On three-stage temperature dependence of elastic wave velocities for rocks

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Received 22 February 2021, revised 9 April 2021
Accepted for publication 5 May 2021

Abstract
For most rocks, the typical temperature behavior of elastic wave velocities generally features a three-stage nonlinear characteristic that could be expressed by a reverse S-shape curve with two inflexion points. The mechanism regulating the slow-to-fast transition of elastic constants remains elusive. The physics of critical points seems related to the multimineral composition of rocks with differentiated thermodynamic properties. Based on laboratory experiments for several rocks with different levels of heterogeneity in compositions, we conduct theoretical and empirical simulations by nonlinear thermoelasticity methods and a S-shape model, respectively. The classical theory of linear thermoelasticity based on the Taylor expansion of strain energy functions has been widely used for crystals, but suffers from a deficiency in describing thermal-associated velocity variations for rocks as a polycrystal mixture. Current nonlinear thermoelasticity theory describes the third-order temperature dependence of velocity variations by incorporating the fourth-order elastic constants. It improves the description of temperature-induced three-stage velocity variations in rocks, but involves with some divergences around two inflexion points, especially at high temperatures. The S-shape model for empirical simulations demonstrates a more accurate depiction of thermal-associated three-stage variations of P-wave velocities. We investigate the physics of the parameters \(a_1\) and \(b_1\) in the S-shape model. These fitting parameters are closely related to thermophysical properties by being proportional to the specific heat and thermal conductivity of rocks. We discuss the mechanism that regulates the slow-to-fast transition in the three-stage nonlinear behavior for various rocks.

Keywords: rocks, elastic wave velocity, three-stage temperature dependence, nonlinear thermoelasticity theory, empirical reverse S-shape model

1. Introduction
The mechanical properties of rocks change significantly with temperatures. The research into temperature-induced velocity variations of elastic waves in rocks is a fundamental influence in engineering fields such as building material, coal mining, nuclear waste storage, geothermal development and superdeep oil/gas exploration. The effect of temperature on elastic wave velocities varies with different types of rock because of their diversities in mechanical properties. The rock velocity variations induced by temperature change typically present in a progressive scale with increasing temperatures, including linear elastic, nonlinear elastic and inelastic deformations. Such a three-stage pattern is closely related to the temperature-induced changes in microstructures and the differentiation of thermophysical properties (e.g. thermal-expansion coefficients) in different
material phases. The typical temperature behavior in rocks has been extensively investigated by both theoretical and empirical models with some fitting parameters. At present, we still lack a convincing correlation between prediction-model parameters and rock thermophysical properties. In this article, we address this issue using various rocks with different levels of heterogeneity in thermophysical properties.

Thermal-associated wave velocities in crystals are generally weak at low temperature, but become obvious at high temperature. The classical thermoelastic theory has related elastic wave velocities to loading temperatures using third-order, as well as higher-order, elastic constants (Hiki & Granato 1966; Loje & Schuele 1970; McSkimin & Andreatch 1972; Garber & Granato 1975a, 1975b; Shrivastava 1980). Based on the small-amplitude bulk acoustic wave propagating in crystal, Sorokin et al. (1999) formulated the first-order linear temperature dependence at low temperatures by taking into account the second-order elastic constants. The theoretical model has been extended using the fourth-order elastic constants for higher temperatures to calculate the nonlinear temperature dependence of elastic wave velocities in cubic crystals (Telichko & Sorokin 2015). These well-established thermoelastic constitutive models for crystals may not be applicable to rocks as a polycrystal mixture with different mineral lithologies, encountering the problem of divergent and deficient predictions in describing thermal-induced velocity variations as the equivalent effect of individual mineral phases.

As demonstrated by numerous experimental measurements for heterogeneous rocks (Li et al. 1986; Zhang et al. 2015; Sirdesai et al. 2018), temperature-dependent wave velocities become complex by presenting strong nonlinear behavior, especially for the P-wave velocity that shows more thermal sensitivity than the S-wave velocity at most temperatures. The typical temperature behavior of rocks is characteristic of a three-stage pattern with two obvious inflexion points, which is attributed to the differentiation of thermal-expansion coefficients in different mineral phases and the temperature-induced change of microstructures (e.g. bedding structures, microcracks, bound fluids etc.) native to natural rocks. In particular, the latter is associated with the deterioration of internal rock structures, followed by variation of mechanical properties, for example, fracture development (Chen et al. 2008; Zhang et al. 2015; Ma & Ba 2020), transform in chemical composition (Moore et al. 1983; Kong et al. 2000) and partial melting reaction (Ito 1990; Jin et al. 1994). The thermal damage to rocks has been extensively studied (Douglit et al. 1977; Wang et al. 1989; Isaak 1992; Tian et al. 2016). Qi et al. (2021) developed a model for temperature effects on the velocity–porosity relationship in rocks. Yang et al. (2019) formulated a third-order nonlinear temperature dependence of wave velocities in rocks based on the decomposition of total strains into the background related to temperature fluctuation and the infinitesimal component induced by wave propagation. Applications to ultrasonic experimental data with three different media (sandstone, granite and olivine) confirm validity of the nonlinear thermoelastic model, but involve some divergences around two inflexion points, especially in rocks with strong heterogeneity in lithology.

Current theoretical models perhaps consider nonlinear elastic deformations under low to moderate temperatures, but cannot describe inelastic deformations in microstructures subject to high temperatures. The literature abounds with empirical models (Yavuz et al. 2010; Zhang et al. 2016; Yang et al. 2017) aimed at describing the nonlinear temperature dependence of wave velocities in rocks, where the polynomial function has been widely used to correlate P-wave velocities and temperatures. Despite these quadratic functions demonstrating more accurate predictions for experimental data than the theoretical models mentioned previously, the fitting parameters lack a correlation with the thermophysical properties of rocks.

In this paper, we first introduce the basic principle of thermoelasticity briefly, as well as the classical linear prediction method. Two kinds of theoretical model for the stress–strain constitutive relationship of wave propagation in thermoelastic media are presented to describe the two-order (Telichko & Sorokin 2015) and third-order (Yang et al. 2019) nonlinear temperature dependence of P-wave velocities. Comparisons with the empirical S-type prediction are given for ultrasonic measurements with four kinds of rock (marble, granite, limestone and sandstone), which demonstrates the accuracies of description by these three prediction models for temperature-induced velocity variations. We investigate the effect of different mineral phases in the rock on the accuracy of prediction. We correlate prediction-model parameters and thermophysical properties of rocks.

2. Thermoelasticity theory

According to Clausius inequality, the stress tensor \( \sigma_{ij} \) is written as

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

where the Helmholtz free energy \( \Psi = \Psi(\gamma_{ij}, \theta^*) \) is a differentiable function of the strain tensor \( \gamma_{ij} \) and the dimensionless temperature \( \theta^* \) defined as \( \theta^* = \frac{T - T_0}{T_0} \) where \( T_0 \) is the the reference temperature and \( T \) is the absolute temperature. The classical thermoelastic theory expands Helmholtz free energy by Taylor power series for the stress–strain constitutive equations of isotropic materials. (Dillon 1962;
\[ \Psi(\gamma, \theta^s) = a_0 + a_1 \gamma + a_2 \gamma^2 + \cdots + a_9 \gamma^9 \]

where \( a_0, a_1, \ldots, a_9 \) are the material constants, and \( I_1, I_2, I_3 \) are the strain invariants defined as:

\[
\begin{align*}
I_1 &= \gamma, \\
I_2 &= \frac{1}{2} (\gamma_a \gamma_b - \gamma_b \gamma_a), \\
I_3 &= \det \gamma.
\end{align*}
\]

Thermophysical properties are not linear with increasing temperatures (Gatewood 1957); that is, the effects of the strain tensors over the third order and the products over the fourth order could be ignored in equation (2). The Helmholtz free energy can be simplified as

\[ \Psi(\gamma, \theta^s) = a_1 + a_2 \theta^s + a_3 \theta^{s2} + a_4 \theta^{s3} + a_5 \theta^{s4} + a_6 \gamma + a_7 \gamma^2 + \cdots, \] (2)

Substituting equation (4) into (5), we rearrange terms to yield:

\[
\sigma_{ij} = \delta_{ij} \left[ a_6 + a_1 \theta^s + a_2 \theta^{s2} + a_3 \theta^{s3} \right] + 2 \left[ a_1 \gamma + a_2 \gamma^2 \right] Y_{ik} \delta_{ij} - \left( \beta_2 \theta^{s2} + \beta_3 \theta^s + \beta_4 \right) \theta \delta_{ij} \] (6)

where \( \delta_{ij} \) is the Kronecker delta and \( a_6 \) is the initial normal stress and could set as zero in the natural state (Hu et al. 2018). By introducing the temperature-dependent constants, equation (6) can be rewritten as

\[
\sigma_{ij} = \delta_{ij} \left( \lambda_1 \theta^{s2} + \lambda_2 \theta^s + \lambda_3 \right) Y_{ik} \delta_{ij} + 2 \left( \mu_2 \theta^{s2} + \mu_3 \theta^s + \mu_4 \right) \gamma_{ij} - \left( \beta_2 \theta^{s2} + \beta_3 \theta^s + \beta_4 \right) \theta \delta_{ij} \] (7)

where \( \lambda \) and \( \mu \) are the Lame constants; \( \lambda_0 = a_{15} + 2a_{10}, \lambda_1 = 2a_{11} + a_{16}, \lambda_2 = 2a_{12} + a_{17}, \mu_0 = -a_{18} - a_{19}, \mu_1 = -a_{20} - a_{21}, \beta_2 \) is the thermostatic coupling coefficient; \( \beta_0 = -\frac{a_7}{a_6}, \beta_1 = -\frac{a_2}{a_6} \).

When the wave is propagating in thermoelastic media, the total strain can be written as a sum of two kinds of strain

\[ \varepsilon_{ij} = \varepsilon_{ij}^1 + \varepsilon_{ij}^2 \] (8)

where \( \varepsilon_{ij}^1 \) is the large background strain related to temperature fluctuations and \( \varepsilon_{ij}^2 \) is the infinitesimal component caused by wave propagation. When the strain follows the hypothesis of effective isotropic temperature change, \( \varepsilon_{ij}^2 \) can be rewritten as

\[ \varepsilon_{ij}^2 = \alpha \delta_{ij} \] (9)

where \( \alpha \) represents the temperature-induced positive strain.

Given a reasonable approximation for linear thermal expansion, we have (Yang et al. 2019)

\[ \alpha = \frac{\beta}{3\lambda + 2\mu} \theta \] (10)

where \( \theta = T - T_0 \) is the temperature increment.

For the small strain \( \varepsilon_{ij}^2 \) induced by P-wave propagation, a P-wave kernel is considered, \( \exp[i \omega_f t - (1 + \alpha) k_p x_1] \) (Ba et al. 2013), to partition \( \varepsilon_{ij}^2 \) into

\[
\begin{cases}
\varepsilon_{ij}^2 = \theta \exp \left[ i \omega_f (t - (1 + \alpha) k_p x_1) \right], & i, j \neq 1, \\
\varepsilon_{ij}^2 = 0, & i, j = 1
\end{cases}
\] (11)

where \( k_p \) is the wave number, \( \omega_f \) is the angular frequency, \( t \) is the propagating time and \( i = \sqrt{-1} \). In general, the wave-induced maximum strain \( \theta \ll \alpha \).

3. Predictive models

3.1. Conventional linear thermoelastic model

The linear thermoelastic model with third-order elastic constants (Sorokin et al. 1999) can be obtained by the Green–Christoffel tensor theory of small-amplitude volume sound waves (BAW) propagation in crystals

\[ \rho V^2_p = \lambda + 2\mu + \psi_1 \alpha \] (12)

with

\[ \psi_1 = 2\lambda + 4\mu + 4v_1 + 10v_2 + 8v_3 \] (13)

where \( (v_1, v_2, v_3) \) are the third-order elastic constants (Toupin & Bernstein 1961; Thurston & Brugger 1964).

3.2. Second-order nonlinear thermoelastic model

Based on the assumption of finite static strain for the BAW propagation, Telichko & Sorokin (2015) consider the fourth-order elastic constants and extend the linear thermoelastic model to account for the second-order nonlinear
Table 1. Thermophysical properties of minerals and cements for common rocks at room temperature

| Mineral component      | $\zeta \times 10^{-6}$ $\cdot$ C$^{-1}$ | $K$ (W $\cdot$ m$^{-1}$ $\cdot$ K$^{-1}$) | $c$ (kJ $\cdot$ kg$^{-1}$ $\cdot$ K$^{-1}$) | $\rho$ (kg $\cdot$ m$^{-3}$) | $\nu$ |
|------------------------|------------------------------------------|------------------------------------------|-------------------------------------------|-----------------------------|------|
| Quartz                 | 16.67                                    | 7.9                                      | 0.7                                       | 2648                        | 0.25 |
| potassium feldspar     | 3.69                                     | 2.3                                      | –                                         | 2620                        | –    |
| anorthose              | 4.17                                     | 1.63                                     | 0.75                                      | 2620                        | –    |
| biotite                | 12.13                                    | 2.02 $\pm$ 0.32                         | 0.78                                      | 3050                        | 0.31 |
| calcite                | 20.1                                     | 3.59                                     | 0.79                                      | 2710                        | 0.316|
| dolomite               | 22.8                                     | 5.51                                     | 0.93                                      | 2860                        | 0.29 |
| illite                 | 48.02                                    | 1.9                                      | –                                         | 2660                        | –    |
| pyroxene               | 21.9                                     | 4.66 $\pm$ 0.31                         | 0.69                                      | 3260                        | 0.25 |
| muscovite              | 10                                       | 2.28 $\pm$ 0.07                         | 0.76                                      | 2790                        | 0.25 |
| tcalc                  | –                                        | 6.10                                     | 0.87                                      | 2784                        | –    |
| amphibole              | 23.8                                     | 2.81                                     | –                                         | 3124                        | 0.29 |
| feldspar               | 3.69                                     | 2.3                                      | –                                         | 2620                        | 0.27 |
| silica cement          | –                                        | 7.7                                      | 0.177                                     | 2650                        | –    |
| clay cement            | –                                        | 1.8                                      | 0.2                                        | 2810                        | –    |
| calcite cement         | –                                        | 3.3                                      | 1.99                                      | 2721                        | –    |
| Dolomite cement        | –                                        | 5.3                                      | 0.204                                     | 2857                        | –    |

Short for properties: coefficient of thermal expansion $\zeta$, thermal conductivity $K$, specific heat $c$, density $\rho$ and Poisson’s ratio $\nu$.

temperature dependence of wave velocities in cubic crystals, as follows

$$\rho V_P^2 = \lambda + 2\mu + \phi_3^{pp}\alpha + \phi_4^{pp}\alpha^2.$$  

where $(\phi_3^{pp}, \phi_4^{pp})$ are the third- and fourth-order elastic constants, respectively.

### 3.3. Third-order nonlinear thermoelastic model

The total strain can be decomposed into the temperature-induced reference and the wave-induced infinitesimal component. Yang et al. (2019) define a third-order nonlinear temperature dependence model based on the fourth-order elastic constant, as follows

$$\rho V_P^2 = \lambda + 2\mu + \phi_1^{pp}\alpha + \phi_2^{pp}\alpha^2 + \phi_3^{pp}\alpha^3,$$

where $(\phi_1^{pp}, \phi_2^{pp}, \phi_3^{pp})$ is the fourth-order elastic constants obtained through the ultrasonic measurement of the best fitting and the least square calculation, the superscripts $p$ refer to P-waves.

### 3.4. Empirical S-type curve model

These theoretical models may be applicable to rocks with elastic and hyperelastic deformations under low to moderate temperatures. However, these models fail to describe inelastic deformations in microstructures subject to high temperatures. Confirmed by a large number of experiments (Yavuz et al. 2010; Yang et al. 2017), the quadratic function is widely used to describe the nonlinear temperature-dependent wave velocities in most rocks features a quadratic trend

$$V_p = a + bT + cT^2,$$

where $(a, b, c)$ are the fitting parameters. The following S-type model has been widely used to correlate P-wave velocities and temperatures.

$$V_P = \frac{V_{\text{max}}}{1 + a_1 T^{b_1}},$$

where $V_{\text{max}}$ is the maximum value of P-wave velocities, and $a_1$ and $b_1$ are the fitting parameters.

The empirical model demonstrates a more accurate prediction to experimental data than the theoretical models for general rocks (Keshavarz et al. 2010; Huang 2014; Zhang et al. 2016). However, the fitting parameters lack a correlation with the thermophysical properties of rocks. To understand the physics of the fitting parameters, we compare both the theoretical and empirical models using various rocks with different levels of heterogeneity in thermophysical properties.

### 4. Applications

In general, rocks are composed of a variety of mineral grains with cements between grains. Different mineral phases have different expansion coefficients. During the heat treatment, the differential deformation of different mineral phases and cements at the same temperature changes the internal structure of rocks (Wu & Liu 2003), apt to induce microcracks around cements at high temperatures. The mechanical properties of rocks will be changed correspondingly. Table 1 shows the thermophysical properties of minerals and cements for common rocks. In terms of whether the lithology is uniform, we select marble (homogeneity), granite (weak heterogeneity), limestone (moderate heterogeneity) and
sandstone (strong heterogeneity) as examples to compare the theoretical and empirical models.

The three-stage behavior of temperature dependence is characteristic of several obvious inflexion points. Different types of rock have inflexion points at different temperatures due to different mechanisms in physics. Generally, these inflexion points correspond to the threshold temperature of thermal damage, mineral decomposition and dewatering. We will clarify the physics of inflexion points for the selected rocks.

4.1. Application to marble as the case of homogeneity in lithology

The experimental data of marble (Liu et al. 2013) are examined with its main components shown in Table 2, including dolomite, calcite, talc and amphibole. According to the international society for rock mechanics (ISRM), the sample is normatively cut into $\Phi50 \text{ mm} \times L100 \text{ mm}$, with an average bulk density of $2.60 \text{ g cm}^{-3}$ at room temperature. Seven groups of samples (three samples per group) are then heated to seven temperatures: 25, 100, 200, 400, 600, 800 and 1000 °C, measured by a RX3-20-12 box-type resistance furnace (heating equipment). The ultrasonic testing instrument sends an ultrasonic pulse to the sample with a slow to constant heating rate $10^\circ \text{C min}^{-1}$ to measure the elastic wave velocity. The thermomechanical analysis curve shows that from 25 to 750 °C, the volume thermal-expansion (VTE) coefficient increases to $4.4 \times 10^{-5}$ (per °C) (Plevova et al. 2010).

As shown in Table 2, the marble is a near homogeneous rock with rather simple components that show little difference in thermal properties from Table 1. Figure 1 compares different prediction models to the experimental P-wave velocities against temperatures. We see that the temperature-induced velocity variation is overall gentle, which can be roughly divided into three stages. For Phase 1 ($T = 20–400^\circ \text{C}$), the P-wave velocity drops slowly because of small damages inside the rock. There is even a slight rise at about 100°C, possibly because some cracks in the rock are closed by heating. For Phase 2 ($T = 400–600^\circ \text{C}$), the P-wave velocity drops a little fast because of some damages inside the marble that gradually becomes darker in color and expands in volume (Liu et al. 2013). Therefore, the inflexion point at about 400°C corresponds to the threshold temperature of thermal damage where the resulting stress peak reaches the threshold of internal damage in the rock. Since the main minerals, such as dolomite, calcite and muscovite, are less affected by temperatures below 600°C, the change in the marble could be related to the transformation of quartz from $\alpha$ phase to $\beta$ phase at 573°C (Sun et al. 2013). The reaction of quartz phase transition at 537°C can be expressed as

$$573^\circ \text{C} \Rightarrow \beta - \text{quartz} \Rightarrow \alpha - \text{cristobalite} + 0.8\%.$$

The phase transition results in the increase of volume microcracks. Therefore, the inflexion point at about 600°C

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Table 2. Mineral composition of four rocks (%)

| Mineral component | Marble | Granite | Limestone | Sandstone |
|-------------------|--------|---------|-----------|-----------|
| Quartz            | 1      | 29      | -         | 91.2      |
| potassium feldspar| -      | 28      | -         | -         |
| anorthose         | -      | 31      | -         | -         |
| biotite           | -      | 12      | -         | -         |
| calcite           | 3      | -       | 93.1      | -         |
| dolomite          | 90     | -       | 2.4       | -         |
| illite            | -      | -       | 4.5       | -         |
| pyroxene          | -      | -       | -         | -         |
| Muscovite         | 3      | -       | -         | -         |
| talc              | 1      | -       | -         | -         |
| amphibole         | 2      | -       | -         | -         |
| feldspar          | -      | -       | 8.8       | -         |
| clay              | -      | a little| calcite and dolomite | a little |
| Cement            | -      | silica  | pyroxene and mica | |

Figure 1. Comparison of the second-order (NT2, black line) and third-order (NT3, green line) thermoelastic models and the empirical S-shape model (blue line) to the experimental P-wave velocities (squares) against temperatures for marble.
corresponds to the threshold temperature of mineral decomposition. The resulting qualitative change in constituents accelerates the drop of P-wave velocity. For Phase 3 ($T = 600–750^\circ C$), the occurrence of partial melting in the marble leads to the fast drop of P-wave velocities (Huang 2003; Zhou et al. 1999; Bai et al. 2002, 2003; Liu et al. 2004).

From 25 to 400°C, all the prediction models agree well with the experimental data. From 400 to 750°C, the third-order thermoelastic model (NT3) seems better than the second-order thermoelastic model (NT2). However, both theoretical models are inferior to the following empirical S-shape model, especially for the temperature range of Phase 3,

$$V_p = \frac{5.1886}{1 + 5.53 \times 10^{-5} T^{1.47845}}.$$  

(19)

4.2. Application to granite as the case of weak heterogeneity in lithology

As shown in Table 2, the mineral components of granite mainly include quartz, feldspar and biotite with a small amount of clay and silica cement. These samples, of which the bulk density is 2.73 g cm$^{-3}$ at room temperature, are cut into 50 × 100 mm cylinders normatively for mechanical tests. The experimental data come from Huang (2014). The heat treatment temperature has a significant influence on the coefficient of VTE, from $1.73 \times 10^{-6}$ (°C) at 60°C to $2.24 \times 10^{-5}$ (°C) at 300°C. The P-wave velocity decreases by 50.3% from 20 to 300°C.

Figure 2 compares different prediction models to the experimental P-wave velocities against temperatures. We see that the temperature-induced velocity variation presents rather nonlinearity, which can be roughly divided into three stages with two inflection points appearing at 60 and 150°C, respectively. For Phase 1 ($T = 20–60^\circ C$), we see a stop of velocity drop. Except for original cracks inside the rock, there are no new cracks occurring before 60°C in terms of granite. Chen et al. (1999) explained the stop of velocity drop by acoustic emission experiments with granite, that is, the threshold temperature for the loss of attached water appears in the range of 60–70°C.

For Phase 2 ($T = 60–150^\circ C$), the P-wave velocity behaves rather abnormally. It presents a trend of first gent rising and then slow decreasing, implying complex changes happening inside the granite. As shown in Table 1, two main minerals (feldspar and quartz) differ in the thermal-expansion coefficient by four times. The differential temperature dependence of P-wave velocities due to polymineral composition perhaps leads to the abnormal change in Phase 2. The temperature-induced change in cement is also attributed to the abnormal change in Phase 2, especially in the range of 80 to 150°C, during which the evaporation of adsorbed and interlayer waters increases the strength of cement in granite (Sun et al. 2013). According to the investigation of fracture-related damages (Li 1988), the formation of new cracks around the cement requires the rather accumulation of elastic strains. Consequently, the cementation effect cancels out part of the thermal-expansion stress, making the P-wave velocity first rise gently and then decrease slowly in this stage.

For Phase 3 ($T = 150–300^\circ C$), the P-wave velocity drops fast because of damages inside the granite that turns red in color with increasing temperatures, indicating that the crystals in the rock undergo phase transition. Therefore, the inflexion point at about 150°C corresponds to the threshold temperature of phase transition. Quartz is the most important constituent mineral of granite. The phase transition of quartz particles with volume changes (Yin 2003) aggravates the thermal fracturing and thermodynamic property of rocks.

From 20 to 300°C, all the prediction models agree roughly with the experimental data. The third-order thermoelastic model (NT3) is better than the second-order thermoelastic model (NT2) especially for Phase 3. In terms of describing velocity variations through temperature increment, however, the following empirical S-shape model seems closer to the actual experimental data than the theoretical models

$$V_p = \frac{4.92335}{1 + 9.17 \times 10^{-5} T^{1.62366}}.$$  

(20)

4.3. Application to limestone as the case of moderate heterogeneity in lithology

Experimental measurements (Li et al. 2016), with the RSSTOIC integrated digital acoustic transmitter and detector for elastic wave velocities, are conducted for the temperature gradually increasing from room temperature to 900°C at a slow and constant heating rate of 5°C min$^{-1}$. In this temperature range the coefficient of VTE increases significantly possibly because of the contribution of calcite cements from
The surface color of limestone changes not much, causing little change in microstructures observed below 200°C. Microcracks begin to develop around 300°C (Zhang et al. 2015), indicating that the chemical composition and crystal structure do not change significantly before 300°C. However, we see a rapid increase of P-wave velocities around 100°C because of the thermal-expansion effect of mineral particles before 100°C on restraining deformation and preventing crack propagation. Some primary fractures close gradually with the shrinkage of pores, which increases the strength of rocks. With increasing temperatures subsequently, the gradual loss of internal adhesion water and mineral bound water increases the porosity of rocks, which makes the P-wave velocity slightly increase at first and then decrease rapidly.

For Phase 2 ($T = 300–600^\circ C$), the surface color of limestone gradually turns to khaki, indicating that there is chemical reaction occurring inside the rock. The trace mineral magnesium carbonate begins to decompose at 520°C, measured with a differential scanning calorimeter (DSC) (Huang 1975; Qi et al. 2002), with its high-temperature decomposition reaction as

$$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2.$$  

(21)

Therefore, the inflexion point at about 300°C corresponds to the threshold temperature of mineral decomposition to induce the peak-stress drop as well as the development of microcracks. The thermodynamic difference of major minerals (dolomite and calcite) as well as the decrease of cement stiffness together deteriorate the mechanical properties of limestone, which reduces P-wave velocities rapidly.

For Phase 3 ($T = 600–900^\circ C$), the surface color of limestone turns white above 700°C, the co-rotating cracks appear at 850°C, and the surface layer exfoliates when the temperature reaches 900°C. The inflection point at about 600°C corresponds to the threshold temperature of softening from brittleness to ductility manifested by its stress–strain relation (Zhang et al. 2006). The rock experiences gradually from serious damage to complete damage. Based on the DSC curve, the dolomite [CaMg(CO$_3$)$_2$] is decomposed into MgO, CO$_2$ and CaCO$_3$ at about 750°C (Huang 1975; Kilic 2006), which, however, counteracts the effect of shear cracks developing gradually. Therefore, the resultant overall variation is rather gentle.

From 25 to 900°C, all the prediction models agree roughly with the experimental P-wave velocities. These models begin to separate at Phase 2 where the following empirical S-shape prediction is much better than the theoretical models.

$$V_P = \frac{6.995}{1 + 3.47 \times 10^{-6} T^{2.03756}}.$$  

(22)

4.4. Application to sandstone as the case of strong heterogeneity in lithology

Like limestone, the mineral composition of sandstone is rather simple as shown in Table 2, but its mineral components show different thermophysical properties. Mineral particles are cemented together by siliceous adhesives that contain amounts of pyroxene and mica. Numbers of studies demonstrate that the existence of such cements across mineral particles has a significant impact on the mechanical properties (Meng et al. 2020; Wu & Liu 2003). The pulse generator and receiving transducer are used to get experimental measurements. The details of the experiment are given by Sirdesai et al. (2018).

Figure 4 compares different prediction models to the experimental P-wave velocities against temperatures. The temperature-induced velocity drop is up to 75.5% from room temperature to 1000°C, which is characterised by a strong nonlinear feature as a typical S-shape trend. The temperature-induced velocity change can be divided into three stages with two inflection points appearing at 500 and 800°C, respectively.

For Phase 1 ($T = 25–500^\circ C$), the P-wave velocity undergoes first a gradual increase and then a rapid decrease. Through a differential thermal analyser in this temperature range, there is no phase transition of main mineral components in sandstone. As a porous rock containing clay...
For Phase 1 ($T = 25–1000^\circ C$), the P-wave velocity experiences a significant decrease after 950°C because of new chemical reactions (Shao et al. 2019). Therefore, the inflection point at about 500°C corresponds to the mineral phase transition in the rock. For example, pyroxene transforms from a monoclinic phase to a tetragonal phase at 500°C. Quartz changes from an alpha phase to a beta phase at 573°C. Sandstone is mainly composed of quartz with its volume increasing during the phase transition (Zhang 2009), resulting in the development of microcracks and decreasing the P-wave velocity rapidly.

For Phase 2 ($T = 500–800^\circ C$), the drop of wave velocities becomes slower because of the expansion and penetration of microcracks. The molten minerals of biotite include garnet, cordierite, plagioclase, monoclase, spinel and potash feldspar (Vielzeuf & Montel 1994; Patino Douce & Beard 1995, 1996). Therefore, the inflection point at about 800°C corresponds to the threshold temperature of the dewatering and melting of biotite (750–850°C). It is worth noting that the P-wave velocity again experiences a significant decrease after 950°C because of new chemical reactions (Shao et al. 2019).

From 25 to 1000°C, all the prediction models agree roughly with the experimental P-wave velocities especially for Phase 1. The following empirical S-shape prediction is much better than the theoretical models beyond 800°C.

$$V_p = \frac{4.00317}{1 + 4.64 \times 10^{-12} T^{2.58225}}.$$ (23)

### 4.5. Correlation of fitting parameters to thermophysical properties

Applications of different prediction models to various rocks demonstrate that the empirical S-shape model is obviously better for rocks with non-uniform lithology. The fitting parameters $a_1$ and $b_1$ play a decisive role in describing the nonlinear temperature dependence of P-wave velocities. The variations of $a_1$ and $b_1$ show certain correlations with the thermophysical properties of rocks.

From the fitting results for four rocks, the temperature range for the heat treatment of granite is very different from the other three rocks. Such a short range cannot embody the global shape feature of the S-shape model. To ensure comparability, we remove granite from the study of this section. Figure 5 shows the correlation of fitting parameters to thermophysical properties for three rocks (marble, limestone and sandstone). We see a strong relevance between them: $a_1$ increases with increasing thermal diffusivities whereas $b_1$ increases with increasing thermal capacities, which could be expressed as

$$a_1 \propto K,$$

$$b_1 \propto c \rho,$$ (24)

where $K$ is the thermal conductivity, $c$ is the specific heat and $\rho$ is the bulk density.

Equation (24) correlates the S-shape fitting parameters $(a_1, b_1)$ with the thermophysical properties $(K, c, \rho)$, indicating the physics of these fitting parameters. $a_1$ represents the degree of thermal diffusivities in rocks, whereas $b_1$ indicates the efficiency of heat transfer. As shown in Table 3, different rocks correspond to different values of $(a_1, b_1)$ that are characteristic of different thermophysical properties, showing that $(a_1, b_1)$ could be alternatives as effective thermophysical properties to characterise the nonlinear temperature-dependent wave elastic constants for rocks. It appears from our results that $(a_1, b_1)$ are related to both microstructures and heterogeneities in lithology. Limited samples limit our investigations on this issue.

From figures 1–4, we see that the temperature dependence of wave velocities is very complicated in the microscopic view, depending on the complexity of rocks. The physics of temperature dependence involves microcracks closure/development, thermal damage, mineral decomposition and dewatering, which occur at different temperatures, respectively, and induce local variations in wave velocities. It is obviously difficult to integrate these mechanisms, with some belonging to the inelastic regime, into one mode only.
However, from the macroscopic view, the combined effect of various temperature behaviors makes the velocity-decrease tendency with temperature a three-stage pattern over the whole temperature domain. Unlike non-physics-based S-curve simulation, two nonlinear thermoelastic models, strictly speaking, could only describe elastic nonlinearity. The physics-based simulation by the theoretical models should be regarded as non-physical for inelastic components.

### 5. Conclusions

Temperature-induced variations in elastic wave velocities for most rocks are generally characteristic of a three-stage nonlinear behavior that could be expressed by a S-shape curve with two inflexion points. We try to interpretate the three-stage velocity variations from ultrasonic measurements with four kinds of rock (marble, granite, limestone and sandstone). We briefly introduce the basic principle of three thermoelastic prediction models to describe one-order linear, two-order nonlinear and third-order nonlinear temperature dependences for the three-stage velocity variations. Comparisons of these theoretical models with the empirical S-type prediction are given for the ultrasonic measurements, which demonstrate different accuracies of prediction for temperature-induced velocity variations. We discuss the effect of different mineral phases in rocks on the prediction. We correlate prediction-model parameters and rock thermophysical properties. The main conclusions can be outlined as follows.

Rocks are not only polymineralic with different mineral phases being of different thermophysical properties, but also heterogeneous in different scales. Experimental data with marble (homogeneity), granite (weak heterogeneity), limestone (moderate heterogeneity) and sandstone (strong heterogeneity) demonstrate the three-stage nonlinear pattern in temperature-induced velocity variations. This is strongly associated with the differential thermal expansion of different mineral phases, the temperature-induced change in microstructures, the loss of internal adhesion water and the decomposition and transition of mineral phases. In particular, different mineral phases produce differential thermal stresses due to uncoordinated deformations.

Traditional one-order linear thermoelasticity has been widely used for crystals with the Taylor expansion of strain energy functions, but suffers from a deficiency in describing thermal-associated velocity changes in rocks. Current second-order and third-order nonlinear thermoelastic models, formulated by effective fourth-order elastic constants, can
improve the description of temperature-induced three-stage velocity variations in rocks, but involve some divergences around two inflexion points, especially at high temperatures. These theoretical models do not account for temperature-induced nonelastic deformations such as the closure and development of microcracks, the loss of internal adhesion water and the decomposition and transformation of mineral phases. The S-shape model with fitting parameters \((a_1, b_1)\) for empirical simulations demonstrates a more accurate depiction of thermal-associated three-stage variations, but with elusive fitting parameters.

Different rocks correspond to different values of \((a_1, b_1)\) that are characteristic of different thermophysical properties. Correlation of fitting parameters to thermophysical properties demonstrates that \(a_1\) and \(b_1\) are correlated linearly with thermal diffusivities and thermal capacities, respectively, indicating that \((a_1, b_1)\) could be an alternative as effective thermophysical properties to characterise the nonlinear temperature dependence of wave velocities in rocks. From our results, \((a_1, b_1)\) seem to be related to both microstructures and heterogeneities in lithology, but we need more samples for investigations in the future.

Acknowledgements

The research is supported by the National Natural Science Foundation of China (grant nos. 41821002 and 41720104006) and 111 Project ‘Deep-Superdeep Oil & Gas Geophysical Exploration’ (grant no. B18055).

Conflict of interest statement

The authors declare that they have no conflict of interest.

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