

4. Equation of State

7. Mie-Grüneisen-Debye equation of state

7.1 Concept of Mie-Grüneisen-Debye equation of state

In this chapter, we introduce Mie-Grüneisen-Debye equation of state, which is the thermal equation of state the most frequently used. This is constructed along the “CH path” (Fig.1), where the volume first decreases at constant temperature (compression stage), and then the temperature increases at constant volume (heating stage). In the heating stage, pressure is also increased, and its change (thermal pressure) is described as follows by using Mie-Grüneisen equation of state:

$$\Delta P_{th} = \gamma_{th} \left(\frac{\Delta E_{th}}{V} \right) \quad (4.7.1)$$

where ΔP_{th} is the increase of thermal pressure, γ_{th} is thermodynamic Grüneisen parameter, ΔE_{th} is the increase of internal energy, and V is the constant volume. Note that E_{th} is calculated from the isochoric heat capacity C_V by Debye approximation described as follows:

$$C_V = 9Nk_B \left(\frac{\Theta_D}{T} \right)^{-3} \int_0^{\Theta_D/T} \frac{x^4 \exp x}{(\exp x - 1)^2} dx \quad (4.7.2)$$

where k_B is Boltzmann constant, and Θ_D is the the Debye temperature. Readers should refer to the previous chapter (S3.7) for the detailed explanations for (4.7.2), or the Debye model.

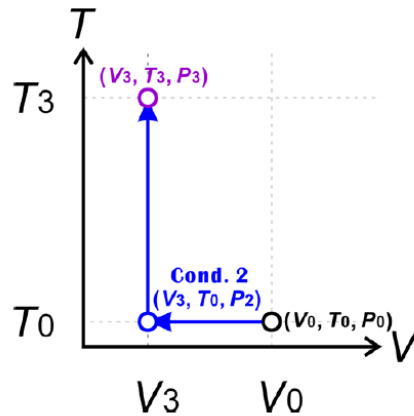


Fig.1 “CH path” considered in the construction of Mie-Grüneisen-Debye equation of state. The body is first compressed along the isothermal path at T_0 and next heated along the isochoric path at V_3 . Note that thermal pressure is loaded to a body expressed by Mie-Grüneisen equation of state during the heating.

Mie-Grüneisen-Debye equation of state is expressed by the following form:

$$P = - \frac{dE_0}{dV} + \gamma_D \frac{E_D}{V} \quad (4.7.3)$$

where E_0 is the internal energy at zero temperature, E_D is the internal energy at high temperature in Debye approximation, and γ_D is the Debye-Grüneisen parameter. The definition of γ_D is described as follows by using the Debye temperature Θ_D :

$$\gamma_D \equiv - \frac{d \ln \Theta_D}{d \ln V} \quad (4.7.4)$$

Note that this new type of “Grüneisen parameter” introduced here is found that be identical to the thermodynamic Grüneisen parameter as discussed later.

7.2 Derivation of Mie-Grüneisen-Debye equation of state

Let us derive Mie-Grüneisen-Debye equation of state. To start the derivation, we defined the pressure P by the [partial derivative](#) of [Helmholtz free energy](#) F with respect to volume V at constant temperature T .

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (4.7.5)$$

Helmholtz free energy F can be divided into zero temperature part F_0 , and [lattice vibration](#) part F_D approximated by the Debye model. Namely,

$$F \cong F_0 + F_D \quad (4.7.6)$$

Considering the definition of F : $F \equiv E - TS$, F_0 can be expressed by the internal energy at zero temperature E_0 . Therefore, (4.7.6) is also written by,

$$F = E_0 + F_D \quad (4.7.6')$$

By substituting (4.7.6') into (4.7.5), P can be described as the following form composing two terms.

$$P = - \left(\frac{\partial (E_0 + F_D)}{\partial V} \right)_T = - \frac{dE_0}{dV} - \left(\frac{\partial F_D}{\partial V} \right)_T \quad (4.7.7)$$

The first term means the zero-temperature pressure, and we can obtain it by isothermal compression at low temperature. On the other hand, the second term which is thermal pressure at high temperature is not measurable, so we need to transform the derivative mathematically to get its value.

$$- \left(\frac{\partial F_D}{\partial V} \right)_T = - \frac{dF_D}{d\theta_D} \frac{d\theta_D}{dV} = \frac{dF_D}{d\theta_D} \frac{\theta_D}{V} \left(- \frac{d\theta_D/\theta_D}{dV/V} \right) = \frac{dF_D}{d\theta_D} \frac{\theta_D}{V} \left(- \frac{d \ln \theta_D}{d \ln V} \right) \quad (4.7.8)$$

Using (4.7.4), the second term of (4.7.7) is equal to the following value.

$$- \left(\frac{\partial F_D}{\partial V} \right)_T = \frac{\gamma_D \theta_D}{V} \frac{dF_D}{d\theta_D} \quad (4.7.9)$$

This means that we need to obtain F_D as a function of θ_D to get the original term. For the preparation for its derivation, we consider the definition of Helmholtz free energy F_D and transform it by using the thermodynamic relation between F_D and the [entropy](#) S .

$$F_D = E_D - TS_D = E_D + T \left(\frac{\partial F_D}{\partial T} \right)_V \quad (4.7.10)$$

In this way, we can derive the relation F_D and internal energy E_D .

$$E_D = F_D - T \left(\frac{\partial F_D}{\partial T} \right)_V = \left(\frac{\partial (F_D/T)}{\partial (1/T)} \right)_V \quad (4.7.11)$$

The transformation from the second to the third side of (4.7.11) is based on the following mathematical operation.

$$\begin{aligned} \left(\frac{\partial \left(\frac{F_D}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_V &= \left(\frac{\partial}{\partial T} \left(\frac{F_D}{T} \right) \right)_V \left(\frac{\partial T}{\partial \left(\frac{1}{T} \right)} \right)_V = (-T^2) \left[\frac{1}{T} \left(\frac{\partial F_D}{\partial T} \right)_V - \frac{F_D}{T^2} \right] \\ &\therefore \left(\frac{\partial \left(\frac{F_D}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_V = F_D - T \left(\frac{\partial F_D}{\partial T} \right)_V \end{aligned} \quad (4.7.12)$$

The internal energy and the entropy of the lattice vibration are in Debye model as follows:

$$E_D = \int_0^T C_V^{\text{Debye}} dT \quad (4.7.13)$$

$$S_D = \int_0^T \frac{C_V^{\text{Debye}}}{T} dT \quad (4.7.14)$$

From (4.7.2), these values are expressed as functions of Θ_D/T in Debye model. Therefore, these are roughly approximated by thermodynamic relations and appropriate functions g and h , respectively.

$$E_D \sim C_V \cdot T \sim T \cdot g\left(\frac{\Theta_D}{T}\right) \quad (4.7.15)$$

$$S_D \sim \frac{C_V}{T} T \sim h\left(\frac{\Theta_D}{T}\right) \quad (4.7.16)$$

By using these relations, (4.7.10) is simplified as follows using a proper function η :

$$F_D = E_D - TS_D = T\eta\left(\frac{\Theta_D}{T}\right) \quad (4.7.17)$$

Then, we substitute (4.7.17) into (4.7.11) and obtain E_D as a function of Θ_D/T .

$$E_D = \left(\frac{\partial(F_D/T)}{\partial(1/T)}\right)_V = \Theta_D \frac{d\eta\left(\frac{\Theta_D}{T}\right)}{d\left(\frac{\Theta_D}{T}\right)} \quad (4.7.18)$$

The derivative of F_D with respect to Θ_D can be described as the following form after some mathematical transformation.

$$\frac{dF_D}{d\Theta_D} = \frac{dF_D}{d\left(\frac{\Theta_D}{T}\right)} \cdot \frac{d\left(\frac{\Theta_D}{T}\right)}{d\Theta_D} = \frac{dF_D}{d\left(\frac{\Theta_D}{T}\right)} \cdot \frac{1}{T} = \frac{d\left(T\eta\left(\frac{\Theta_D}{T}\right)\right)}{d\left(\frac{\Theta_D}{T}\right)} \cdot \frac{1}{T} = \frac{d\eta\left(\frac{\Theta_D}{T}\right)}{d\left(\frac{\Theta_D}{T}\right)} \quad (4.7.19)$$

Then, (4.7.18) provides the derivative.

$$\frac{dF_D}{d\Theta_D} = \frac{E_D}{\Theta_D} \quad (4.7.20)$$

We can finally obtain the derivative of F_D with respect to T by using (4.7.9) and (4.7.20).

$$-\left(\frac{\partial F_D}{\partial V}\right)_T = \frac{\gamma_D \Theta_D}{V} \frac{dF_D}{d\Theta_D} = \frac{\gamma_D \Theta_D}{V} \frac{E_D}{\Theta_D} = \gamma_D \frac{E_D}{V} \quad (4.7.21)$$

Therefore, Mie-Grüneisen-Debye equation of state is produced in the following form.

$$P = -\left(\frac{\partial(E_0 + F_D)}{\partial V}\right)_T = -\frac{dE_0}{dV} + \gamma_D \frac{E_D}{V} \quad (4.7.22)$$

The first term is usually reckoned with third-order [Birch-Murnaghan](#) or [Vinet equation of state](#) explained in the previous chapters.

7.3 Equivalency of thermodynamic and Debye Grüneisen parameters

Debye-Grüneisen parameter which we newly introduced in the previous part is equivalent to thermodynamic Grüneisen parameter. Now, we consider the partial derivative of thermal pressure with respect to T at constant V using Mie-Grüneisen-Debye equation of state to reveal the equivalency.

$$\left(\frac{\partial P}{\partial T}\right)_V \cong \left(\frac{\partial}{\partial T}\left(-\frac{dE_0}{dV} + \gamma_D \frac{E_D}{V}\right)\right)_V \cong \frac{\gamma_D}{V} \left(\frac{\partial E_D}{\partial T}\right)_V = \frac{\gamma_D}{V} C_V \quad (4.7.23)$$

Note that we assume here γ_D and V are constant to T . On the other hand, thermal pressure is also expressed by the [thermal expansion](#) α and the [bulk modulus](#) K_T as following.

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T \quad (4.7.24)$$

Therefore, we obtain the following relation from (4.7.23) and (4.7.24) showing Debye-Grüneisen parameters is identical to thermal Grüneisen parameter γ_{th} .

$$\gamma_D = \frac{V}{C_V} \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha K_T V}{C_V} = \gamma_{th} \quad (4.7.25)$$

7.4 Volume dependence of Grüneisen parameter

Thermal pressure has dependences on the [confining pressure](#) (or volume), and we need to correct its effects. Fig.4 (see section 4.7.5) shows the confining-pressure dependence of integrated thermal pressure of MgSiO₃ [bridgmanite](#) from 300 K in isothermal conditions from 500 K to 1900 K. This diagram indicates that thermal pressure decreases with the confining pressure increase, or compression. In other words, we need to consider the pressure (or volume) dependence of Grüneisen parameter γ and correct it, especially in high pressure. The dependence is usually expressed using the V exponent

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0}\right)^q \quad (4.7.26)$$

or, equivalently, q value

$$q \equiv \frac{d \ln \gamma}{d \ln V} \quad (4.7.27)$$

where γ_0 and V_0 are Grüneisen parameter and volume at zero pressure (or no compression), respectively. This value is also described by the Debye temperature by combining (4.7.4) and (4.7.27).

$$\frac{\gamma}{q} = -\frac{d \ln \Theta_D}{d \ln V} / \frac{d \ln \gamma}{d \ln V} = -\frac{d \ln \Theta_D}{d \ln \gamma} = -\frac{d \ln \Theta_D}{d \gamma / \gamma} = -\gamma \frac{d \ln \Theta_D}{d \gamma} \quad (4.7.28)$$

Namely, we obtain:

$$\frac{d \ln \Theta_D}{d \gamma} = -\frac{1}{q} \quad (4.7.29)$$

By integrating (4.7.29), the Debye temperature is expressed by γ and q as the following relation:

$$\ln \Theta_D(V) - \ln \Theta_{D,0} = -\frac{1}{q} (\gamma(V) - \gamma_0) = \frac{\gamma_0 - \gamma(V)}{q} \quad (4.7.30)$$

or exponential expression:

$$\Theta_D(V) = \Theta_{D,0} \exp \left[\frac{\gamma_0 - \gamma(V)}{q} \right] \quad (4.7.31)$$

where $\Theta_D(V)$ and $\gamma(V)$ are the Debye temperature and Grüneisen parameter under compression, and $\Theta_{D,0}$ and γ_0 are under no compression, respectively. In practical processes, we make plots of these parameters v.s. compressional volume change to obtain the initial parameters which are the [intercepts](#) of plots at no compressional condition, and we can calibrate the dependence for the equation of states.

7.5 Examples of geoscientific application of Mie-Grüneisen-Debye equation of state

Let us show some geoscientific examples of Mie-Grüneisen-Debye equation of state in this section. The reference material of examples is MgSiO₃ [bridgmanite](#). Fig.2 shows pressure changes with respect

to the compressional volume change at various temperature conditions and the parameters determined from the relation.

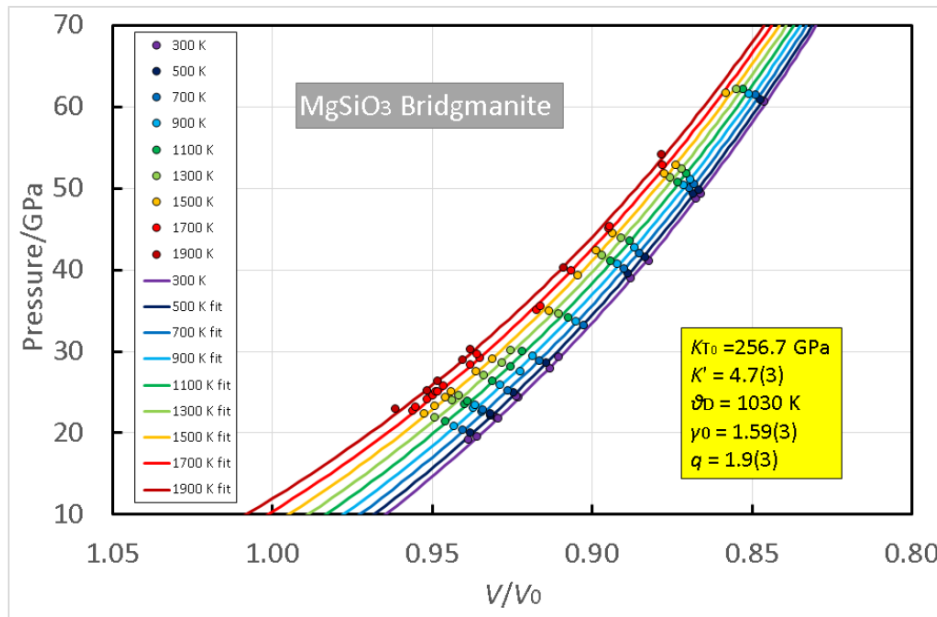


Fig.2 P - V - T relations of MgSiO_3 bridgmanite in Mie-Grüneisen-Debye equation of state. Dots show the experimental data and lines are their fitting curves. The parameters of the EoS are also provided as shown in the figure.

From these data, changes of the Grüneisen parameter and the Debye temperature to compression are estimated in Fig.3. The Grüneisen parameter has a negative slope to compression while the Debye temperature has a positive as expected from (4.7.26) and (4.7.31). We can also obtain the initial parameters $\Theta_{D,0}$ and γ_0 from the intercept of the curve at $V/V_0 = 1.0$, where no compression was loaded on the body, here, $\Theta_{D,0} = 1030$ K and $\gamma_0 = 1.59$, respectively, and q is estimated at 1.9 as well.

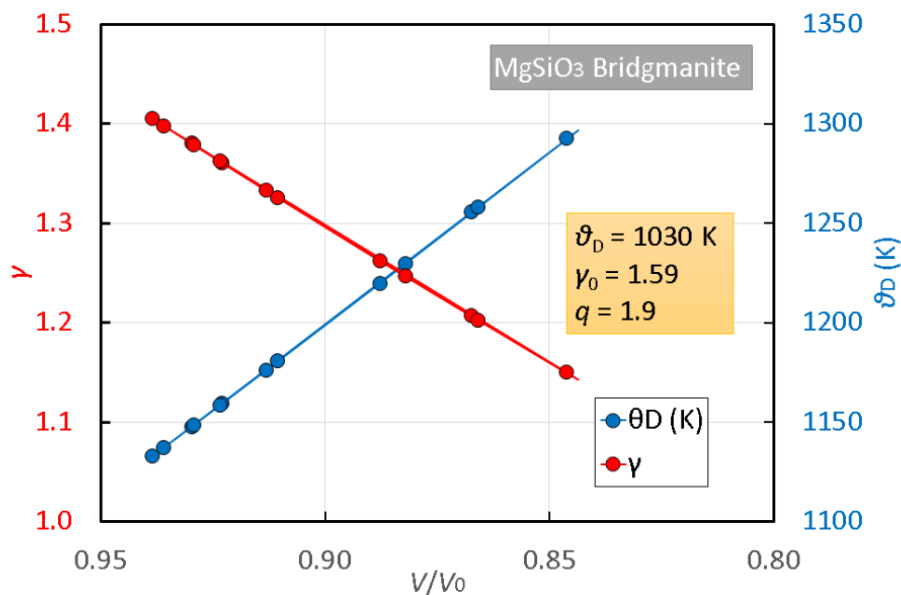


Fig.3 The changes of the Grüneisen parameter and the Debye temperature to compressional volume change. Grüneisen parameter gets smaller as the body is compressed while the Debye temperature

becomes larger. The initial parameters are also obtained from this plot referring to the values at no compression and q value is estimated from these values.

Fig.4 shows integrated thermal pressure change from 300 K to some temperature conditions with respect to the confining pressure computed by the following:

$$\Delta P_{th} = \int_{300}^T \frac{\gamma}{V} C_V^{Debye} dT \quad (4.7.32)$$

This again indicates thermal pressure decreases as the pressure increases. Note that thermal pressure is much smaller than confining pressure even in the [mantle](#) temperature.

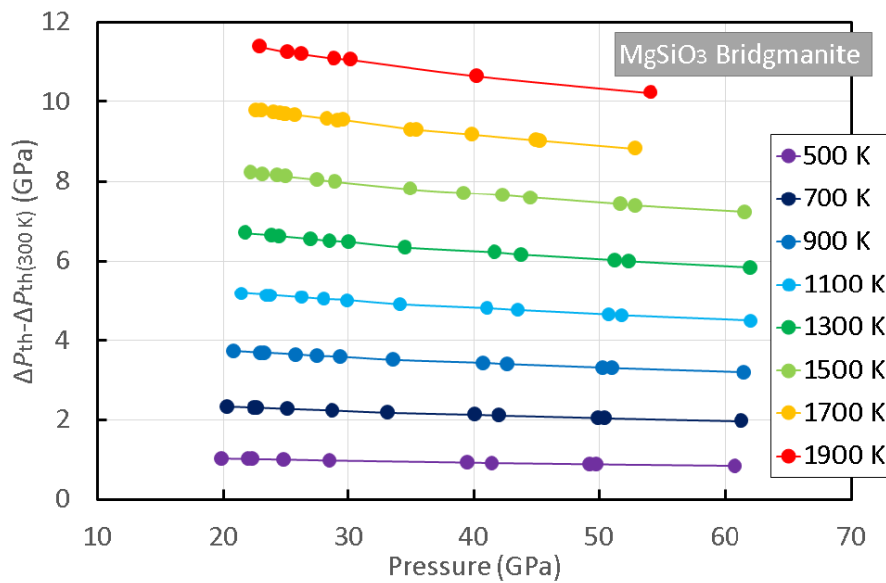


Fig.4 Integrated thermal pressure change from 300 K to some temperature conditions to the confining pressure. This shows thermal pressure decreases as the pressure increases. It is important thermal pressure is much smaller than confining pressure even in high temperatures.