Xia et al. 2004; Yang et al. 2017; Zhang et al. 2017) for high-temperature thermal treatments consists of three stages: (i) exposing the specimen to a specified temperature at a constant heating rate of 5°C min\(^{-1}\), (ii) maintaining the temperature for 2 or 3 h and (iii) cooling naturally to room temperature below the heating rate to avoid thermal shock inside the rock. All the mechanical and physical properties of the dry samples were measured after cooling. The heating rate significantly affects the thermomechanical properties. Using a relatively low heating rate can prevent undesirable widespread damages and thermal shocks inside the rock due to the appearance of thermal stresses (Rathnaweera et al. 2018). The purpose of maintaining the temperature for 2 or 3 h is to ensure sufficient and evenly distributed heating to the specified temperature.

4. Results and discussions

4.1. Application to marble

We used the marble experimental data (Xia et al. 2004) to obtain the material constants and equivalent elastic moduli. The marble samples, which were collected from a mining area in Henan Province, in central and eastern China, were exposed to temperatures of up to 800°C. Heat treatment was conducted in an SX\(_2\)–4–10 high-temperature furnace, and the temperature was maintained with the KSW4–11 automatic thermostat console. The parallelism of the upper and lower surfaces was within 0.05 mm, and the flatness was less than 0.02 mm. During the uniaxial compressive experiment, the axial and the lateral deformation displacement sensors were set to 0–5 and 0–2.5 mm, respectively.

By fitting equation (14) to the experimental data, we obtained six material constants, \(a_i (i = 10 \sim 12, 15 \sim 17)\), in equation (12). Table 2 lists the material constants and corresponding determination coefficients. Figure 1 shows the plot of the \(m(\theta^*)\) and \(n(\theta^*)\) coefficients versus dimensionless temperatures. The fitting and experimental results appear to be in good agreement. An empirical formula, a quadratic tendency with dimensionless temperatures, can be used to determine the \(m(\theta^*)\) and \(n(\theta^*)\) values, with resulting correlation coefficients of 0.943 and 0.906, respectively, indicating that \(m(\theta^*)\) and \(n(\theta^*)\) can be expressed
by thermally coupled constitutive relations, i.e. a quadratic formula.

Figures 2 and 3 show the equivalent elastic moduli as the temperature increases, as calculated using different theoretical equations. Except for 500°C, we discovered that all other points are significantly consistent. The following factors can be used to explain this. On the one hand, different minerals have different thermal expansion coefficients even at the same temperature. Due to uncoordinated deformations, the differential expansion induces thermal stress, loosening grain arrangements and generating new microcracks. Provided that high thermal gradients or thermal shocks are not considered, two main mechanisms of thermal stress have been identified, namely thermal expansion anisotropy related to a single mineral and thermal expansion mismatch related to different mineral phases (Browning et al. 2016). That is, new microcrack extensions may form when the maximum thermal stress exceeds the ultimate shear or compressive strength limits of the rock. In addition, differences in the coefficients of thermal expansion along different crystallographic axes of the same mineral can also cause structural damage on heating, with boundary cracks appearing between quartz and feldspar grains and transgranular cracks emerging in feldspar grains (Somerton 1992). On the other hand, the internal rock composition may change as the temperature increases, including magnesium carbonate (MgCO₃) decomposing into...
MgO and CO₂ at approximately 500°C (Huang 1979). In conclusion, thermal stress appears and internal rock composition changes as the temperature increases, resulting in structural damages.

### 4.2. Application to granite

We applied the equivalent thermally coupled constitutive relations to temperature-related granite experimental data (Yang et al. 2017). The granite samples were collected in Rizhao City, Shandong Province. According to the experimental procedure, the temperature is gradually increased from room temperature to 800°C. The high-temperature treatments were conducted using the model SGM.M10 high-temperature furnace. The granite samples consisted mainly of feldspar, biotite and quartz at room temperature, as determined by X-ray powder diffraction (XRD). The mineral composition remains unchanged as the temperature increases. In addition, the AE output was continuously monitored to observe the microcrack evolution characteristics in the deformed samples using the DS2 full information AE measuring system.

Similarly, Table 3 presents the calculated material constants from the experimental data of the granite samples and their corresponding determination coefficients. Figure 4 shows the variations in the $m(\theta^*)$ and $n(\theta^*)$ coefficients as functions of dimensionless temperature, which could be well represented by the empirical formula of a quadratic tendency. The resulting correlation coefficients are up to 0.901 and 0.916, respectively, indicating that the fitting and experimental results are in good agreement.

As depicted in figures 5 and 6, the equivalent elastic moduli of the granite sample as a function of the temperature change, which were calculated from the material constants, are in good agreement with the experimental measurements except at 200 and 300°C. This behavior is extremely complex and could be possibly explained as follows. The attached water can escape between 70 and 100°C, bound water vaporizes at temperatures above 100°C and crystal water evaporates at temperatures less than 400°C (Zhang et al. 2016). Variations in water properties affect granite features, causing the collapse of mineral skeletons and great defects. The presence or absence of water, as well as its state, has a noticeable effect on Poisson’s ratio of rocks (Ito et al. 1979; Yang et al. 2019b). Poisson’s ratio decreases from 0.127 at room temperature to 0.038 at 600°C, indicating that it is affected by temperature. Furthermore, thermal stresses can cause internal crack propagation, resulting in structural damage to rocks and anisotropic properties in constituting minerals. The vertical and horizontal cross sections of the granite samples at room temperature demonstrated that the crack aperture thicknesses in some local regions are significantly lower than those at 300°C with some lateral tensile cracks; both grain boundary and transgranular cracks form at 400°C, and the AE counts increase as the temperature increases (Yang et al. 2017). Therefore, rock thermal damages may

![Figure 3. Comparison of the shear modulus of the marble sample as a function of dimensionless temperature.](https://i.imgur.com/3J5Q5Q.png)

### Table 3. Material constants and the resulting correlation coefficients of the granite sample

| Parameters | Material constants | Results (GPa) | Correlation coefficient |
|------------|--------------------|--------------|------------------------|
| $m(\theta^*)$ | $a_{10}$ | 19.06456 | 0.901 |
| | $a_{11}$ | 0.43022 | |
| | $a_{12}$ | −0.03904 | |
| | $a_{13}$ | | |
| | $a_{14}$ | $a_{15}$ | −32.63931 | 0.916 |
| | $a_{16}$ | −0.88539 | |
| | $a_{17}$ | 0.06947 | |

As depicted in figures 5 and 6, the equivalent elastic moduli of the granite sample as a function of the temperature change, which were calculated from the material constants, are in good agreement with the experimental measurements except at 200 and 300°C. This behavior is extremely complex and could be possibly explained as follows. The attached water can escape between 70 and 100°C, bound water vaporizes at temperatures above 100°C and crystal water evaporates at temperatures less than 400°C (Zhang et al. 2016). Variations in water properties affect granite features, causing the collapse of mineral skeletons and great defects. The presence or absence of water, as well as its state, has a noticeable effect on Poisson’s ratio of rocks (Ito et al. 1979; Yang et al. 2019b). Poisson’s ratio decreases from 0.127 at room temperature to 0.038 at 600°C, indicating that it is affected by temperature. Furthermore, thermal stresses can cause internal crack propagation, resulting in structural damage to rocks and anisotropic properties in constituting minerals. The vertical and horizontal cross sections of the granite samples at room temperature demonstrated that the crack aperture thicknesses in some local regions are significantly lower than those at 300°C with some lateral tensile cracks; both grain boundary and transgranular cracks form at 400°C, and the AE counts increase as the temperature increases (Yang et al. 2017). Therefore, rock thermal damages may
significantly affect the experimental result of the equivalent elastic moduli. In general, the appearance of thermal stress and the continuous evaporation of the internal moisture as the temperature increases result in the formation of more microcracks, eventually contributing to the degradation or weakening of rocks (Brotóns et al. 2013).

4.3. Application to limestone

The equivalent thermally coupled theories are applied to limestone (Zhang et al. 2017). The limestone samples used in this study were collected from Linyi City, Shandong Province. Heat treatment was conducted in a CTM300A high-temperature furnace at $1^\circ C$ resolution, and pore characteristic parameters were measured using an Auto-Pore IV9510 automatic mercury injection equipment. According to the XRD analysis, the primary minerals in these limestone samples are dolomite and calcite. The average bulk density and effective porosity are 2.710 g/cm$^{-3}$ and 0.17% at room temperature, respectively.

Table 4 presents the material constants and corresponding determination coefficients of the limestone samples. Figure 7 shows the $m(\theta^*)$ and $n(\theta^*)$ coefficients as functions of dimensionless temperature, which could be well described using the empirical formula of a quadratic tendency. The resulting correlation coefficients are up to 0.876 and 0.976,
Figure 6. Comparison of the shear modulus of the granite sample as a function of dimensionless temperature.

Table 4. Material constants and the resulting correlation coefficients of the limestone sample

| Parameters | Material constants | Results (GPa) | Correlation coefficient |
|------------|--------------------|---------------|-------------------------|
| $m(\theta^*)$ | $a_{10}$ | 47.89134 | 0.876 |
| | $a_{11}$ | −3.31565 | |
| | $a_{12}$ | 0.06250 | |
| $n(\theta^*)$ | $a_{15}$ | −59.21827 | |
| | $a_{16}$ | 3.26645 | 0.976 |
| | $a_{17}$ | −0.04576 | |

respectively, indicating that $m(\theta^*)$ and $n(\theta^*)$ can also be expressed by a quadratic formula.

Figures 8 and 9 show the equivalent elastic moduli of the limestone sample as a function of temperature. Except for those at the first three points, the theoretical predictions by equations (8) and (9) are observed to be in good agreement with the experimental measurements, particularly for the equivalent Young’s modulus. Similarly, intricate factors can be used to explain this. The absorbed water vaporizes at approximately 100°C, the interlayer water vaporizes between

Figure 7. Variation parameters of the limestone sample with dimensionless temperature for (a) $m(\theta^*)$ and (b) $n(\theta^*)$. 
100 and 300°C, the crystal water escapes at temperatures less than 400°C and the structural water evaporates at temperatures above 300°C (Sun et al. 2015). The influence of water–rock interactions on rock properties causes Poisson’s ratio to increase from 0.248 at room temperature to 0.309 at 100°C and subsequently decrease to 0.177 at 600°C. Some studies (Géraud 1994) have demonstrated that high temperatures can increase the crack density of crystals and accelerate the development of anisotropy, decreasing the elastic properties, particularly for Young’s and shear moduli and the peak strength (Tufail et al. 2007), and increasing the crack damage and spatial structural heterogeneity of rocks (Lin 2002). By gradually increasing the thermal treatment temperature, the inside and outside of limestone may become unevenly exposed, inducing microdefects. Rock expansion is responsible for the development of microcracks to macrocracks within grains. In addition, at approximately 200°C, Ca(HCO₃)₂ in the rock begins to decompose into H₂O, CO₂ and CaO, and CO₂ gas released from preexisting isolated pores after thermal treatments may enhance its internal porosity (Yang et al. 2019b).

5. Conclusions
Thermally coupled constitutive relations are critical in determining the material constants and equivalent elastic moduli of solid media. In this study, the Taylor power series of the Helmholtz free energy function within dimensionless temperatures and the thermoelastic equivalent constitutive equations based on the generalized Hooke’s law were used to
develop the thermally coupled constitutive relations. Material constants associated with the thermally coupled constitutive relations were determined by fitting experimental results at different temperatures. The thermoelastic equivalent constitutive equations were used to derive the theoretically equivalent Young’s modulus and shear modulus for solid rocks with the dimensionless temperature. The following are the findings of the investigation:

(i) The theoretically derived moduli have a quadratic dependence on the dimensionless temperature, as demonstrated by applications to geologic materials. The theoretical results are in good agreement with the experimental results, and strong nonlinearity is observed.

(ii) Material constants could be determined by fitting experimental data using the axisymmetric stress and strain fields at different temperatures, taking into account the effects of Young’s modulus and Poisson’s ratio.

(iii) The appearance of thermal stresses, internal moisture evaporation and changes in the internal rock composition could significantly influence the experimental results.

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