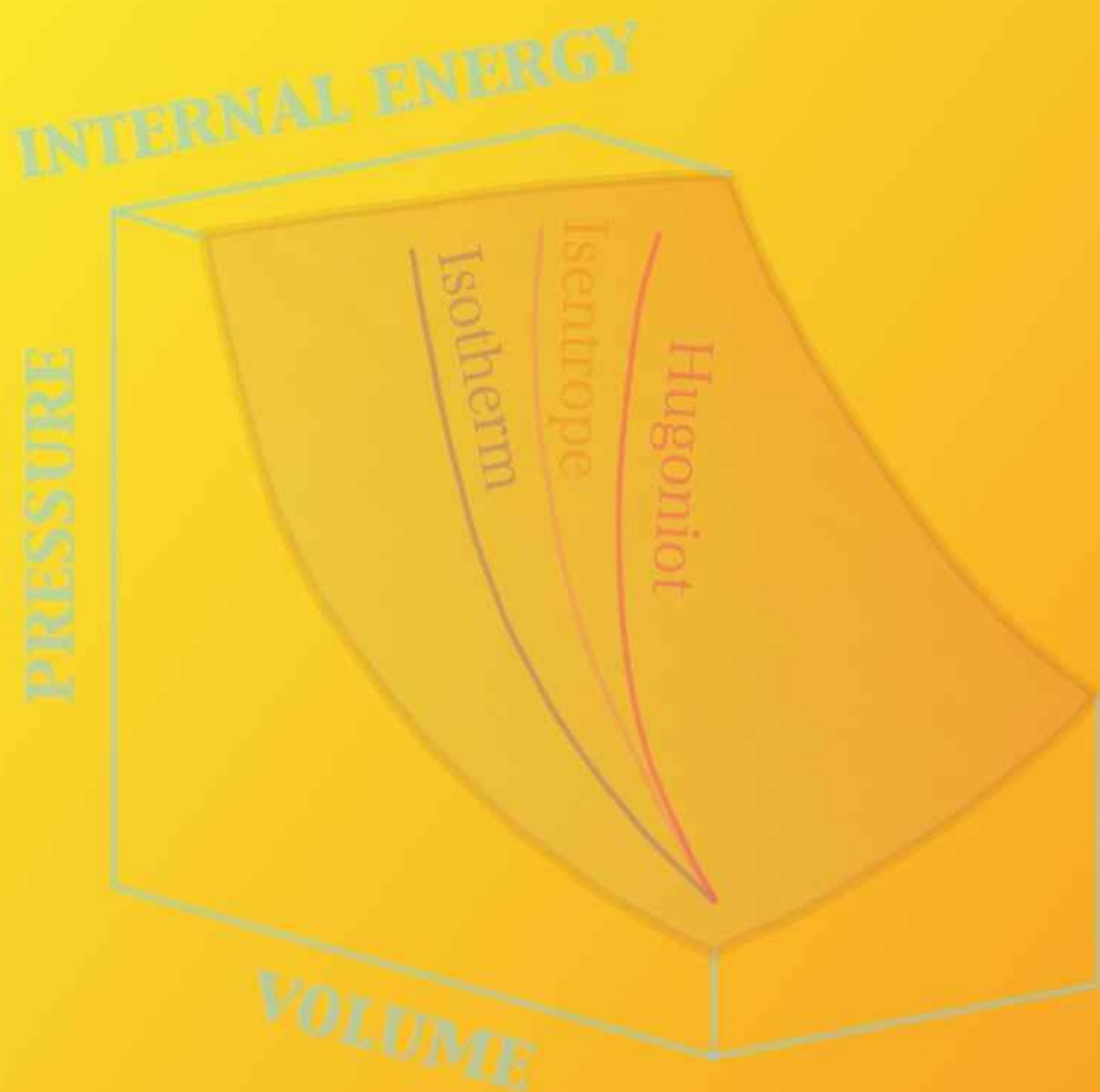


**AN INTRODUCTION TO THE
GRÜNEISEN EQUATION OF STATE
AND
SHOCK THERMODYNAMICS**



KUNIHITO NAGAYAMA

Introduction to the Grüneisen Equation of State and Shock Thermodynamics

Kunihito Nagayama

First Kindle Edition, November 2011

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Dedication

To my family.

Author's acknowledgment

Thank you for Prof. Tsutomu Mashimo for his encouragements during the course of this study and writing this book. He also wishes to thank Dr. Yasuhito Mori and Dr. Shiro Kubota for their useful discussions on several of the topics.

Preface

This is a monograph on the Grüneisen equation of state basically used for condensed substance at high pressures and temperatures. The Grüneisen type equation of state, in a wide sense, has been used for a long time in high-pressure physics or in shock wave physics and detonation physics especially for condensed media. This book covers most of the works of the author on this EOS and its application to several dynamic problems including shock wave propagation.

Thermodynamic definition of the Grüneisen parameter is a non-dimensional parameter characteristic of an aspect of materials mechanical degrees of freedom. This fact indicates that no self-similarity holds for the EOS. Thermodynamic formulation of the equation of state provides a strong constraint on the interrelationship between the Grüneisen parameter and the specific heat at constant volume.

New thermal variables have been derived to describe the compressed state of condensed substance attained by the application of high pressure. Thermodynamic formulation based on new variables has been developed for idealized Debye solids, anharmonic solids, and three-term EOS for solids at extremely high pressures and temperatures. Possibility of the law of corresponding states concerning a new thermal variable has been pursued.

A numerical procedure is proposed to estimate the volume dependence of the Grüneisen parameter based on three theoretical models. Numerical examples are presented to discuss the results on the Grüneisen parameter and cold potential energy function by comparing them with DAC data and/or theoretical calculations. All the above treatments rely on the shock wave data, and precise shock wave physics discussion has been described in this book.

Shock wave compression provides appreciable irreversible heating as well as appreciable volume compression. Importance of shock wave data is due to the fact that shock Hugoniot compression curve is a most reliable succession of high-pressure states on the state surface of the substance.

Detailed discussions on the shock compression, shock Hugoniot, irreversible heating together with the estimation of shock Hugoniot states based on the Grüneisen equation of state have been made. As one of the important applications of the Grüneisen type equation of state, detonation of condensed high explosives is described. And finally, some of the flow problems including shock wave propagation have been described.

This book totally ignores the following important topics such as high-pressure polymorphic transformation and elastic-plastic transition. They are interesting topics in shock wave science and readers can find excellent books or reviews on these subjects. The reason why these are omitted is simply because the author has no appreciable contributions to this area. In this sense, we stick to hydrostatic pressure in the realm of equilibrium thermodynamics where the equation of state is defined.

Fukuoka, Japan

Kunihito Nagayama

October 5, 2011

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Chapter 1 Introduction

1.1. Equation of State and Thermodynamics

We will start with the discussion of thermodynamics. One of the fundamental equations for specific internal energy can be written as

$$d\varepsilon = TdS - pdv, \quad (1.1)$$

where ε , p , v , T and S denote the specific internal energy, the pressure, the specific volume, the temperature and the specific entropy, respectively. This can be regarded as various meanings. One of them is such that specific entropy and specific volume are the particular choice of independent variable for the specific internal energy. Furthermore, as noted in the textbooks of thermodynamics, the first term of rhs of Eq.(1.1) corresponds to the heat added to the system, while the second term to the mechanical work made to the system. This simple explanation means that pressure and specific volume are regarded as mechanical state variables and they are conjugate with each other. Temperature and entropy can also belong to the group of thermal variables and be conjugate. As one of physical explanations of Eq.(1.1), thermodynamic potential function can be expressed by two terms, thermal degree of freedom and mechanical degree of freedom.

We can consider an equation of state in terms only of mechanical state variables as

$$f(p, v, \varepsilon) = 0. \quad (1.2)$$

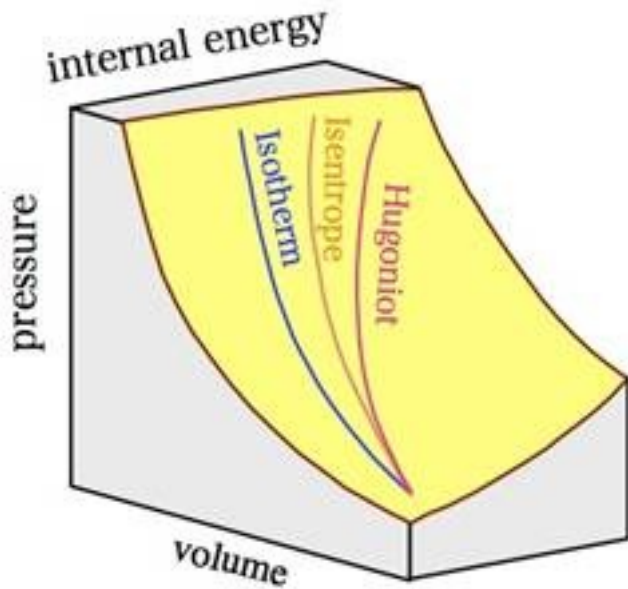


Fig. 1.1 Equation of state surface in terms of p , v , and ε .

By giving an equation of state only in terms of mechanical variables, Eq.(1.2) apparently is not a complete self-closed equation of state. We need further equation of state to describe full thermodynamic properties of materials. We will discuss this topic in a later section. Grüneisen equation of state belongs to this type of equation of state as shown schematically in Fig. 1.1. (Brush 1967, Zharkov and Kalinin 1971, Eliezer, Ghatak and Hora 1986, Zel'dovich and Raizer 1966, Godwal 1982, Bethe 1942) This choice of variables has the advantage in that mechanical behavior of materials can be described by those EOS including deformation and/or flow behavior. This discussion will be made again in the sections of shock waves. (Bethe 1942, McQueen et al 1970, Nagayama 2001, Nagayama 1992)

If so, every property associated with material flow can be expressed by this type of equation of state. For example, sound velocity as a fundamental quantity of the isentropic flow can be written as

$$\begin{aligned}
a^2 &= \left(\frac{\partial p}{\partial \rho} \right)_s = -v^2 \left(\frac{\partial p}{\partial v} \right)_s = -v^2 \left[\left(\frac{\partial p}{\partial v} \right)_\epsilon + p \left(\frac{\partial p}{\partial \epsilon} \right)_v \right] \\
&= -v^2 \left(\frac{\partial p}{\partial \epsilon} \right)_v \left[\left(\frac{\partial p}{\partial v} \right)_\epsilon \left(\frac{\partial \epsilon}{\partial p} \right)_v + p \right] \\
&= -v^2 \left(\frac{\partial p}{\partial \epsilon} \right)_v \left[p - \left(\frac{\partial \epsilon}{\partial v} \right)_p \right]
\end{aligned} \tag{1.3}$$

As shown in Eq.(1.3), rhs expressions contain terms which can be evaluated by using the equation of state of the form, Eq.(1.2).

1.2. Simple Representation of Compressed States

In order to obtain intuitive grasp of the EOS surface of crystalline solids, we will consider extremely simplified model for the compression of lattice. Crystalline lattice is considered to be a network of mass points combined by a potential function so-called lattice potential. This potential stems originally from the repulsive potential and attractive potential between atoms and/or molecules.

Qualitative representation of the atomic potential is illustrated in Fig.1.2. An atom in between two atoms feel two potentials from the adjacent two atoms, and eventually the superposed potential has a deep valley, the bottom of which corresponds to the mechanically equilibrium position with no force from atoms. This superposed potential is an oversimplified representation of periodic lattice potential.

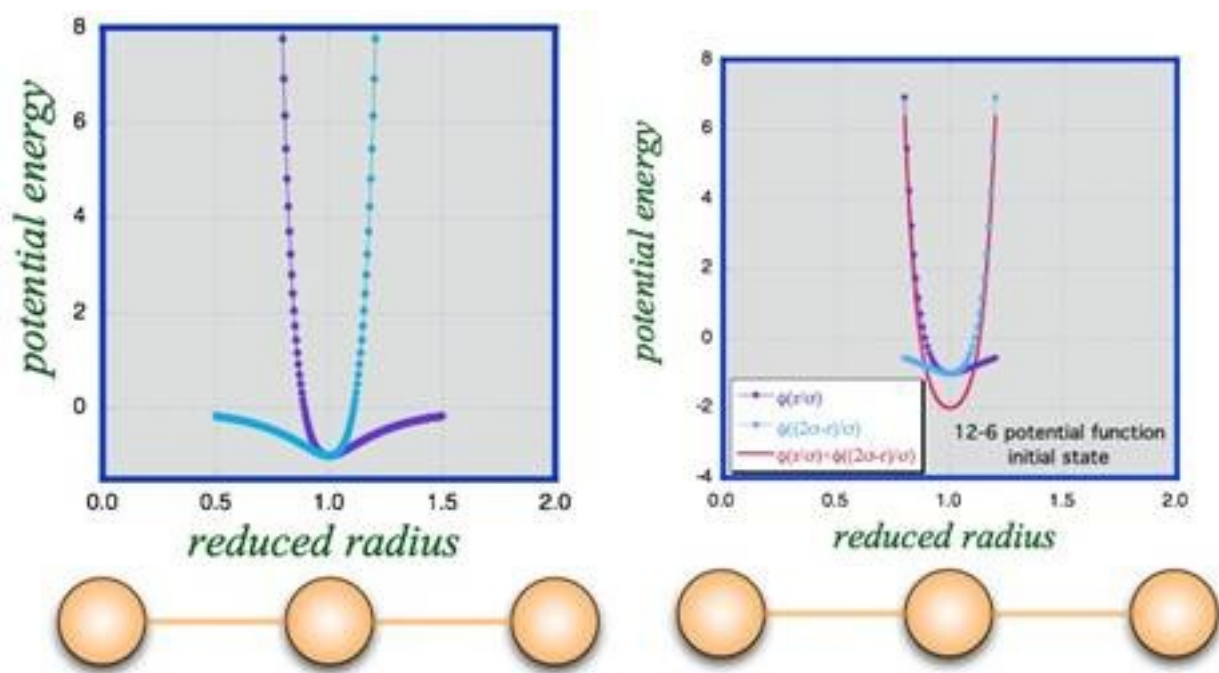


Fig. 1.2 Lennard-Jones atomic potential function of an atom in the middle of two adjacent atoms and their superposed potential form (red line).

If the crystalline solid is compressed hydrostatically, distance between atoms decreases. Figure 1.3 shows the change in the superposed potential function from the original form to the deformed one, as one intentionally squeezes distance 0.9 times that of original one. Apparently, potential well still exists and the bottom position shifts to 0.9. One may see two distinctive changes in the potential; that is, (i) potential value at the bottom increases by compression, and (ii) potential becomes to have a sharper valley.

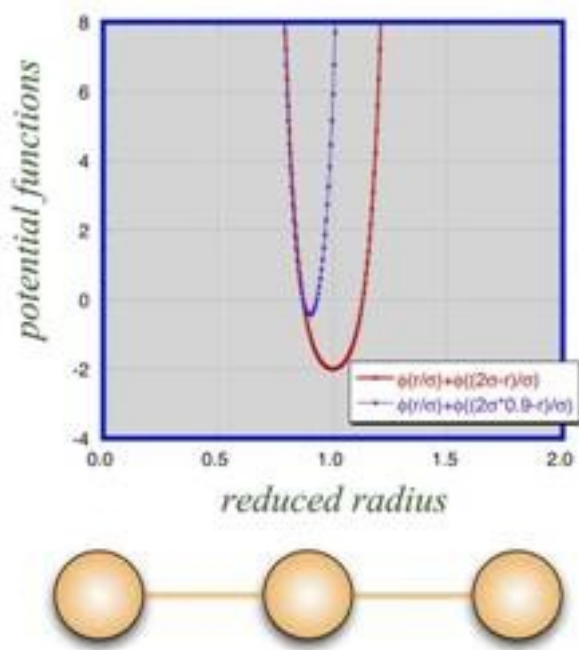


Fig. 1.3 Change in the potential function of an atom by the compressive displacement of adjacent atoms to the position, 0.9 times that of original equilibrium position.

These changes can be interpreted in physical terms as

- (1) Compression makes energy of crystalline solids increase, and this is interpreted as the increase in the internal energy of solids by compression,
- (2) Internal energy increase by compression will take place even at zero temperature, and should be a function of volume only.
- (3) Sharper form of the potential function under compression indicates the increase in elastic modulus by compression.
- (4) Increase in elastic modulus leads to the increase in eigen frequency of lattice vibration, i.e., eigen frequency increases by compression.

Conclusions obtained by the present model are seen to be valid at least qualitatively in later sections. Internal energy of solids under compression must be an isotherm or an isentrope at zero Kelvin. The form of this cold energy should have close connection with the change in eigen frequency of lattice vibration.

1.3. Definition of Grüneisen parameter

Grüneisen parameter is defined in thermodynamics terms as a material parameter with no dimension as

$$\gamma = v \left(\frac{\partial p}{\partial \varepsilon} \right)_v, \tag{1.4}$$

where we will define the fundamental thermodynamic state variables, p, v, ε as the pressure, the specific volume, and the specific internal energy of a condensed substance. Since the parameter has no dimension, and can be defined in any thermodynamics state of materials, it should be a state parameter with some physical meaning describing an aspect of condensed matter. As will be explained later, this definition is usually called ‘Grüneisen law’ and not used as a definition. It is stressed here that we use this the thermodynamic definition of the Grüneisen parameter, since it always is regarded as one of material parameters in terms of mechanical thermodynamic state variables.

It can also be described by some of other thermodynamic quantities as

$$\begin{aligned} \gamma &= v \left(\frac{\partial p}{\partial \varepsilon} \right)_v = v \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial \varepsilon} \right)_v = - \frac{v}{C_v} \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p \\ &= - \frac{v^2}{C_v} \left(\frac{\partial p}{\partial v} \right)_T \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{v \kappa_T \beta}{C_v} = \frac{v \kappa_S \beta}{C_p} \end{aligned} \tag{1.5}$$

where C_v, κ_T, κ_S and β denote the specific heat at constant volume, the isothermal bulk modulus, the isentropic bulk modulus and the thermal expansion coefficient, respectively. Suffices, T and S denote the entropy and temperature, respectively. Final expression of Eq.(1.5) contains several thermodynamic quantities, which can be measured experimentally. Figure 1.4 shows the periodicity of the Grüneisen parameter evaluated by the thermodynamic measurements using Eq.(1.5). One may refer to Tables in Appendix for various parameters of elements.

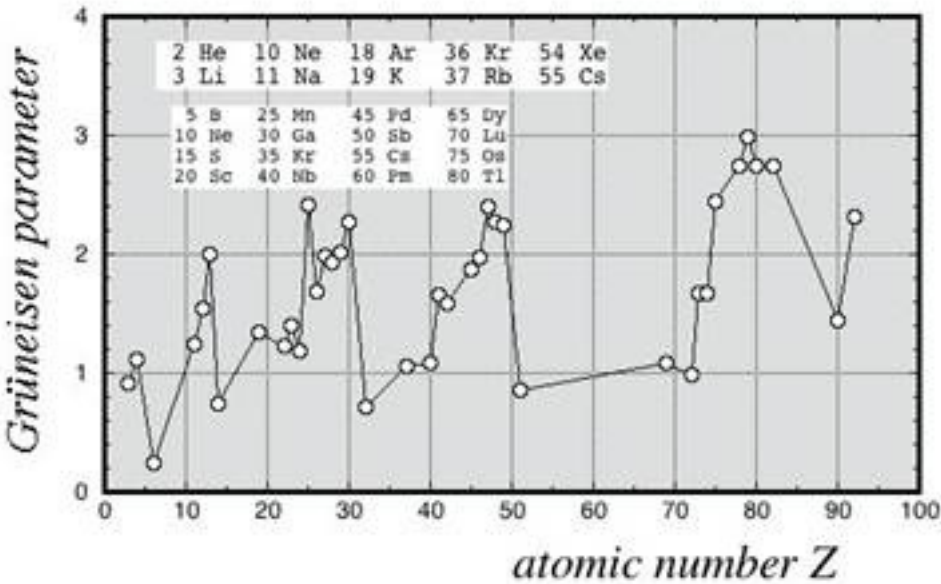


Fig. 1.4 Periodicity of the Grüneisen parameter γ as a function of the atomic number. The values are estimated at the atmospheric pressure condition.

Crystalline solids have their inherent frequencies due to the lattice vibration. Statistical mechanics of solid materials have revealed that we can define another non-dimensional parameter γ_j as a microscopic counterpart of the thermodynamically defined Grüneisen parameter, which is

$$\gamma_j = - \left(\frac{d \ln \omega_j}{d \ln v} \right), \quad (1.6)$$

where ω_j shows the j-th mode of eigen frequency of lattice vibration. This is sometimes called mode Grüneisen parameter and is introduced later in chapter 2 in the treatise of the lattice vibration based on statistical mechanics. Simple assumption on the behavior of microscopic Grüneisen parameter leads to the thermodynamic definition of the Grüneisen parameter.

In this book, however, thermodynamic definition, Eq.(1.4) is adopted as the most preferable definition of the Grüneisen parameter due to the following reasons. That is,

(i) The value given by Eq.(1.4) can be defined in every state of every substance including anharmonic and extreme conditions where EOS may become complicated, so that Eq.(1.4) is most flexible as the definition of a material parameter.

(ii) The definition may contain the definition given by Eq.(2.6) in chapter 2, i.e. $\gamma = \gamma(v)$ widely used assumption.

(iii) Microscopic definition, Eq.(1.6) also converges to Eq.(1.4) or Eq.(2.6) under a simple assumption as shown later.

1.4. Physical Models for Grüneisen parameter and Cold Potential Function

As schematically shown in Section 1.2, potential energy or internal energy at zero Kelvin increases by compression, and changes its form. At temperatures higher than zero temperature, lattice vibration will take place at various frequencies according to the form of the lattice potential function. This means that compression gives the extent of the change in lattice potential, and thereby determines modes of lattice vibration. In other words, volume determines cold internal energy of solids, and determines modes of lattice vibration, and eventually the Grüneisen parameter given by Eq.(1.4).

It is therefore natural that the Grüneisen parameter should be determined by the form of cold potential energy function. Based on the microscopic assumptions, three independent theoretical models have been proposed so far, which make the Grüneisen parameter related to the cold pressure. They are Slater model (Slater 1939, Gilverry 1956b), Dugdale-MacDonald model (Dugdale and MacDonald 1953) and Vaschenko-Zubarev model (Vaschenko and Zubarev 1963). These three models have been conveniently represented as the following single equation

$$\gamma(v) = \frac{t-2}{3} - \frac{v}{2} \frac{\frac{d^2}{dv^2} \left[p_c v^{\frac{2}{3}t} \right]}{\frac{d}{dv} \left[p_c v^{\frac{2}{3}t} \right]} \quad (1.7)$$

by using a parameter t being 0, 1, 2 for three models in the cited order. Various examinations of these models with the experimental estimation of the Grüneisen parameter of many solids suggests that none of these models have proved to have better explanation to the real behavior of gamma than the other models. (Nagayama and Mori, 1994) Furthermore, these models have no significant difference in the high-pressure behavior of gamma at very high pressures. Migault and Romain et al suggested parameter t appeared in Eq. (1.7) may be a material parameter having continuous values. (Migault 1971, Migault 1972, Migault and Romain, 1977, Romain, Migault, and Jacquesson, 1976)

Further efforts of estimating the Grüneisen parameter have been made by various authors. (Parciauskas 1975, Segletes and Walters 1998, Bodryakov and Povzner 2003, Burakovsly and Preston 2004, Shanker et al 2007) Some of these as well as efforts of obtaining equation of state for solids will be given briefly also in Chapter 2.

Chapter 2 Grüneisen Equation of State

2.1. Grüneisen law and Grüneisen Equation of State

2.1.1. Scope of the law

Definition of the Grüneisen parameter in Eq.(1.4) shows that the Grüneisen parameter is regarded as a thermodynamic state variable as a function of specific volume and specific internal energy. To discuss the dependence of the Grüneisen parameter on these variables, we will start with the following thermodynamic identity

$$\frac{dT}{T} = -\left(\frac{\partial p}{\partial \varepsilon}\right)_v dv + \frac{1}{C_v} dS = -\frac{\gamma}{v} dv + \frac{1}{C_v} dS \quad (2.1)$$

showing that temperature change is expressed as the change in specific volume and that of entropy. Maxwell's relation pertaining this equation is written as

$$\frac{1}{v} \left(\frac{\partial \gamma(v, S)}{\partial S} \right)_v = \frac{1}{C_v^2} \left(\frac{\partial C_v(v, S)}{\partial v} \right)_S. \quad (2.2)$$

This equation shows the close relationship between the Grüneisen parameter and the specific heat at constant volume. One may also see that the same formula can be represented in several different forms such as

$$\left(\frac{\partial \gamma(v, T) C_v(v, T)}{\partial \ln T} \right)_v = \left(\frac{\partial C_v(v, T)}{\partial \ln v} \right)_T \quad (2.3)$$

$$\left(\frac{\partial \gamma(v, T)}{\partial \ln T} \right)_v = \left(\frac{\partial C_v(v, S)}{\partial \ln v} \right)_S \quad (2.4)$$

Physical model for the specific heat and that for the Grüneisen parameter are not independent but related through the relationship of Eqs.(2.2)-(2.4). It should also be confirmed that any other relationships involving the Grüneisen parameter and the specific heat at constant volume must be identified equivalent to Eq. (2.2).

From here, we will develop various thermodynamic formulations based on several assumptions. Some of them are of physics basis and others are of no physical basis. As noted in the Introduction, material functions at zero Kelvin must have close relationship with Grüneisen parameter as well as the specific heat at constant volume. Fig.2.1 shows the schematic diagram of zones separated by the used assumptions, and sometimes simplified assumptions. Zone 1 contains no assumptions and therefore the most complete area, although sometimes it is unpractical to stick to this region. But we will show later the examples of zone 1. Zone 2 must be the most discussed area for a long time. We will describe this region rather in great detail. Zone 2 is divided into 2 zones, whether the theoretical models between cold functions and the Grüneisen parameter. Zone 3 is discussed in detail in this chapter. In Zone 4, very simple assumptions for the Grüneisen parameter which has almost no physical meaning. These assumptions, however, have used for a long time due to their simplicity and convenience.

Zone1 $\gamma(v, S) \Leftrightarrow C_v(S, v)$ They are not independent. $\left(\frac{\partial}{\partial S} \left(\frac{\gamma(v, S)}{v} \right) \right)_v = \frac{1}{C_v^2} \left(\frac{\partial C_v}{\partial v} \right)_S$	Coupled γ and C_v models should be integrated along reliable compression curve such as shock Hugoniot. All kinds of quantities including thermal variables are determined simultaneously.
Zone2 $\gamma(v) \Leftrightarrow C_v(S)$ <i>They are independent.</i> New thermal variables $\Theta(v)$: characteristic temperature $C(S)$: conjugate variable to $\Theta(v)$ <i>Relation between $\epsilon_c(v)$ and $\gamma(v)$</i>	If γ model is compatible with C_v model, cold functions such as $\epsilon_c(v)$, $\gamma(v)$, and other volume functions are determined simultaneously . Thermal variables need C_v model, and are determined separately.
Zone3 Theoretical models $\epsilon_c(v)$ and $\gamma(v)$ $\Rightarrow$ <i>complete Grüneisen EOS</i>	
Zone4 <i>Simple assumptions</i> (i) $\rho\gamma = \rho_0\gamma_0 = \text{const}$ (ii) $\gamma = \gamma_0 = \text{const}$	Cold functions are determined by a differential equation. Thermal variables need C_v model to be determined.

Fig. 2.1 Zone schematic of various levels of possible models based on thermodynamic constraints on them.

Various theoretical models for the specific heat of crystalline solids at constant volume has been proposed so far (Gopal 1966), although we will not go into details in this book. Later, we will choose the simple Debye model for the specific heat in this book, since more complicated theories are considered to be too delicate for the present data of high pressure science to apply. As is explained in a later section, in case of the Debye model, the specific heat is a function of entropy only and not a function of volume. In that case, rhs of Eq.(2.2) is zero, so that the Grüneisen parameter must be a function of volume only. One may prove that left condition leads to the right condition, and vice versa, i.e.,

$$\gamma = \gamma(v) \Leftrightarrow C_v = C_v(S) \quad (2.5)$$

At least, it is really desirable to find a reliable way to measure the specific heat at constant volume along the isentropic compression curve, or to measure the temperature dependence of the Grüneisen parameter under high pressure along an isochoric. Although both measurements are not easy tasks. Unless we have a reliable evidence that the Grüneisen parameter is a function of entropy as well as volume, or the specific heat at constant volume is a function of volume as well as entropy, we will stick to the constraint, Eq. (2.5).

Experimental estimation of the value γ of various solid materials as a function of temperature at atmospheric pressure reveals that it is almost unchanged with temperature, i.e., (Steinberg 1981)

$$\gamma = \gamma(v) \quad (2.6)$$

which we call here the ‘Grüneisen law’. Usually, thermodynamic relationship, Eq.(1.5) is called the ‘Grüneisen law’. This name apparently comes from the original definition of the Grüneisen parameter such

that it is given by the volume dependence of eigen frequency of lattice vibration. In this book, however, we adopt the thermodynamic definition of the Grüneisen parameter by Eq.(1.4). By the use of this definition, Eq. (1.5) is a thermodynamic identity. Instead, we use the term of the Grüneisen law described by Eq.(2.6). As a thermodynamic quantity, the Grüneisen parameter γ will change its value with compression up to high density states, although its measurements under high pressure is generally very difficult, and the information on the change of γ is quite limited.

This expression can be reached by once expressing the Grüneisen parameter as a function of volume and temperature, then the property of γ of temperature independence is applied. If we will discuss the pressure dependence of it, it should be careful to see that it depends on temperature as well as pressure. This is due to the fact that choice of independent variables to describe the thermodynamics of γ is important. We will again remind that the Grüneisen parameter is temperature independent, that means it is a function of volume only. Experimentally, for many of the materials, the value is almost constant with temperature almost up to the melting temperature. (Steinberg 1981)

It is also noted that definition of the Grüneisen parameter by Eq.(1.4) can be valid for liquids and even for gases. For liquid states, the Grüneisen parameter is believed to be dependent also on temperature. For gases, especially for ideal gases, we have a very simple result

$$\gamma = v \left(\frac{\partial p}{\partial \varepsilon} \right)_v = v \left(\frac{\partial \left[(\Gamma - 1) \frac{\varepsilon}{v} \right]}{\partial \varepsilon} \right)_v = \Gamma - 1, \quad (2.7)$$

where Γ denotes the ratio of the two specific heats for ideal gases. Apparently, the value of γ for gases is almost constant over wide range of thermodynamic states.

2.1.2. Grüneisen equation of state (EOS) based on the Grüneisen law

If the Grüneisen parameter is temperature independent, the definition, Eq.(1.4) can be integrated along an isochoric curve as (Nagayama 2008)

$$\frac{\gamma(v)}{v} d\varepsilon = dp \quad \text{with } v = \text{constant} \quad (2.8)$$

The result is

$$p = f(v) + \frac{\gamma(v)}{v} \varepsilon, \quad (2.9)$$

where function $f(v)$ is an integration constant. Volume dependence of it comes from the fact that the integration is along an isochoric. This is a very general expression of the equation of state for condensed substance under pressure in terms of pressure, volume and internal energy. This combination of state variables has a physical meaning in various ways. One of the consequences of this form of the equation of state is that sound velocity of the substance can be discussed or determined as in Eq.(1.6).

To specify the precise functional form of the EOS by Eq.(2.9), we have to know the functions, $f(v)$ and $\gamma(v)$. Goal of the theory in the Grüneisen equation of state (EOS) is to determine these two functions for the materials desired.

One of the important clue to understand the structure of the EOS in the form of Eq.(2.9) can be obtained by considering the zero-temperature state of the material. At absolute zero, we have one relationship from Eq.(2.9) as

$$p(v, T = 0) = f(v) + \frac{\gamma(v)}{v} \varepsilon(v, T = 0) \quad , \quad (2.10)$$

we have introduced here the pressure and internal energy at absolute zero temperature. Even in this condition, they can be a function of volume. In another words, they will change value by compression even at zero Kelvin. We call these values or functions, cold pressure and cold internal energy. In this in mind, Eq. (2.10) can be rewritten formally as

$$p_c(v) = f(v) + \frac{\gamma(v)}{v} \varepsilon_c(v) \quad . \quad (2.11)$$

Note that this equation contains volume functions only. This equation determines the meaning of the integration constant, the function $f(v)$. By using this expression with Eq.(2.9), we obtain the EOS in the form,

$$p = f(v) + \frac{\gamma(v)}{v} \varepsilon$$

$$f(v) = p_c(v) - \frac{\gamma(v)}{v} \varepsilon_c(v) \quad (2.12)$$

In this expression, now we have to know three functions, $p_c(v)$, $\varepsilon_c(v)$ and $\gamma(v)$.

Formulation of the Grüneisen equation of state not for crystalline solids but for fluids under the assumption of 'Grüneisen law' requires another formulation. It will be given in later chapters.

2.1.3. Cold and thermal part of the Grüneisen EOS

One can see the difference in the total pressure and cold pressure, or that in the total internal energy and cold internal energy by rewriting Eq.(2.12) as

$$p - p_c(v) = \frac{\gamma(v)}{v} [\varepsilon - \varepsilon_c(v)] \quad . \quad (2.13)$$

From this expression, we can define the thermal contribution of pressure and internal energy as

$$p_T(v, T) = p(v, T) - p_c(v, T)$$

$$\varepsilon_T(v, T) = \varepsilon(v, T) - \varepsilon_c(v, T) \quad (2.14)$$

where the suffix T indicates the quantity of thermal origin.

By writing in the following, we have for the full internal energy and pressure

$$p(v, T) = p_c(v, T) + p_T(v, T)$$

$$\varepsilon(v, T) = \varepsilon_c(v, T) + \varepsilon_T(v, T) \quad (2.15)$$

it can be said that the pressure and the specific internal energy of condensed media obeying the Grüneisen law consist of two different contributions, cold and thermal.

A relationship between the cold contributions is derived by applying the thermodynamic identity to zero temperature together with the definition of cold contribution. That is,

$$d\varepsilon = TdS - pdv, \text{ with } T = 0 \quad (2.16)$$

$$p_c(v) = -\frac{d\varepsilon_c(v)}{dv} . \quad (2.17)$$

The relation is simply the relationship between the potential energy and the force derived from it. Cold pressure comes from the repulsive force between atoms, if it is forced to be in close contact with each other.

New meaning of the Grüneisen parameter is seen in the following expression

$$p_T(v, T) = \frac{\gamma(v)}{v} \varepsilon_T(v, T) , \quad (2.18)$$

which states that thermal pressure is linearly dependent on the thermal internal energy, and the Grüneisen parameter determines how thermal energy contributes pressure, if the heated body tries to expand in a confined situation. Microscopic meaning for all the formulae in this section will be discussed in a later section based on the statistical mechanics.

Thermal contribution will increase apparently by heating materials. If the material is confined in limited space, thermal pressure exerts the confined wall. Even by the 300K increase from zero Kelvin to room temperature, increase in thermal pressure of the substance amounts to about 1 GPa (10 kbar=10000 atm), which is normally larger than the elastic strength of many solid materials. Invention of variety of high pressure apparatus makes it possible to compress solid material up to very high pressures far larger than the elastic strength of materials. In that case, cold contribution plays a major contribution to the total pressure of the substance.

Very high thermal pressure can be realized not by high-pressure apparatus, but by a dynamic method, the shock compression method, which drives high pressure into materials. Irreversible heating of materials can reach very high temperature possibly higher than several thousand Kelvin or higher. In such cases, thermal contribution is estimated to be comparable to or larger than cold contribution.

2.2. New thermal variables for Grüneisen solids

2.2.1. Introduction of the new variables

The author introduced new thermal variable set for condensed substances obeying the Grüneisen law. (Nagayama, 1994, 2008) Rather in the extended version of the formulation, the same result will be assured for the substances that do not obey the Grüneisen law. This variable set is an alternative of the temperature and entropy. In this section, derivation of these variables and discuss some of the resultant relationships.

Suppose that the function $f(v)$ is determined by experiment. Then we have the relationship

$$p_c(v) - \frac{\gamma(v)}{v} \varepsilon_c(v) = -\frac{d\varepsilon_c(v)}{dv} - \frac{\gamma(v)}{v} \varepsilon_c(v) = f(v), \quad (2.19)$$

where Eq.(2.11) and Eq.(2.17) are used. For a given functional form of $f(v)$, Eq.(2.19) can be considered to be a differential equation for $\varepsilon_c(v)$ with respect to specific volume. Cold internal energy is described by the solution of this differential equation.

A differential equation of the same form is derived for the total internal energy as

$$p(v,S) - \frac{\gamma(v)}{v} \varepsilon(v,S) = -\left(\frac{\partial \varepsilon}{\partial v}\right)_S - \frac{\gamma(v)}{v} \varepsilon(v,S) = f(v). \quad (2.20)$$

In this case, however, the differential equation should be integrated along an isentrope. General solution of the differential equation should consist of two solutions, like

$$\varepsilon(v,S) = \varepsilon_c(v) + \varepsilon_T(v,S), \quad (2.21)$$

where the first term, $\varepsilon_c(v)$ is a particular solution of the differential equation, Eq.(2.19). While the second term of Eq.(2.21) is a general solution of the differential equation, Eq.(2.19) with $f(v)=0$. This is obtained in the following way. By starting the differential equation,

$$\left(\frac{\partial \varepsilon_T}{\partial v}\right)_S + \frac{\gamma(v)}{v} \varepsilon_T = 0, \quad (2.22)$$

we have the general solution as

$$\varepsilon_T = C(S)\Theta(v), \quad (2.23)$$

$$\Theta(v) = \Theta(v_0) \exp\left[-\int_{v_0}^v \frac{\gamma(v')}{v'} dv'\right], \quad (2.24)$$

where function $\Theta(v)$ is the general solution, and $C(S)$ is an integration constant. Since the integration is along an isentrope, the integration constant can be a function of entropy.

At this point, the derived results are summarized as follows:

- (1) At least experimentally, the Grüneisen parameter and cold internal energy are determined at the same time by Eq.(2.19).
- (2) General expression for the total internal energy consists of two terms, one of which is a volume function, while the other is function of volume and entropy.

(3) The first term should be the cold contribution, while the second term corresponds to thermal part.

(4) Thermal part of internal energy is found to be a product of two functions, one of which is a function of volume, and the other that of entropy. Dependence of thermal part of the specific internal energy on volume and entropy is found to be completely separated.

(5) Volume function of the thermal internal energy, $\Theta(v)$ is determined by the volume dependence of the Grüneisen parameter.

As discussed in later section, the Grüneisen parameter is in close connection with the cold internal energy. Eq.(2.19), the differential equation for the cold part gives additional constraint from the thermodynamic law. Statement (3) can be understood by the following consideration. Zero-Kelvin isotherm is one of the isentrope as well as isotherm, and that the entropy at zero Kelvin is zero by the third law of thermodynamics. Entropy term, therefore, appears only in the thermal contribution. One may also note that the statement (4) stems from the Grüneisen law.

We defined the volume function, $f(v)$ by using the cold function as in Eq.(2.19). Arbitrary thermodynamic states, described by pressure and internal energy should satisfy the equality, Eq.(2.20). This means that any compression curve, $p(v)$ and $\varepsilon(v)$ on the state surface can be combined to give the volume function, $f(v)$, such as an isotherm, $p(v, T_0)$ and $\varepsilon(v, T_0)$ or as an isentrope, $p(v, S_0)$ and $\varepsilon(v, S_0)$. It should be emphasized here that any succession of thermodynamic states which are described by $p(v)$ and $\varepsilon(v)$ on the state surface can be used to define the function $f(v)$. Solution of the thermal function derived as Eq.(2.22)-(2.24) is the difference between arbitrary state and cold component. By the consideration that the integration process is formally along an isetrope, one may see that choice of isentropes for the definition of $f(v)$ is most natural. We will see, however, some examples of choices of compression curve other than isentropes to define $f(v)$ in chapter 3 and 4.

2.2.2 Thermodynamics in terms of new thermal variables

To discuss further thermodynamic relationships in terms of newly introduced thermal variables, we will begin with the following expression for the equation of state for condensed media,

$$\varepsilon(v, S) = \varepsilon_c(v) + C(S)\Theta(v). \quad (2.25)$$

Noting that the internal energy is given by a function of volume and entropy, thermodynamically this form of the equation of state contains all the information for the materials. In other words, Eq.(2.25) contains information both on thermic and caloric equation of state for the substance. For example, the pressure is derived as

$$\begin{aligned} p &= -\left(\frac{\partial \varepsilon}{\partial v}\right)_S = -\frac{d\varepsilon_c(v)}{dv} - C(S)\frac{d\Theta(v)}{dv} \\ &= p_c(v) + \frac{\gamma(v)}{v}C(S)\Theta(v) \end{aligned} \quad (2.26)$$

Although it is natural to reach the final expression for pressure just the same as Eq.(2.18) or other related expressions, this derivation requires the knowledge of Eq.(2.24) derived in the previous section.

This discussion gives the following conclusion. That is, for the complete thermodynamic knowledge of the substance, we will determine the functional forms of $C(S)$, $\gamma(v)$ and $\varepsilon_c(v)$. These three functions are all needed to specify. We have to note again that those conclusions stem only from the Grüneisen law. Another important conclusion can be obtained from the thermodynamic identity. If we calculate the heat added to the system dQ , we have

$$\begin{aligned}
\delta Q &= TdS = d\varepsilon + pdv \\
&= d\varepsilon_c + d[C(S)\Theta(v)] + p_c dv + \frac{\gamma(v)}{v} C(S)\Theta(v)dv \\
&= -p_c dv + C(S)d\Theta(v) + \Theta(v)dC(S) \\
&\quad + p_c dv + \frac{\gamma(v)}{v} C(S)\Theta(v)dv \\
&= C(S)d\Theta(v) + \Theta(v)dC(S) - C(S)\frac{d\Theta(v)}{dv}dv \\
&= \Theta(v)dC(S)
\end{aligned} \tag{2.27}$$

In short,

$$\delta Q = TdS = \Theta(v)dC(S). \tag{2.28}$$

From this expression, we can conclude the following:

(1) In this expression, $\Theta(v)$ plays a role of the integrating denominator.

(2) $\Theta(v)$ and $C(S)$ are, therefore, mutually conjugate thermodynamic variables just like temperature and entropy.

(3) Although $\Theta(v)$ is a function of volume only, it can be a state variable, which can be a characteristic temperature of the system.

(4) Two variables, $\Theta(v)$ and $C(S)$ are thermodynamic state variables, which can be an alternative of temperature and entropy.

(5) This expression can be valid for most of the condensed substance over wide range of thermodynamic states subject to Grüneisen law.

Statement (3) looks surprising, since a volume function cannot be a measure of temperature of the system. Even so, we found a state variable set which can be chosen as an alternative of temperature and entropy. Since the variable $\Theta(v)$ is determined solely by the behavior of the Grüneisen parameter, the Grüneisen parameter determines part of the thermal part of the system. Remind that it has a close connection with the cold contribution, it plays a role of connecting cold and thermal contribution.

By rewriting Eq.(2.28), we have

$$dC = \frac{d\varepsilon + pdv}{\Theta(v)}. \tag{2.29}$$

This equation states that the variable $C(S)$ can be calculated by knowing the ε - p - v equation of state and $\gamma(v)$. Variable $\Theta(v)$ can be determined from the knowledge of $\gamma(v)$ through Eq.(2.24). Then one can calculate $C(S)$ by integrating Eq.(2.29) for the given ε - p - v equation of state. Since thermal variables like temperature and entropy cannot be calculated not only by the given ε - p - v equation of state, this relationship is surprising. Although we need other kind of information like the Debye model for the specific heat, some of the general relationships can be derived in this level of knowledge. That is, from the definition of the specific heat at constant volume, we have

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_v = \Theta(v) \left(\frac{\partial C(S)}{\partial T} \right)_v = \frac{\Theta(v)}{\left(\frac{\partial T}{\partial C(S)} \right)_v}$$

$$= \frac{\Theta(v)}{\left(\Theta(v) \frac{\partial}{\partial C(S)} \frac{dC(S)}{dS} \right)_v} = \frac{1}{\frac{d}{dC(S)} \frac{dC(S)}{dS}} = \frac{\frac{dC(S)}{dS}}{\frac{d^2 C(S)}{dS^2}} \quad (2.30)$$

This equation states that specific heat is a function only of entropy, and this result is the direct consequence of the Grüneisen law. (Nagayama 1994)

To know the volume dependence of the Grüneisen parameter $\gamma(v)$ is not an easy task. Experimental determination of $\gamma(v)$ under high pressure is found to be quite difficult. Theoretical models or molecular dynamic simulations may be useful, but not perfect.

2.2.3. Statistical mechanics and physical interpretation of the variables

Thermodynamic analysis developed so far gives fundamental relationships or necessary constraints that state variables for the system will satisfy. Even so, physical meaning and concrete value of each variable should be calculated by the microscopic theory. Equilibrium thermal properties of condensed systems can be discussed by statistical mechanics.

Thermal energy of crystalline solids is modeled by the collection of almost independent harmonic oscillators. Thermal properties are represented by the statistical properties of this dynamical system. Since the energy level of a harmonic oscillator is given by

$$\varepsilon_j = \left(n_j + \frac{1}{2} \right) \hbar \omega_j, \quad (2.31)$$

where ω_j denotes the frequency of lattice vibration of j -th mode.

Total number of harmonic oscillators of the system is $3N$. Without assuming the spectrum of lattice vibration frequencies, we will first calculate the total internal energy of solid for a state with the excited number set $(n_1, n_2, \dots, n_{3N})$ as

$$\varepsilon_j(n_1, n_2, \dots, n_{3N}) = \sum_{j=1}^{3N} \left(n_j + \frac{1}{2} \right) \hbar \omega_j + \varepsilon'_c, \quad (2.32)$$

where the cold energy of solid, ε'_c is introduced. This is regarded as the same concept as that appeared in Eq.(2.10). Since the energy of zero-point vibration is a function of volume, it is often incorporated into the cold part. Thus, we have

$$\varepsilon_j(n_1, n_2, \dots, n_{3N}) = \sum_{j=1}^{3N} n_j \hbar \omega_j + \varepsilon_c, \quad (2.33)$$

where the cold internal energy ε_c is introduced.

Partition function of the system is then calculated as

$$\begin{aligned}
Q &= \sum_{(n_1, n_2, \dots, n_{3N})} \exp[-\beta \varepsilon(n_1, n_2, \dots, n_{3N})] \\
&= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} \exp[-\beta n_j \hbar \omega_j - \beta \varepsilon_c] \\
&= \exp[-\beta \varepsilon_c] \sum_{n_1=0}^{\infty} \exp[-\beta n_1 \hbar \omega_1] \sum_{n_2=0}^{\infty} \exp[-\beta n_2 \hbar \omega_2] \\
&\quad \cdots \sum_{n_{3N}=0}^{\infty} \exp[-\beta n_{3N} \hbar \omega_{3N}] \\
&= \exp[-\beta \varepsilon_c] \prod_{j=1}^{3N} [1 - \exp(-\beta \hbar \omega_j)]^{-1}
\end{aligned} \tag{2.34}$$

where

$$\beta = \frac{1}{k_B T}, \tag{2.35}$$

with k_B the Boltzmann constant. From this partition function, the Helmholtz free energy, and internal energy of the system are given by

$$F = -k_B T \ln Q = \varepsilon_c + k_B T \sum_{j=1}^{3N} \ln [1 - \exp(-\beta \hbar \omega_j)] \tag{2.36}$$

$$\varepsilon = \varepsilon_c + \sum_{j=1}^{3N} \frac{\hbar \omega_j}{\exp[\beta \hbar \omega_j] - 1}. \tag{2.37}$$

Pressure is derived from Eq.(2.36) as

$$p = -\left(\frac{\partial F}{\partial v}\right)_T = -\frac{d\varepsilon_c}{dv} + \frac{1}{v} \sum_{j=1}^{3N} \frac{\gamma_j \hbar \omega_j}{\exp[\beta \hbar \omega_j] - 1}, \tag{2.38}$$

where the microscopic Grüneisen parameter for the mode j is defined as

$$\gamma_j = -\left(\frac{\partial \ln \omega_j}{\partial \ln v}\right)_T. \tag{2.39}$$

Since the frequency of lattice vibration increases with compression, this quantity represents the rate of increment of frequency of each mode upon compression.

Modes of vibration are apparently a function of volume, which is determined by the lattice potential field with the constraint provided by the given volume. In a simplified situation, they are independent on temperature, or in other words, they are not dependent on the amplitude of vibration. This is a naive explanation of the Grüneisen law.

Furthermore, if the change of each oscillation takes place in a self-similar fashion, the above quantity is independent of mode itself. For a given volume, potential force field should be fixed, and each eigen

frequency is determined quantum mechanically. In this sense, each Grüneisen parameter is ideally a function only of volume. Then we have

$$\gamma = \gamma(v). \quad (2.40)$$

In this case, the angular frequency ω_j can be written as

$$\omega_j = \omega_j^0 \exp \left[- \int^v \frac{\gamma(v')}{v'} dv' \right] = \omega_j^0 \Theta(v), \quad (2.41)$$

where we have introduced a material function $\Theta(v)$ independent on a particular mode of vibration. This function is exactly the same functional dependence as in that described in Eq.(2.24).

To discuss the physical meaning of these relations, we will examine the entropy of the system which is written in the following form

$$\begin{aligned} S &= k_B \sum_{j=1}^{3N} \left[\frac{\beta \hbar \omega_j}{\exp[\beta \hbar \omega_j] - 1} - \ln \left\{ 1 - \exp[-\beta \hbar \omega_j] \right\} \right] \\ &= k_B \sum_{j=1}^{3N} \left[\frac{\hbar \omega_j^0 \beta \Theta(v)}{\exp[\hbar \omega_j^0 \beta \Theta(v)] - 1} - \ln \left\{ 1 - \exp[-\hbar \omega_j^0 \beta \Theta(v)] \right\} \right] \end{aligned} \quad (2.42)$$

Parameters that depends on the macroscopic variable appeared in Eq.(2.42) are β and $\Theta(v)$. Note that they appeared only by one combination

$$\varsigma = \beta \Theta(v) = \frac{\Theta(v)}{k_B T}. \quad (2.43)$$

Other parameters contained in the expression (2.42) are mode dependent. From these considerations, variable ζ should be a function of entropy. By using Eqs.(2.40), (2.41) and (2.43), Eqs.(2.37) and (2.38) can be rewritten as

$$\begin{aligned} \varepsilon &= \varepsilon_c + \sum_{j=1}^{3N} \frac{\hbar \omega_j^0 \Theta(v)}{\exp[\hbar \omega_j^0 \beta \Theta(v)] - 1} = \varepsilon_c + \sum_{j=1}^{3N} \frac{\hbar \omega_j^0 \Theta(v)}{\exp[\hbar \omega_j^0 \varsigma(S)] - 1} \\ &= \varepsilon_c(v) + \Theta(v) \sum_{j=1}^{3N} \frac{\hbar \omega_j^0}{\exp[\hbar \omega_j^0 \varsigma(S)] - 1} \\ &= \varepsilon_c(v) + \Theta(v) C(S) \end{aligned} \quad (2.44)$$

$$\begin{aligned}
p &= -\frac{d\varepsilon_c}{dv} + \frac{1}{v} \sum_{j=1}^{3N} \frac{\gamma_j \hbar \omega_j}{\exp[\beta \hbar \omega_j] - 1} \\
&= -\frac{d\varepsilon_c}{dv} + \frac{\gamma(v)}{v} \sum_{j=1}^{3N} \frac{\hbar \omega_j}{\exp[\beta \hbar \omega_j] - 1} \\
&= p_c(v) + \frac{\gamma(v)}{v} \Theta(v) C(S)
\end{aligned} \tag{2.45}$$

where $C(S)$ is defined as

$$C(S) = \sum_{j=1}^{3N} \frac{\hbar \omega_j^0}{\exp[\hbar \omega_j^0 \zeta(S)] - 1} . \tag{2.46}$$

Thus we arrived at Eqs.(2.25), and (2.26) based on the statistical mechanics of harmonic oscillator system. Now we have the microscopic expression for $C(S)$ as well as $\Theta(v)$. In some sense, thermodynamically derived formulae for new variables have no restrictions for the physical models for condensed media. To provide a clear physical concept for new variables, microscopic modeling is inevitable. Up to this point, assumptions we have made to derive the results, Eqs.(2.44), (2.45) are as follows: (1) internal energy is made up of the cold potential energy plus the energy of harmonic oscillators, (2) the Grüneisen law, Eq.(2.40). Discussions described in this section reveals that the new variables defined thermodynamically can be introduced quite naturally also in the microscopic basis.

2.2.4. Debye model for specific heat and a new variable C and law of corresponding states in high-pressure physics

In this section, relationship between new thermal variables and the Debye model for the specific heat at constant volume. Since we do not need the Debye model for the discussion or the derivation of new variables, we would like to know the concrete functional relationship between entropy and the new variable C . Only for this purpose, we will introduce the Debye model for the specific heat. The most important drawback of the adoption of the Debye model is the underestimation of the effect of sound dispersion to the density of states of lattice vibration.

Debye model, however, gives appropriate description of thermal energy of crystalline solids, even when its spectrum of density of states does not look like that of Debye model. Thermodynamics in terms of new thermal variables does not need the introduction of the Debye model, and Debye model is used only to have concrete functional form, $C(S)$ and the discussion of the corresponding states. (Beke et al 1981, Parsafar and Mason 1994, Nagayama 1994a)

The Debye model uses a specific parameter defined as

$$\chi = \frac{\Theta_D}{T} = \frac{\Theta(v)}{T} , \tag{2.47}$$

where Θ_D denotes the Debye temperature. In the Debye model, this parameter is proved to be a function of entropy. The result is already evident by the present formulation particularly in Eq.(2.43) and succeeding consideration. The result is thus not the characteristics of the Debye model, but that of the Grüneisen law.

Thermal internal energy of solids in the Debye model is written as

$$\varepsilon_T = 3nk_B TD_3(x)$$

$$D_3(x) = \frac{3}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} \quad (2.48)$$

where $D_3(x)$ is a Debye function. From this equation, the new variable is obtained

$$C(S) = \frac{\varepsilon_T}{\Theta_D} = \frac{3nk_B TD_3(x)}{\Theta_D} = 3nk_B \frac{D_3(x)}{x} \quad (2.49)$$

We will stress here that this relationship is universal in that the formula contains no material parameter. Similar expression has already been derived in this model for the specific heat and entropy as a function of x as

$$S = 3nk_B \left[\frac{4}{3} D_3(x) - \ln(1 - e^{-x}) \right] \quad (2.50)$$

$$C_v = 3nk_B \left[4D_3(x) - \frac{3x}{e^x - 1} \right] \quad (2.51)$$

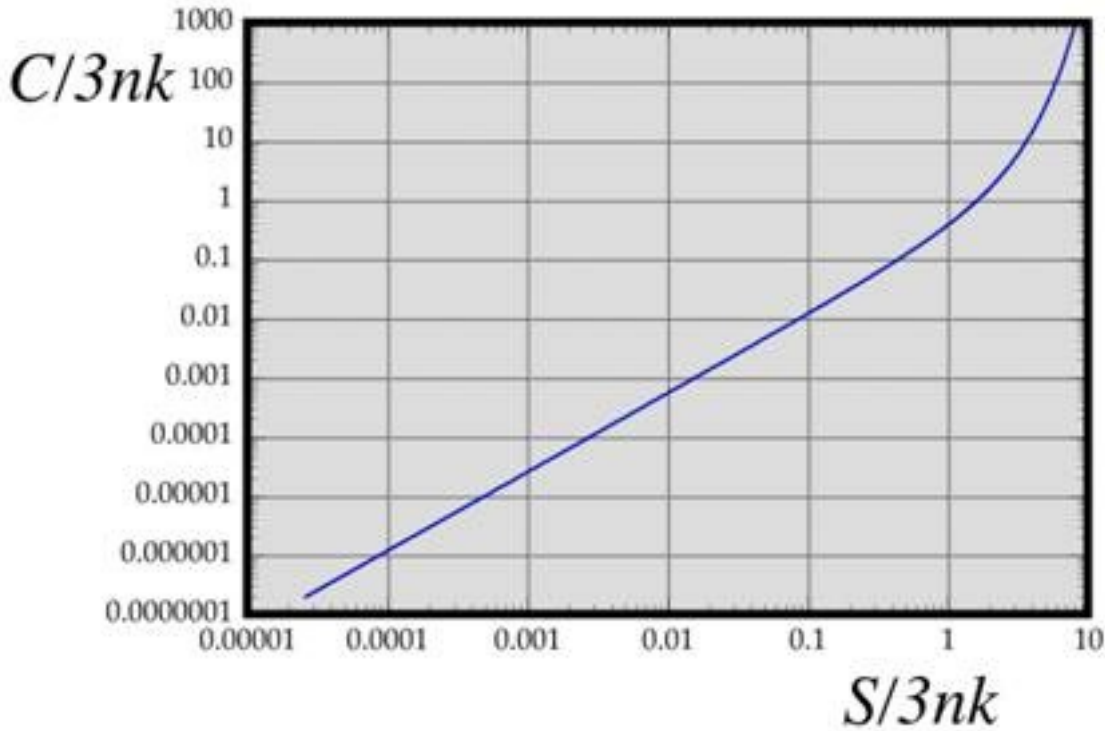


Fig. 2.2 New variable C as a function of entropy S based on the Debye model.

In this way, variable C is a function of x , or S or C_v , and vice versa. These mutual relationships are universal in that they do not contain any material parameters.

Figure 2.2 shows the calculated C - S relationship calculated by Eqs.(2.50) and (2.51). The relationship might be universal. As seen in Fig. 2.1, variable C changes faster than S . In other words, C is more sensitive to the change of state.

Figure 2.3 shows new variable C as a function of $x = \Theta(v)/T = \Theta_D(v)/T$ and entropy S as a function of x .

Debye model for the specific heat combined with the statistical mechanics of harmonic oscillator system is proved to be a very good approximation to the temperature behavior of the lattice specific heat of many elements. This fact proposes an example of the law of corresponding states for the value of specific heat as a function of temperature divided by Debye temperature Θ_D .

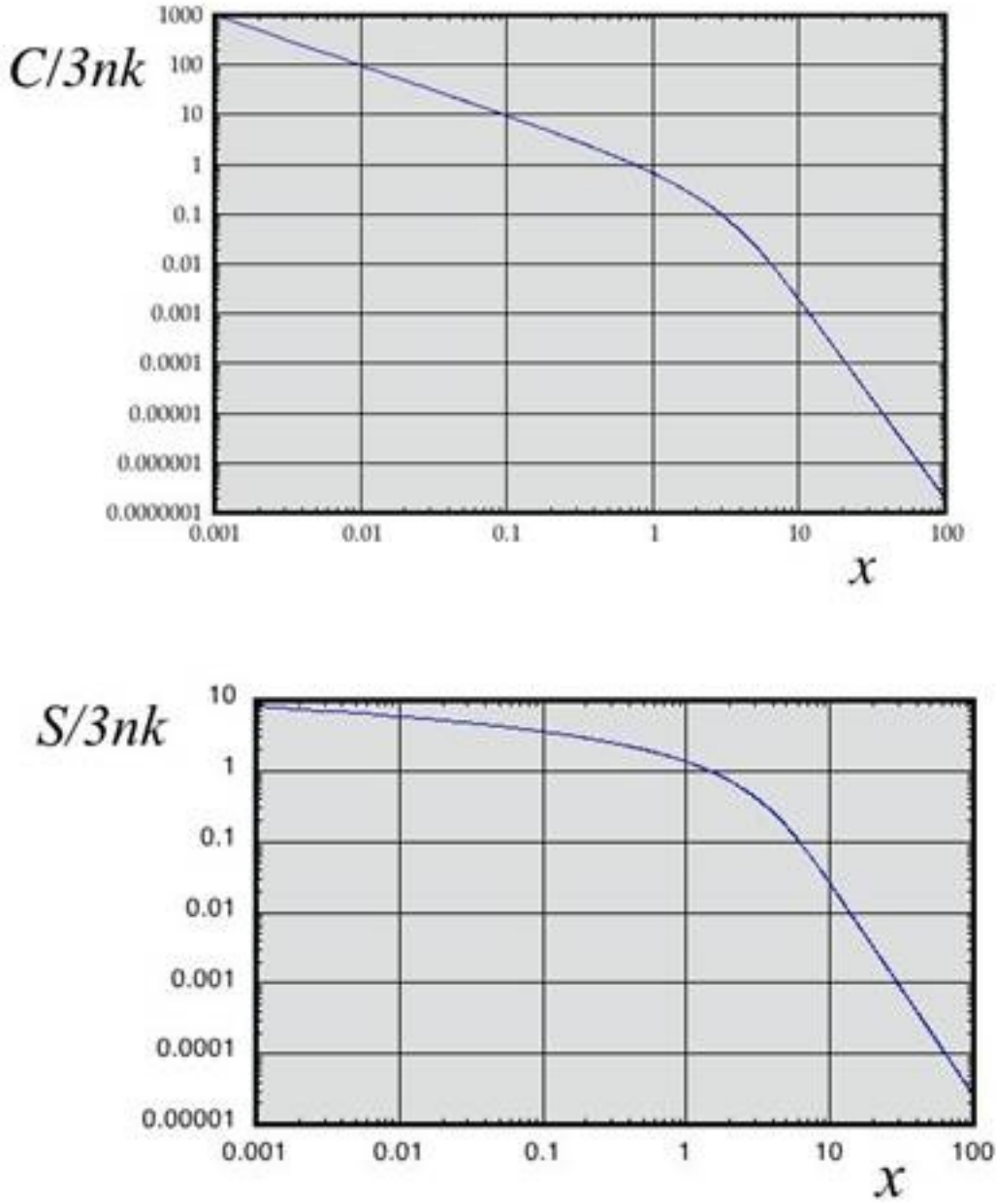


Fig. 2.3 New variable C and entropy S as a function of $x=\Theta/T$.

Unlike gases, law of corresponding states for crystalline solids has been discussed not so extensively. (Beke et al 1981, Parsafar and Mason 1994) We will discuss here the possibility of the law of corresponding states for other combination of thermal variables without assuming the Debye model. Suppose that the specific heat C_V is expressed as a function of the variable y defined as

$$y = \frac{T}{\Theta_D(v)} = \frac{dC(S)}{dS} \quad . \quad (2.52)$$

In this case, the function $C_V(y)$ is assumed to be a universal function irrespective of material. Then, the entropy S and the new thermal variable C can be calculated also as a function of y exactly as

$$S(y) = \int^y \frac{C_v(y')}{y'} dy' , \quad (2.53)$$

$$C(y) = \int^y C_v(y') dy' . \quad (2.54)$$

If the function $C_v(y)$ is universal, the function $S(y)$ and $C(y)$ is proved to be universal as well.

In other words, two more functions, $C_v(S)$ and $C(S)$ are also proved to be universal, starting from the assumption above. The discussion here is based only on thermodynamics, and not on the microscopic theory. The result, however, should also be interpreted microscopically. The success of the Debye model for the specific heat will support the existence of the other universal law presented here.

It should be stated that the universal law of the specific heat as a function of temperature divided by Debye temperature is proved to be valid almost at atmospheric pressure conditions. It should be noted that the functional relationship $C_v(y)$ is once established by the experimental data for the specific heat at atmospheric pressure, then the universal relationship $C_v(S)$ and $C(S)$ are also derived from the function $C_v(y)$.

In case of constant volume process, more specific results have been obtained by the application of the equations, (2.53) and (2.54). In this case, Eq.(2.54) can be rewritten as

$$\frac{\varepsilon_T(v, T)}{\Theta_D(v)} = C(S) = \frac{1}{\Theta_D} \int^T C_v \left(\frac{T}{\Theta_D} \right) dT . \quad (2.55)$$

This result can be interpreted that the thermal internal energy $\varepsilon_T(v, T)$ divided by a material constant Θ_D or by some characteristic temperature as the Debye temperature of the substance should be a universal function of (T/Θ_D) . The specific functional form of several universal functions will be calculated by the help of the Debye theory, although the present results does not dependent on it.

It is not easy to give precisely the range of validity of the law of corresponding states described here. Naturally, these rules will become invalid where the Grüneisen assumption cannot be applied. The range of validity of the Grüneisen assumption has been examined by Steinberg. (Steinberg 1981) He has concluded that in most metals the temperature effects of the Grüneisen parameter is within or less than several percent up to until the melting temperature. The limitation of the rules will be attributed to the effect of anharmonicity of lattice potential at the strongly compressed and/or high temperature states.

2.3 Theoretical treatment of the Grüneisen parameter under compression

2.3.1. Theoretical models

As explained in the Introduction, the cold potential energy function and the Grüneisen parameter may have close connection, and theoretical models have been proposed the relationship between them. Based on the microscopic assumptions, three independent theoretical models have been proposed so far, which make the Grüneisen parameter related to the cold pressure. They are Slater model (Slater 1939), Dugdale-MacDonald model (Dugdale and MacDonald 1953) and Vaschenko-Zubarev model (Vaschenko and Zubarev 1963). These three models have been conveniently represented as the following single equation

$$\gamma(v) = \frac{t-2}{3} - \frac{v}{2} \frac{\frac{d^2}{dv^2} \left[p_c v^{\frac{2}{3}t} \right]}{\frac{d}{dv} \left[p_c v^{\frac{2}{3}t} \right]} \quad (2.56)$$

by using a parameter t being 0, 1, 2 for three models in the cited order. These models have no significant difference in the high-pressure behavior of gamma at very high pressures. Migault and Romain et al suggested parameter t appeared in Eq.(2.56) may be a material parameter having continuous values. (Migault 1971, Migault 1972, Migault and Romain 1977)

This equation can be combined with Eq.(2.19) to close the system of equation for the two unknown functions of $p_c(v)$ and $\gamma(v)$ or $\varepsilon_c(v)$ and $\gamma(v)$. One of the possible procedures of calculating the Grüneisen parameter has been explained for example by Eliezer et al. (Eliezer, Ghatak and Hora 1986) If the Grüneisen parameter is eliminated from these two equations, the resultant equation for $\varepsilon_c(v)$ is a non-linear differential equation of the third order. In this procedure, both $\gamma(v)$ and $\varepsilon_c(v)$, and also $p_c(v)$ can be obtained by the integration. In order for the numerical integration of the differential equation, three initial values, i.e., the value of $\varepsilon_c(v)$, and its derivatives are required. These values are those on the zero-Kelvin isotherm, which are one of the objectives of integration. In this sense, the choice of these values may contain some ambiguities or errors, which may affect the result of integration.

We will explain the derivation of the Slater model briefly. Only this model among three is based on the Debye model for the specific heat. One may note, however, that the resultant model formula does not mean to contain the Debye model. In this sense, formula for the Slater model as in Eq.(2.56) with $t=0$ can be discussed apart from the Debye model.

Debye temperature is given by the following formula

$$\Theta_D = \frac{\hbar}{k_B} \bar{c} \left(\frac{3N}{4\pi V} \right)^{1/3} \quad (2.57)$$

where Θ_D , N , V denote the Debye temperature, number of particles and volume, respectively. Derivation of this equation can be found in various textbooks on statistical mechanics. Averaged sound velocity in Eq. (2.57) is defined by

$$\frac{3}{\bar{c}^3} = \frac{1}{c_\ell^3} + \frac{2}{c_t^3} \quad (2.58)$$

where c_ℓ and c_t denote the longitudinal and transverse sound velocity, respectively. In this case, the

Grüneisen parameter is given by

$$\gamma = -\frac{d \ln \Theta_D}{d \ln v} = \frac{1}{3} - \frac{d \ln \bar{c}}{d \ln v} \quad (2.59)$$

By using the bulk sound velocity c_b and Poisson's ratio π , the averaged sound velocity can be rewritten to the following equation

$$\bar{c} = 3^{5/6} c_b \zeta(\pi) \quad (2.60)$$

$$c_b = v \left\{ - \left(\frac{\partial p}{\partial v} \right)_s \right\}^{1/2} \quad (2.61)$$

$$\zeta(\pi) = \left(\frac{1-\pi}{1+\pi} \right)^{1/2} \left[1 + 2^{5/2} \left\{ \frac{1-\pi}{1-2\pi} \right\}^{3/2} \right]^{-1/3} \quad (2.62)$$

By applying these equations to Eq.(2.59), we obtain

$$\gamma = \gamma_{Slater} - \frac{d \ln \zeta(\pi)}{d \ln v} = \gamma_{Slater} + \delta \quad (2.63)$$

where

$$\gamma_{Slater} = \frac{1}{3} - \frac{d \ln \bar{c}_b}{d \ln v} = -\frac{2}{3} - \frac{v \left(\frac{\partial^2 p}{\partial v^2} \right)_s}{2 \left(\frac{\partial p}{\partial v} \right)_s} = -\frac{2}{3} - \frac{v \frac{d^2 p_c}{dv^2}}{2 \frac{dp_c}{dv}} \quad (2.64)$$

$$\delta = v \frac{d\pi}{dv} \left[\frac{1}{1-\pi^2} + \frac{2^{2/3}}{(1-2\pi)^2} \frac{\left(\frac{1-\pi}{1-2\pi} \right)^{1/2}}{1 + 2^{5/2} \left(\frac{1-\pi}{1-2\pi} \right)^{3/2}} \right] \quad (2.65)$$

In the derivation of Eq.(2.64), thermal contribution to the second term of third equation in Eq.(2.64) is neglected. This might be a good approximation except for extremely high pressure region. Inclusion of thermal term has been discussed by the author based on three theoretical models. (Nagayama, 1997) Slater model is obtained by neglecting the volume dependence of Poisson's ratio, although Poisson's ratio will be an increasing function of volume. Whether the quantity δ appeared in Eq.(2.63) is much smaller than the 1st term, however, is not very clear, although volume dependence of Poisson's ratio has also been discussed for a long time. (Razarus, 1949, Romain, Migault and Jacquesson 1976, Migault and Romain 1977)

Combining Eqs.(2.57), (2.60) and (2.61), we have the following relationship between cold pressure, $p_c(v)$ or cold potential energy, $\varepsilon_c(v)$ and Debye temperature or Debye limiting frequency or characteristic temperature, $\Theta_D(v)$ as

$$\Theta_D = -Cv^{\frac{2}{3}} \frac{dp_c(v)}{dv} = +Cv^{\frac{2}{3}} \frac{d^2 \epsilon_c(v)}{dv^2} \quad (2.66)$$

This equation states that limiting frequency is proportional to the second derivative of cold potential energy function, which will be the reflection of the form of lattice potential.

According to Eq.(2.58), averaged sound velocity by Eq.(2.58) is almost determined not by the longitudinal sound velocity but by the transverse sound velocity. Number of the density of states attributed to the transverse vibrational modes is much larger than that to the longitudinal one. In order to see the relative importance of longitudinal and transverse modes, the ratio of the density of states with and without omission of longitudinal modes can be estimated by the following.

$$\frac{\frac{2}{c_t^3}}{\frac{1}{c_l^3} + \frac{2}{c_t^3}} = \frac{1}{1 + \frac{c_l^3}{2c_t^3}} = \frac{1}{1 + \frac{1}{2^{5/3}} \left(\frac{1-2\pi}{1-\pi} \right)^{3/2}} \quad (2.67)$$

Figure 2.4 shows the ratio of Eq.(2.67) against Poisson's ratio. Ratio of the value of Grüneisen parameter estimated with and without omission of the longitudinal modes.

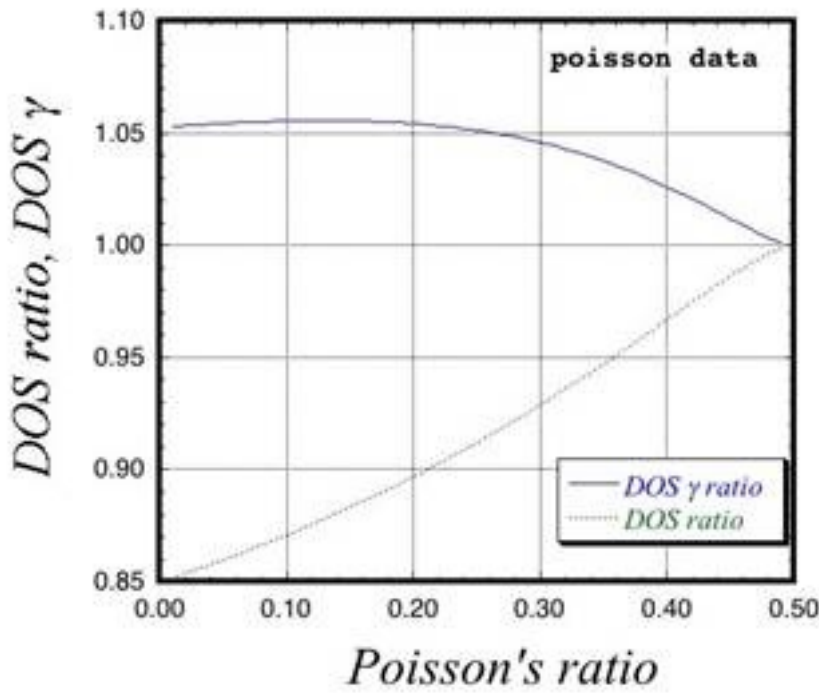


Fig. 2.4 Ratio of the density of states with and without omission of longitudinal vibrational modes, and that for the estimation of the Grüneisen parameter.

2.3.2. New procedure of calculating compression behavior of the Grüneisen parameter and further analytical models

Nagayama and Mori have developed a new procedure of calculating the Grüneisen parameter fully compatible with the shock Hugoniot data. (Nagayama and Mori 1994) The most important idea of the present method is that we can choose the measured shock Hugoniot compression curve as the integration path instead of the zero-Kelvin isotherm by the following reason. Firstly, zero-Kelvin isotherm itself is one of the targets to know how it is, and therefore, the parameters on the isotherm initially required for integration can

be estimated only approximately. This might give some errors to the integrated values of both the isotherm and the Grüneisen parameter. Second reason is that if the Grüneisen parameter is introduced as a function of volume, we can choose any thermodynamic path on the state surface, if the path can be described as a function of volume. In the present method, we adopt the shock Hugoniot curve as the integration path, since the Hugoniot curve may be a curve most reliable in very high pressure range on the state surface. Then, we will expect that if this can be possible, the result of integration may be more reliable than the previous procedures.

We will first define a new variable for a later use, that is,

$$q_S = \left[\partial \left\{ p \left(\frac{\rho}{\rho_0} \right)^{-2t/3} \right\} / \partial \rho \right]_S \quad (2.68)$$

The quantity in the parenthesis of the numerator is a quantity appearing in Eq.(2.56), and this variable is defined as the derivative with respect to density along an "isentropes". The meaning of this definition will be understood soon. This variable is included in the following thermodynamic identity.

$$\begin{aligned} d \left[p \left(\frac{\rho}{\rho_0} \right)^{-2t/3} \right] &= q_S d\rho + \left(\frac{\rho}{\rho_0} \right)^{-2t/3} \left(\frac{\partial p}{\partial S} \right)_\rho dS \\ &= q_S d\rho + \left(\frac{\rho}{\rho_0} \right)^{-2t/3} \left(\frac{\partial p}{\partial \epsilon} \right)_v \left(\frac{\partial \epsilon}{\partial S} \right)_v dS \\ &= q_S d\rho + \left(\frac{\rho}{\rho_0} \right)^{-2t/3} \left(\frac{\partial p}{\partial \epsilon} \right)_v T dS \\ &= q_S d\rho + \left(\frac{\rho}{\rho_0} \right)^{-2t/3} \left(\frac{\partial p}{\partial \epsilon} \right)_v [d\epsilon + p dv] \end{aligned} \quad (2.69)$$

Note that all the quantity contained in this equation can be estimated in terms of energy, pressure and volume, by the Grüneisen equation of state.

Applying this equation to the states on the shock Hugoniot, we have

$$q_S = \left[\frac{d \left\{ p \left(\rho / \rho_0 \right)^{-2t/3} \right\}}{d\rho} \right]_H - \left(\frac{\rho}{\rho_0} \right)^{-\frac{2t}{3}} \left(\frac{\partial p}{\partial \epsilon} \right)_v \left[\frac{d\epsilon + p dv}{d\rho} \right] \quad (2.70)$$

Since most of the shock Hugoniot have been represented as a relation between shock velocity u_s and particle velocity u_p , we will rewrite the above expression in terms of u_s and u_p .

By the help of the shock jump conditions explained in chapter 3, we obtain for the variable, q_S as

$$q_S = \left[\frac{u_s - u_p}{u_s} \right]^{\frac{2t}{3}} \frac{u_s - u_p}{u_s - u_p \frac{du_s}{du_p}} \left[u_s + u_p \frac{du_s}{du_p} - \frac{2t}{3} \frac{u_p \left[u_s - u_p \frac{du_s}{du_p} \right]}{u_s - u_p} - \gamma \frac{u_p^2 \frac{du_s}{du_p}}{u_s - u_p} \right] \quad (2.71)$$

where the thermodynamic relation for the Grüneisen parameter and various shock wave relations are used to derive Eq.(2.71). Eq.(2.71) states that the variable q_S can be described by the Grüneisen parameter and shock wave parameters.

While Eq.(2.56) can be described in terms of q_S as,

$$\gamma = \frac{t+1}{3} + \frac{\rho}{2} \frac{\left(\frac{\partial q_S}{\partial \rho} \right)}{q_S} \quad (2.72)$$

Furthermore, this equation can be again rewritten in terms of shock wave parameters as

$$\gamma = \frac{t+1}{3} + \frac{u_s (u_s - u_p)}{2 \left[u_s - u_p \frac{du_s}{du_p} \right]} \left(\frac{\partial \ln q_S}{\partial u_p} \right)_H \quad (2.73)$$

Eq.(2.71) and Eq.(2.73) form a closed set of differential equations for q_S and γ with the independent variable of u_p . These equations can be integrated over u_p with appropriate initial conditions. For the simplest choice, the necessary initial values for the integration are all that u_s - u_p Hugoniot compression curve. The initial value of the Grüneisen parameter γ_0 , the quantity $q_S(0)$ are given automatically by using the differential equations with the condition of $u_p = 0$.

We have calculated the volume dependence of the Grüneisen parameter for selected element materials. Some of the results are shown in Fig. 2.5. In these calculations, we used available shock Hugoniot data for the calculated materials. Details of the shock Hugoniot and the integration along shock Hugoniot will be given in the next chapter on the shock thermodynamics.

Calculations of the integration along shock Hugoniot should be made by using the polynomial formula for the Grüneisen parameter with respect to small compression, which is given by

$$\gamma = \gamma_{01} + \gamma_{02} \frac{u_p}{A} + \gamma_{03} \left(\frac{u_p}{A} \right)^2 \quad (2.74)$$

where

$$\gamma_{01} = 2B - \frac{2}{3} - \frac{t}{3} \quad (2.75)$$

$$\gamma_{02} = B(B-2) - B\gamma_{01} - \frac{t}{3} \left[1 - 4B + \frac{2t}{3} \right] \quad (2.76)$$

$$\gamma_{03} = B \left[B(B-1) - \frac{B+1}{2} \gamma_{01} - \frac{3}{2} \gamma_{02} \right] + 4 \left(B - \frac{t}{3} \right)^3 + \gamma_{01} B \left(B - \frac{t}{3} \right) \quad (2.77)$$

As shown in Fig. 2.5, rate of decrease of the Grüneisen parameter decreases with compression, but has some deflection of curvature at some degree of compression. This is a common tendency of various materials. Initial value of the parameter depends on the model as seen in Fig. 2.5.

Along with the calculation of the Grüneisen parameter, various Hugoniot parameters as well as other state variables can be obtained simultaneously. Details of the procedures and results are given in the next chapter.

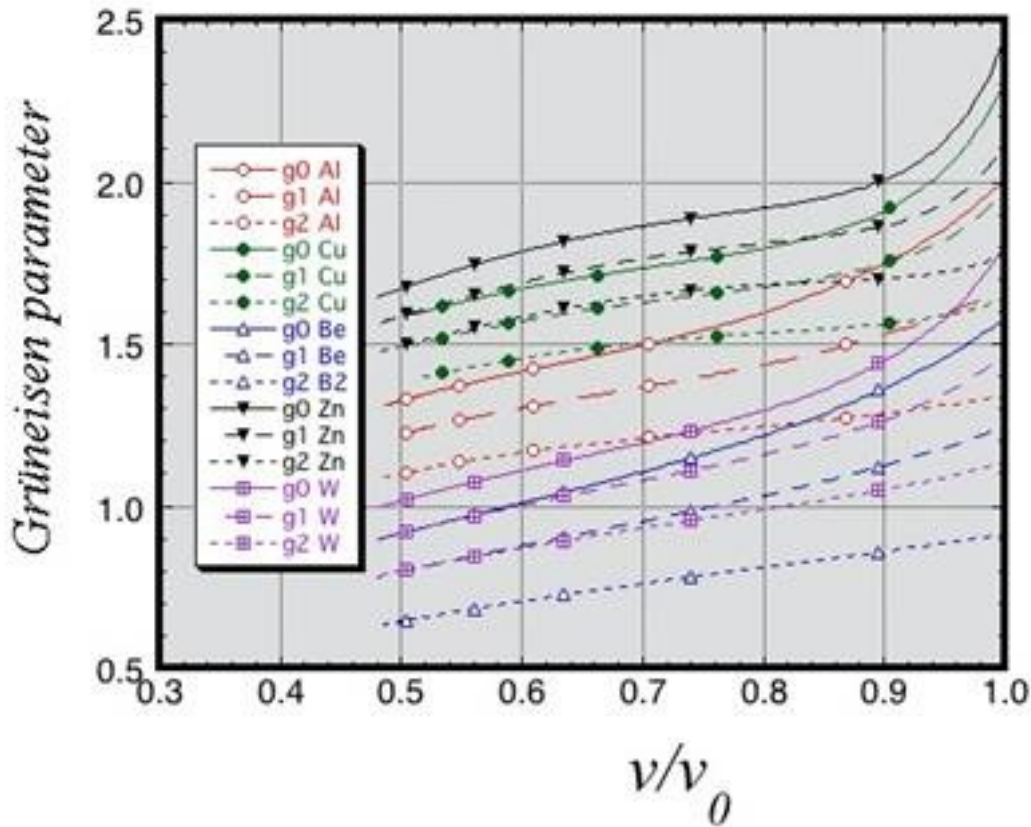


Fig. 2.5 Calculated Grüneisen parameter as a function of volume for selected elements. Notations used such as g0, g1, and g2 indicate the value of Grüneisen parameter by Slater, D-M and V-Z models, respectively.

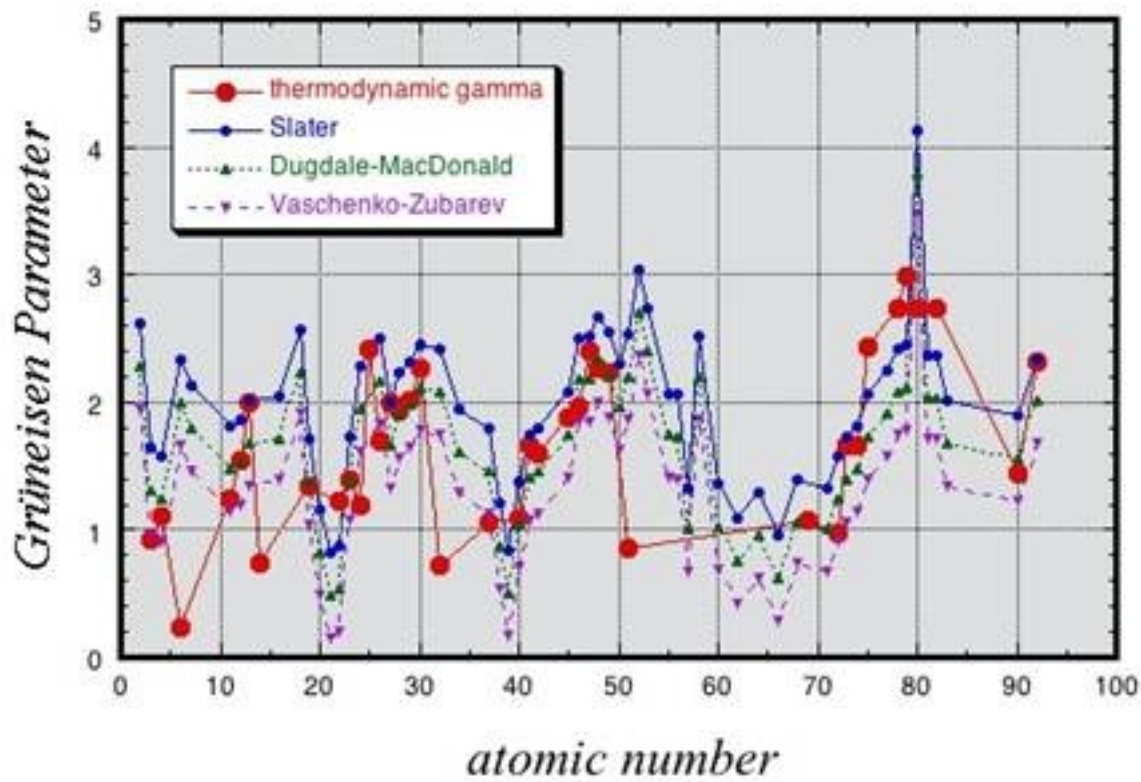


Fig. 2.6 Periodic table of calculated Grüneisen parameter based on three theoretical models compared with thermodynamic value. All theories can describe periodic changes, although the agreement between theory and experiment is not always very good.

As stated in the previous section, the Grüneisen parameter is a very difficult quantity to measure, theoretical estimation of the value is quite necessary. In this method, necessary data for calculation are the initial value of the Grüneisen parameter, and the shock Hugoniot data of the material. In case of the structural phase transition at high pressure, even the initial value of calculation cannot be provided by the experiment.

Figure 2.6 shows the comparison of the periodicity of thermodynamic Grüneisen parameter with that of the calculated values based on three theoretical models. Theoretical prediction shows clear periodic properties against the atomic number. Trends of the change of the results based on three models looks similar to the thermodynamically determined values of the Grüneisen parameter. However, three results resemble to each other, and no one may be the closest to the thermodynamic values.

As explained in Chapter 2, theoretical models, especially, Slater model ignores the change of Poisson's ratio with compression. Provided the appropriate contribution of the Poisson's ratio on the Grüneisen parameter, theoretical value for the volume derivative of the Grüneisen parameter is interesting to compare for three theories.

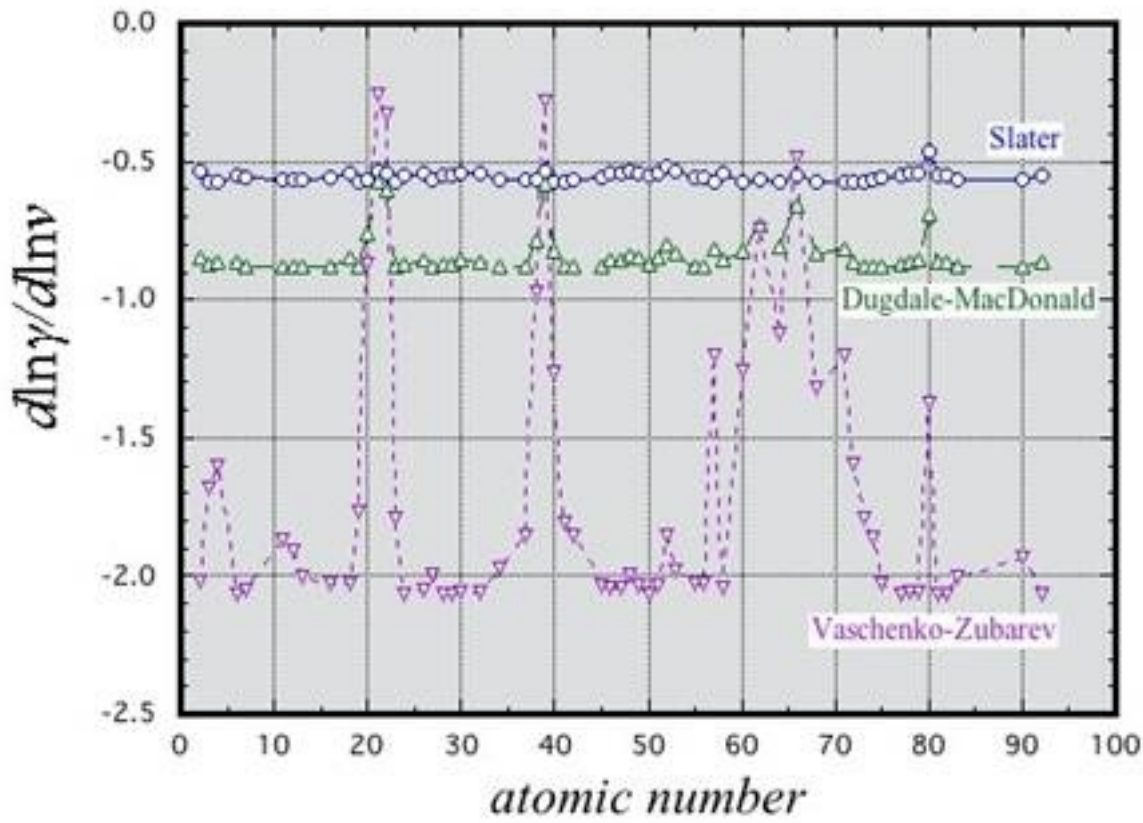


Fig. 2.7 Initial volume derivative of the Grüneisen parameter calculated by three theoretical models.

Figure 2.7 shows the periodic properties of volume derivative of Grüneisen parameter for three theoretical models. Three models have different base value, although the periodic nature itself is almost similar. Magnitude of the Grüneisen parameter and also their derivative has the value for Slater model, Dugdale-MacDonald model and Vaschenko-Zubarev models in this order. The initial slope of Grüneisen parameter against compression is given by

$$\left. \frac{d \ln \gamma}{d \ln v} \right|_0 = - \frac{\gamma_{02}}{\gamma_{01}} \quad (2.78)$$

Procedure of calculation for the Grüneisen parameter in this section will be discussed also in the next chapter in the sense that various quantities other than the Grüneisen parameter can be calculated simultaneously in the calculations of Grüneisen parameter. What quantities can be estimated simultaneously depends on the models used and its combination. These issues will also be explained in the next chapter.

2.3.3. Further analytical models of the Grüneisen parameter

In this section, proposals of further analytical expression for the Grüneisen parameter are briefly described. Romain, Migault and Jacquesson have discussed two Grüneisen parameters pertaining to longitudinal and transvers vibrations. (Romain et al 1976) They studied the possibility of determining the parameter t in Eq.(2.56) for each vibrational modes. By using Morse type interatomic potential in their analysis, they found that the difference in two Grüneisen parameters must be very small. One may note that difference in two Grüneisen parameters give difference in two associated characteristic temperatures. In this case, the overall Grüneisen parameter must be a function of temperature as well as volume. This aspect of the Grüneisen parameter will be discussed in the example of energetic materials treated in chapter 4.

First principle calculations have been made to obtain equation of state information for various materials under high pressures. (Friedli and Ashcroft 1975, Lam and Cohen 1983, Albers et al 1985, Nellis et al 1988, Bercegeay and Bernard 2005) These calculations have been compared with precision DAC (diamond anvil cell) based experimental dataset obtained for many materials until recently. (Greene et al, 1994, Dewaele et al 2004) Even now, value of the Grüneisen parameter is not an easy parameter determined in high precision, although various attempts or procedures of measuring Grüneisen parameter have been exploited. (for example, McQueen et al 1982, Anderson et al 2001) Cold pressure function, however, can be well compared obtained for various theoretical or experimental methods. Present method explained in this chapter can also be compared with these reports, and this discussion will be included in section 3.2.3 of chapter 3.

Several attempts have been proposed to provide analytical formula for the Grüneisen parameter as a function of volume in very wide pressure range. (Segletes and Walters 1998, Nie 2000, Bodryakov and Povzner 2003, Burakovsly and Preston 2004, Shanker et al 2007, Srivastava and Sinha 2009) Among various reports, Burakovsky and Preston have tried to give a simple analytical formula for the Grüneisen parameter. In order to match the change in the parameter t in Eq.(2.56) suggested by several authors, they proposed the value of 2.5 at least in very high pressure region. Further high pressures, the formula approaches to the value of 0.5 suggested by theory. Further matching can be done to the melting curve for solids governed by the Lindeman law.

According to the Lindemann's postulate, solids melt when the root-mean-square amplitude of lattice vibrations of atoms about their equilibrium positions becomes a critical fraction of the interatomic spacing. Criterion of Lindemann' melting law is written such that melting temperature under compression is determined by thermodynamic Grüneisen parameter which must be an average of mode Grüneisen parameters. (Gilverry 1956, Gilverry 1956a, Parciauskas 1976, Romain et al 1980, Burakovsky and Preston 2004) It is therefore possible to discuss the volume dependence of the Grüneisen parameter by the theoretical or experimental determination of melting temperature under compression.

2.4. Grüneisen EOS for anharmonic solids

2.4.1. Universal theory for the Grüneisen EOS

Author developed a quite generalized formulation which will define the Grüneisen parameter in any thermodynamic state for any form of substances. (Nagayama 1997a) Such a universal treatment of the EOS under arbitrary high pressure condition was made by starting the discussion with the thermodynamic definition of pressure. This generalized theory is intended to obtain much more physical insight of the meaning of two new variables introduced in the previous section. As explained in the previous section, the definition of the Grüneisen parameter has applied equally into the range of ideal gases as well as condensed phase of the substance.

In the following, a formulation is presented to define two new thermodynamic state variables. Let us begin with the thermodynamic definition of hydrostatic pressure, p

$$p = -\left(\frac{\partial \varepsilon}{\partial v}\right)_s. \quad (2.79)$$

Since the cold pressure, p_c which is the difference between the total pressure and thermal pressure, should be the function of volume and is the volume derivative of the cold energy, ε_c , thermal pressure can be expressed by the following equation

$$p_T = -\left(\frac{\partial \varepsilon_T}{\partial v}\right)_s = f(v, \varepsilon_T), \quad (2.80)$$

where the thermal pressure is described by two independent state variables, the volume and the thermal energy.

This equation can be regarded as a first order differential equation for the thermal internal energy along an isentrope. The formal but general solution of this differential equation can be written as

$$\varepsilon_T = \varepsilon_T(v, C(S)), \quad (2.81)$$

where $C(S)$ corresponds to the integration constant. Since, the differential equation is first order, we have one integration constant. The integration constant can be a function of entropy, because the integration is performed along an isentrope. How this entropy function is contained in the thermal energy function depends on the form of the differential equation, Eq.(2.80).

The solution, Eq.(2.81) can always be rewritten into the form

$$\varepsilon_T = C(S) \frac{\varepsilon_T(c, C(S))}{C(S)} = C(S) \Theta(v, C(S)). \quad (2.82)$$

In this form, the thermal internal energy can be always subdivided into the multiplication of two functions, one of which is always a function of entropy. Soon, why this splitting has a meaning will be established. From Eq.(2.82) combined with the definition of thermal pressure, we obtain

$$\begin{aligned}
p_T &= -\left(\frac{\partial \varepsilon_T}{\partial v}\right)_S = -C(S)\left(\frac{\partial \Theta(v, C(S))}{\partial v}\right)_S \\
&= -C(S)\left(\frac{\partial \Theta(v, C(S))}{\partial v}\right)_{C(S)} . \quad (2.83)
\end{aligned}$$

In order to see the physical meaning of the splitting of thermal energy into two functions, we will calculate the heat added to the system, i.e., $dQ = TdS$,

$$TdS = d\varepsilon_T + p_T dv = \Theta_0(v, C(S))dC(S), \quad (2.84)$$

where another function $\Theta_0(v, C(S))$ is introduced as

$$\Theta_0(v, C(S)) = \Theta(v, C(S)) + C(S)\left(\frac{\partial \Theta(v, C(S))}{\partial C(S)}\right)_v. \quad (2.85)$$

Eq.(2.84) states that the function $\Theta_0(v, C(S))$ can be an integrating denominator of the differential of heat like temperature, while $C(S)$ should be a state variable conjugate to the integrating factor, $\Theta_0(v, C(S))$ just like temperature and entropy. In this case, of course, these two variables, $C(S)$ and $\Theta_0(v, C(S))$ can be the entropy S and the absolute temperature T . If they are not S and T , other possible state variable conjugate to the integrating factor should be limited to a function of entropy. The above is a simple proof of this property for general thermodynamic systems. We will later discuss possible and important set of new state variables, $C(S)$ and $\Theta_0(v, C(S))$ other than S and T . All of these possibilities of new state variables are common to any phase of simple materials.

According to the above thermodynamic discussions, two new thermal variables introduced in this section might have the dimension of temperature and entropy. That is, the variable Θ or Θ_0 has the dimension of temperature, and $C(S)$ has the dimension of entropy. Although this seems a natural choice of dimensions, there can be alternative choice of dimensions, i.e., the variable Θ or Θ_0 has non-dimension, while $C(S)$ has the dimension of energy instead of entropy. These pure thermodynamic discussions cannot answer this question, rather one has to define these variables depending on how convenient these can describe thermodynamic states. In order to define these variables as universal variables for the description of matter in a wide range of thermodynamic states, however, one should have suitable reduction of these variables to have non-dimensional variable set. We will discuss later what kind of parameter should be chosen to reduce these variables.

In this generalized discussion, the Grüneisen parameter is a non-dimensional state variable defined as

$$\begin{aligned}
\gamma(v, \varepsilon) &= v\left(\frac{\partial p}{\partial \varepsilon}\right)_v = \gamma(v, \varepsilon_T) = v\left(\frac{\partial p_T}{\partial \varepsilon_T}\right)_v \\
&= -v\frac{\left(\frac{\partial \Theta_0(v, C(S))}{\partial v}\right)_{C(S)}}{\Theta_0(v, C(S))} = -\left(\frac{\partial \ln \Theta_0(v, C(S))}{\partial \ln v}\right)_{C(S)} \quad (2.86)
\end{aligned}$$

where later part of the calculation is made by using the new functions introduced in the previous paragraph. Since this parameter has a value dependent on the material, the law of corresponding states for gases and liquids cannot hold in the sense stated for fluids. Rather the value characterizes the condensed matter.

From the form of Eq.(2.86), one can infer that the variable $\Theta_0(v, C(S))$ could correspond to the Debye

limiting frequency or the Debye temperature in the Debye model for the specific heat of the harmonic solids. More generally, the variable can be regarded as a variable representing some characteristic temperature. This characteristic temperature can be introduced in any phase of the substance.

From Eq.(2.83) and (2.84), differential of temperature T is expressed as

$$dT = \left[\left(\frac{\partial \Theta_0}{\partial C} \right)_v \left(\frac{dC}{dS} \right)^2 + \Theta_0 \frac{d^2 C}{dS^2} \right] dS + \left(\frac{\partial \Theta_0}{\partial v} \right)_S \frac{dC}{dS} dv \quad (2.87)$$

By combining Eq.(2.87) with Eq.(2.84), specific heat at constant volume can be derived as

$$\begin{aligned} \frac{1}{C_v} &= \frac{1}{T} \left(\frac{\partial T}{\partial S} \right)_v = \frac{1}{\Theta_0} \frac{dS}{dC} \left[\left(\frac{\partial \Theta_0}{\partial C} \right)_v \left(\frac{dC}{dS} \right)^2 + \Theta_0 \frac{d^2 S}{dC^2} \right] \\ &= \frac{\frac{d^2 C}{dS^2}}{\frac{dS}{dC}} + \frac{1}{\Theta_0} \left(\frac{\partial \Theta_0}{\partial C} \right)_v \frac{dC}{dS} \end{aligned} \quad (2.88)$$

This equation for the specific heat and Eq.(2.86) for the Grüneisen parameter naturally satisfies the thermodynamic constraint, Eq.(2.2).

2.4.2. Formulation of the anharmonic Grüneisen EOS

In this section, somewhat realistic formulation for Grüneisen EOS for condensed media under pressure was developed. We will present an example of the theoretical formulation presented in the previous section. Such a formulation seems often sufficient to examine the anharmonic contribution to EOS.

Frequency of the lattice vibration will change with compression. This will take place by at least two reasons. One is the effect of the change in lattice potential energy function by volume compression, even if the form of the potential can be regarded as harmonic. This contribution has already been incorporated into the Grüneisen type equation of state by the volume dependence of the Grüneisen parameter. The other is the effect of increase in the energy of lattice vibration. This is the contribution of the anharmonic portion of the lattice potential energy function. In order to include this kind of anharmonic contribution into the equation of state for solids, which appears in the relatively high temperature region, it is assumed here that the Grüneisen parameter has energy dependence expressed by

$$\gamma(v, \epsilon) = \gamma_0(v) + 2\gamma_1(v)\epsilon, \quad (2.89)$$

where two volume functions are defined. The function $\gamma_1(v)$ in this definition has dimension of the reciprocal of energy. Practically, the Grüneisen parameter is a function of volume and temperature. Thermodynamic formulation of the equation of state for solids, the combination of the variables, volume and energy is convenient for the Grüneisen type equation of state. In the above equation, the Grüneisen parameter itself has two contributions, from the volume function and energy term. At zero temperature, the second term gives $2\gamma_1(v)\epsilon_c(v)$. In Eq.(2.89), the second term, therefore, is not assumed to be small.

By combining this equation with the thermodynamic definition of the Grüneisen parameter, Eq.(1.4), it is possible to integrate it over ϵ along an isochoric to obtain an expression of the equation of state for pressure as a function of (ϵ, v) as

$$p = F(v) + \rho\gamma_0(v)\epsilon + 2\rho\gamma_1(v)\epsilon^2. \quad (2.90)$$

In this equation, function $F(v)$ corresponds to the integration constant, which can be an arbitrary function of volume.

Furthermore, it is assumed here that the specific internal energy of an anharmonic solid can be decomposed into two terms as

$$\varepsilon = \varepsilon_c(v) + \varepsilon_T(v, S), \quad (2.91)$$

where the suffices c and T indicates the value of cold and thermal parts. In this equation, two energy functions are described as functions of volume and entropy. These two independent variables are the natural set of variables for internal energy by the usual equilibrium thermodynamics.

Rewriting the equation of state, (2.90) by inserting Eq.(2.91) into Eq.(2.90),

$$\begin{aligned} p = & \left[F(v) + \rho\gamma_0(v)\varepsilon_c(v) + \rho\gamma_1(v)\varepsilon_c^2(v) \right] \\ & + \rho \left[\gamma_0(v) + 2\gamma_1(v)\varepsilon_c(v) \right] \varepsilon_T(v, S) \\ & + \rho\gamma_1(v)\varepsilon_T^2(v, S) \end{aligned} \quad (2.92)$$

consequently, we have

$$p(v, S) = p_c(v) + \rho\gamma_{00}(v)\varepsilon_T(v, S) + \rho\gamma_1(v)\varepsilon_T^2(v, S), \quad (2.93)$$

where the cold pressure and a new volume function

$$p_c(v) = F(v) + \rho\gamma_0(v)\varepsilon_c(v) + \rho\gamma_1(v)\varepsilon_c^2(v), \quad (2.94)$$

$$\gamma_{00}(v) = \gamma_0(v) + 2\gamma_1(v)\varepsilon_c(v), \quad (2.95)$$

are introduced. Function $\gamma_{00}(v)$ corresponds to the Grüneisen parameter at zero temperature, and therefore is the one normally used in the Grüneisen type equation of state. In this sense, the second term in Eq.(2.93) corresponds to the harmonic contribution.

From the equation of state, Eq.(2.93), it states that the thermal pressure consists of two terms. The last term of Eq.(2.93) corresponds to the anharmonic contribution to the pressure, which is proportional to the square of the thermal internal energy. According to the law of Dulong-Petit, the specific heat tends to the constant value at high temperatures. In this sense, specific internal energy, ε_T is directly proportional to the temperature T . The last term of Eq.(2.93) proportional to T^2 can also be regarded as the contribution from electronic contribution. In this thermodynamic analysis, it does not need to discriminate the difference in the anharmonic effect and electronic effect.

Since the thermal pressure, p_T is given by

$$p_T = p(v, S) - p_c(v) = - \left(\frac{\partial \varepsilon_T}{\partial v} \right)_S. \quad (2.96)$$

Combining Eq.(2.96) with Eq.(2.93), we obtain

$$\left(\frac{\partial \varepsilon_T}{\partial v} \right)_S + \rho\gamma_{00}(v)\varepsilon_T(v, S) + \rho\gamma_1(v)\varepsilon_T^2(v, S) = 0, \quad (2.97)$$

which can be regarded as a differential equation for the thermal internal energy.

It is shown that this equation can be integrated formally to have general solution as

$$\varepsilon_T(v, S) = \frac{C(S)\Theta(v)}{1 + C(S)\int^v \rho\gamma_1(v')\Theta(v')dv'} , \quad (2.98)$$

where a volume function

$$\Theta(v) = \Theta(v_0) \exp \left[- \int_{v_0}^v \frac{\gamma_{00}(v')}{v'} dv' \right] , \quad (2.99)$$

is introduced. In this expression, the function of entropy, $C(S)$ corresponds to the integration constant. To specify the integration constant, we choose the solution which has an analogous form as the harmonic equivalent. This is the reason why the function, $C(S)$ appears twice in Eq.(2.98). As is seen in Eq.(2.98), this tends to the harmonic solution, if the anharmonic term tends to zero.

By introducing a new function,

$$\Theta_0(v, S) = \frac{\Theta(v)}{1 + C(S)\int^v \rho\gamma_1(v')\Theta(v')dv'} , \quad (2.100)$$

thermal internal energy can be expressed as

$$\varepsilon_T = \Theta_0(v, C(S))C(S) . \quad (2.101)$$

By comparing this expression with the harmonic solution, we notice that thermal internal energy still have the form of the product of two functions. In appearance, the change from harmonic to anharmonic appears only in the function $\Theta_0(v, C(S))$. In this sense, the two functions, introduced in this expression will also be two new thermal variables.

By discussing the physical meaning of these variables, we will again calculate the heat added to the isolated system, $\delta Q = TdS$,

$$\begin{aligned} \delta Q &= TdS = \left(\frac{\partial \varepsilon_T}{\partial S} \right)_v dS \\ &= \frac{\Theta_0^2(v, C(S))}{\Theta(v)} dC(S) \end{aligned} \quad (2.102)$$

consequently, we have

$$TdS = \frac{\Theta_0^2(v, C(S))}{\Theta(v)} dC(S) . \quad (2.103)$$

This indicates that function $\Theta_0^2(v, C(S))/\Theta(v)$ plays a role of integrating factor of the differential form δQ , and function $C(S)$ corresponds to a state variable conjugate to $\Theta_0^2(v, C(S))/\Theta(v)$. Therefore, the following quantity should be a function of entropy,

$$\frac{T\Theta(v)}{\Theta_0^2(v, C(S))} = \frac{dC(S)}{dS} . \quad (2.104)$$

This result indicates that the quantity $\Theta_0(v, C(S))$ is not exactly corresponding to some sort of characteristic

temperature such as the Debye temperature.

In order to calculate the specific heat at constant volume, we will first calculate the differential of temperature as

$$\begin{aligned} \frac{dT}{T} &= 2 \frac{d\Theta_0(v, S)}{\Theta_0(v, S)} - \frac{d\Theta(v)}{\Theta(v)} + \frac{\frac{d^2 C}{dS^2}}{\frac{dC}{dS}} dS \\ &= \left[\frac{2}{\Theta_0} \left(\frac{\partial \Theta_0}{\partial v} \right)_S - \frac{1}{\Theta(v)} \frac{d\Theta(v)}{dv} \right] dv + \left[\frac{2}{\Theta_0} \left(\frac{\partial \Theta_0}{\partial S} \right)_v + \frac{\frac{d^2 C}{dS^2}}{\frac{dC}{dS}} \right] dS \end{aligned} \quad (2.105)$$

From this equation, specific heat at constant volume is given by

$$C_v = \frac{1}{\frac{\frac{d^2 C}{dS^2}}{\frac{dC}{dS}} - \frac{\Theta_0}{\Theta} \frac{dC}{dS} \int^v \rho \gamma_1(v') \Theta(v') dv'} \quad (2.106)$$

It is shown from this expression that the specific heat at constant volume is not a function of entropy only, that is the case for the harmonic approximation. The first parenthesis of the second line of Eq.(2.105) is proved to be equal to $-\rho\gamma$ calculated from Eq.(2.89).

The new thermal variable $C(S)$ is shown to be determined by mechanical variables, pressure and volume, i.e., as

$$\frac{dC(S)}{C^2(S)} = \frac{\Theta(v)}{\varepsilon_T(p, v)} \left[d\varepsilon_T(p, v) + p_T dv \right], \quad (2.107)$$

which is derived from Eq.(2.103) and Eq.(2.102) combined within a thermodynamic identity. Where thermal internal energy $\varepsilon_T(p, v)$ is given by solving Eq.(2.93) as a quadratic equation for $\varepsilon_T(p, v)$ as,

$$\varepsilon_T = \sqrt{\left| \frac{\gamma_{00}(v)}{2\gamma_1(v)} \right|^2 + \frac{p - p_c(v)}{\rho\gamma_1(v)}} - \frac{\gamma_{00}(v)}{2\gamma_1(v)}. \quad (2.108)$$

Eq.(2.107) combined with Eq.(2.108) indicates that the thermal variable $C(S)$ introduced in this analysis can be determined only by the mechanical variables, p and v . In this sense, the situation is the same as the harmonic case described in the previous section. It is again noteworthy that this variable $C(S)$ is only one thermal variable that can be determined by the pure mechanical variables. So, this variable can link the mechanical variables to the other thermal variables like temperature and entropy. Another caloric equation of state or microscopic model, however, is required to estimate the temperature and entropy.

Although the assumption of Eq.(2.89) is considered not to be of universal form, it may cover almost all the pressure region of interest. In this sense, the results obtained in this analysis seem to be quite universal. Extreme contribution of anharmonicity in very high temperature states at extreme high pressure can be replaced by another approach which takes account of various phase transformations. In this sense, this

discussion does not aim at the formulation of the equation of state for extreme wide range of states. At least this theory gives evidence that the variable $C(S)$ might be a fundamental thermal variable even in the anharmonic case.

We have to mention that very high temperature causes the excitation of electrons to higher energy states, which will alter the lattice potential function, and electronic energy will give appreciable contribution to the total internal energy of the substance. Above analysis will be used to simulate these behaviors only for the case that the electronic contribution is smaller than that of lattice vibration. Further analysis of the inclusion of the electronic energy will be presented in the next section.

2.5. Three Term EOS at high pressures and temperatures

2.5.1. Equation of state of matter at extremely high pressures and temperatures attained by very strong shock compression

To describe the extremely high pressure states of solids, the three term equation of state has been used in several circumstances. (Al'tshuler 1960, Zel'dovich and Raizer 1966, Zharkov and Kalinin 1971, Eliezer et al 1986) This is an intuitive assumption that the total pressure and total internal energy are composed of the cold contribution, the lattice thermal contribution and the electronic contribution. The electronic contribution can be imaged in the case of metals. Since in metallic elements, free electrons may acquire thermal energy, which could be a part of the internal energy of metals. The situation can safely be approximated by the statistical mechanical theory of Fermi gas. Their specific heat, the corresponding pressure can then be calculated in the framework of the theory. In very low temperatures, electronic specific heat is a dominant contribution to the total specific heat of metals, since the electronic specific heat is proportional to temperature, while lattice specific heat is proportional to the third power of temperature.

Situation will change with temperature. Lattice contribution may become the second largest contribution of the internal energy of condensed substances. This is the case at room temperature. Strong compression of materials up to several tens of GPa, and to several thousand Kelvin, brings the substances to a high energy density states, which can be described by almost two major contributions of cold and lattice contribution, that is described in several previous sections.

Situation changes again with further temperature increase. Very high pressure and very high temperature state of condensed substance can be realized by the strong shock compression of solids. Shock pressures of more than several hundreds of GPa, electronic contribution will increase again to a value which is comparable to that of lattice vibration. This is simply due to the fact that the lattice specific heat at very high temperature have almost constant value, while the electronic specific heat is supposed to be still proportional to temperature. In other words, the lattice thermal energy is proportional to temperature, while electronic energy is proportional to the square of temperature. At extremely high temperatures of more than several electron volts (several tens of thousand Kelvin, i.e., Fermi temperature), electronic contribution dominates that of lattice thermal contribution.

How can we imagine the states of electrons and motions of ions, the constituents of the substance? At such a high temperature, condensed substances can be described by the picture of lattice vibration and free electrons. If the extremely high temperature is associated with a very strong compression of lattice, the above picture may not be altered appreciably. To describe the high temperature and high pressure state of solid materials other than metals, the same concept of three term equation of state has been assumed. The equation of state is based on the same physical assumption of electron gas.

In this section, we will therefore start the discussion of pure electron gas and its equation of state at high pressure with special emphasis to define a corresponding new thermal variables for the electron gas.

2.5.2. Equation of state of electron gas

Consider an ideal Fermi gas. (Eliezer et al 1986) Internal energy of the Fermi gas, its pressure, and its specific heat can be found in many books on the statistical mechanics as

$$C_{ve} = \beta T \quad (2.109)$$

$$\varepsilon_e = \frac{1}{2} \beta T^2 \quad (2.110)$$

$$p_e = \rho \gamma_e \varepsilon_e = \frac{\gamma_e}{v} \frac{1}{2} \beta T^2 \quad (2.111)$$

where suffix e denotes the contribution due to electronic excitation. The formulae are valid for the Fermi gas whose temperature is less than the Fermi temperature. Since the electronic Grüneisen parameter is defined as in Eq.(2.111) and not by Eq.(1.1), it should be a function of volume only. Its value for ideal electron gas is $2/3$, so in this case, the pressure is given by

$$p_e = \rho \gamma_e \varepsilon_e = \frac{1}{3} \rho \beta T^2 \quad (2.112)$$

The possible volume dependence of parameters appeared in these expressions is examined in later sections.

Entropy for the system are also given by

$$S_e = \beta T \quad (2.113)$$

which is equal to the specific heat. Due to this fact, the electronic Grüneisen parameter is again restricted to be a function only of volume as shown in Sec.2.1.

2.5.3. Physical models for the three term EOS and underlying assumptions

Al'tschuler et al have presented an equation of state model to describe high pressure high temperature shocked state including the contribution of free electrons,

$$\varepsilon = \varepsilon_c(v) + \varepsilon_T(v, T) + \varepsilon_e(v, T) \quad (2.114)$$

$$\begin{aligned} p &= p_c(v) + p_T(v, T) + p_e(v, T) \\ &= p_c(v) + \frac{\gamma_T}{v} \varepsilon_T(v, T) + \frac{\gamma_e}{v} \varepsilon_e(v, T) \end{aligned} \quad (2.115)$$

where the suffix e denotes the contribution of free electrons induced by extremely high temperature. (Al'tshuler 1960, Zel'dovich and Raizer 1966, Zharkov and Kalinin 1971, Eliezer et al 1986) Internal energy and pressure is assumed to be composed of three terms, cold, lattice and electronic contribution. The equation is, therefore, called 3-term equation of state. In the pressure equation, two Grüneisen parameters are also defined.

In the following, thermodynamic aspects as well as its consistency is discussed. By differentiating Eq. (2.114) with respect to temperature under constant volume, we have the specific heat at constant volume

$$C_v(v, T) = C_{vT}(v, T) + C_{ve}(v, T) \quad (2.116)$$

In this equation, it is apparent that specific heat is composed of lattice and electronic contribution. If the thermodynamic definition of the Grüneisen parameter is used, we need to evaluate the change in pressure and internal energy along an isochoric. That is, under the constraint, $dv=0$, the change in the specific internal energy and pressure can be read

$$\begin{aligned} d\varepsilon &= d\varepsilon_T(v, T) + d\varepsilon_e(v, T) = C_v(v, T) dT \\ &= C_{vT}(v, T) dT + C_{ve}(v, T) dT \end{aligned} \quad , \quad (2.117)$$

$$\begin{aligned}
dp &= dp_T(v, T) + dp_e(v, T) \\
&= \frac{\gamma_T(v)}{v} d\varepsilon_T(v, T) + \frac{\gamma_e(v)}{v} d\varepsilon_e(v, T) \\
&= \frac{\gamma_T(v)}{v} C_{vT}(v, T) dT + \frac{\gamma_e(v)}{v} C_{ve}(v, T) dT \\
&= \left[\frac{\gamma_T(v)}{v} C_{vT}(v, T) + \frac{\gamma_e(v)}{v} C_{ve}(v, T) \right] dT
\end{aligned} \tag{2.118}$$

In the derivation of this equation, two Grüneisen parameters are supposed to be a function only of volume, since the parameters are introduced not by the thermodynamic definition, Eq.(1.4), but in the equation of state by Eq.(2.115). Thermodynamically defined Grüneisen parameter for the system is calculated by using the definition, Eq.(1.4) as

$$\gamma = v \left(\frac{\partial p}{\partial \varepsilon} \right)_v = \frac{\gamma_T(v) C_{vT}(v, T) + \gamma_e(v) C_{ve}(v, T)}{C_{vT}(v, T) + C_{ve}(v, T)} \tag{2.119}$$

Overall Grüneisen parameter γ is given by a weighted sum of two Grüneisen parameters. In order to investigate the consistency of these relationship, we will then examine the relationship, Eq.(2.1). In this case, Eq.(2.1) can be rewritten as

$$\begin{aligned}
\frac{dT}{T} &= -\frac{\gamma}{v} dv + \frac{1}{C_v} dS \\
&= -\frac{1}{v} \left[\frac{\gamma_T C_{vT} + \gamma_e C_{ve}}{C_{vT} + C_{ve}} \right] dv + \frac{1}{C_{vT} + C_{ve}} dS
\end{aligned} \tag{2.120}$$

By multiplying the total specific heat, we have

$$\left[C_{vT} + C_{ve} \right] \frac{dT}{T} = -\frac{1}{v} \left[\gamma_T C_{vT} + \gamma_e C_{ve} \right] dv + dS \tag{2.121}$$

Entropy change in this system stems from lattice vibration and acquiring energy by free electrons. The entropy change in this system is assumed to be the sum of the contributions from lattice vibration and from the electronic.

$$dS = dS_T + dS_e \tag{2.122}$$

By substituting this equation to the entropy term in Eq.(2.121), one may see that lattice and electronic contribution can be split up to the equation of the same form

$$C_{vT} \frac{dT}{T} = -\frac{\gamma_T C_{vT}}{v} dv + dS_T, \tag{2.123}$$

$$C_{ve} \frac{dT}{T} = -\frac{\gamma_e C_{ve}}{v} dv + dS_e, \quad (2.124)$$

These equations give rise to the same form as Eq.(2.1), and eventually have the same Maxwell relationships. Thus we have the equation for the electronic contribution

$$\frac{1}{v} \left(\frac{\partial \gamma_e(v, S_e)}{\partial S_e} \right)_v = \frac{1}{C_{ve}^2(v, S_e)} \left(\frac{\partial C_{ve}(v, S_e)}{\partial v} \right)_{S_e} \quad (2.125)$$

In the next section, this relation leads to the conclusion that electronic Grüneisen parameter γ_e must also be a function only of volume, which is a consequence of the first assumption of introducing the electronic Grüneisen parameter by Eq.(2.115).

2.5.4. Electronic Grüneisen parameter

The coefficient β as well as the electronic Grüneisen parameter may change upon compression. (Zharkov and Kalinin 1971, Eliezer et al 1986) In this case, electronic terms can be written as

$$\varepsilon_e(v, T) = \frac{1}{2} \beta(v) T^2 \quad (2.126)$$

$$p_e(v, T) = \frac{\gamma_e(v)}{v} \frac{1}{2} \beta(v) T^2 \quad (2.127)$$

Eq.(2.127) is an equation of state for the electronic contribution in terms of p - v - T , i.e., thermic equation of state. This equation of state has a constraint on the ε - v - T (caloric) equation of state through the thermodynamic identity

$$\left(\frac{\partial \varepsilon}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p \quad (2.128)$$

By inserting Eq.(2.126) and (2.127) into Eq.(2.128), we have the differential equation for β ,

$$\frac{d\beta(v)}{dv} = \frac{\gamma_e(v)}{v} \beta(v), \quad (2.129)$$

which is integrated to be

$$\beta(v) = \exp \left[\int^v \frac{\gamma_e}{v} dv \right] \quad (2.130)$$

Again we can define a characteristic temperature function as

$$\Theta_e(v) = \exp \left[- \int^v \frac{\gamma_e(v)}{v} dv \right] \quad (2.131)$$

Characteristic temperature function may have its counterpart, the new entropy function, $C_e(S_e)$. By

noting the expression for electronic entropy, Eq.(2.113), Eq.(2.126) can be rewritten to

$$\begin{aligned}\varepsilon_e(v, T) &= \frac{1}{2} \beta(v) T^2 = \frac{1}{2} \frac{(\beta(v) T)^2}{\beta(v)} \\ &= \frac{1}{2} \frac{S_e^2}{\beta(v)} = \Theta(v) C(S_e)\end{aligned}\quad (2.132)$$

where the corresponding new thermal variable is defined as

$$C(S_e) = \frac{1}{2} S_e^2 \quad (2.133)$$

There are discussions concerning the behavior of the electronic Grüneisen parameter upon compression. Change in value is estimated to be relatively gradual, so that sometimes γ_e is simply assumed to be a constant. In this case, function $\beta(v)$ can be given by

$$\beta(v) = \beta(v_0) \left(\frac{v}{v_0} \right)^{\gamma_e} = \beta_0 \left(\frac{v}{v_0} \right)^{\gamma_e} \quad (2.134)$$

By using this equation, electronic contributions can be rewritten to

$$\varepsilon_e = \frac{1}{2} \beta_0 \left(\frac{v}{v_0} \right)^{\gamma_e} T^2 \quad (2.135)$$

$$\begin{aligned}p_e &= \frac{\gamma_e}{v} \varepsilon_e = \frac{\gamma_e}{v} C(S_e) \Theta_e(v) \\ &= \frac{\gamma_e}{v} \frac{1}{2} \beta_0 \left(\frac{v}{v_0} \right)^{\gamma_e} T^2\end{aligned}\quad (2.136)$$

$$C_{ve} = \beta_0 \left(\frac{v}{v_0} \right)^{\gamma_e} T, \quad (2.137)$$

These formulations are known to be in harmony with very high pressure data of up to several hundred GPa region obtained by shock wave method. In the region of further increase in pressure or temperature, one may consider the atom models such as Thomas-Fermi or Thomas-Fermi-Dirac models.

Chapter 3 Shock Thermodynamics

This chapter is devoted to the basics of shock compression physics followed by various numerical examples of equation of state (EOS) calculations based on the shock wave data. Part of the calculations, especially the behavior of the Grüneisen parameter, etc were already displayed in chapter 2. There, we already have used shock wave data to calculate γ . In the calculation, it is also possible to obtain some of the variables other than Grüneisen parameter.

Since the Grüneisen type equation of state is not a complete equation of state in the sense of equilibrium thermodynamics, it cannot describe all the thermodynamic behaviors of substance. For example, calculation of temperature is impossible only by the Grüneisen EOS. A model for the specific heat is also a necessary information for the temperature calculation. As is noted later, the Grüneisen EOS contains enough information on the isentropic change of state, isentropes and isotherms have relatively larger discrepancies in their calculation using Grüneisen EOS.

Theories or models to estimate what kind of variables depend on the variables to be calculated. Various combinations of used models at least together with the Grüneisen type equation of state are summarized already in Fig. 2.1.

In this chapter, calculations in zone 3 and zone 4 in Fig. 2.1 are presented with full use of the shock wave data. Later, we will see the procedures of calculations in zone 3 and zone 4 is quite different.

3.1. Thermodynamics of Shock Hugoniot

3.1.1. Shock jump conditions

In this chapter, we will discuss the high pressure high temperature states attained by strong shock compression of solids. Shock compressed data for condensed substance is very important not only for its interests in physics, but also for the precision of the attained state variables due to the reliability of the data. High precision of shock wave data stems from the application of the conservation laws across shock transition. Shock-compressed states of matter apparently depend on the properties of matter, especially the equation of state for the material. Various numerical examples of the equation of state and its parameters of several materials attained by shock compression are presented in this chapter.

Shock compressed states or its succession, shock Hugoniot curve is one of most reliable curves in the state surface of matter at high pressures and temperatures. Most of the calculations of EOS, therefore made along this curve.

As stated in chapter 1, the Grüneisen type equation of state is quite suitable to describe flow problems including shock wave propagation. In this sense, we will start here with the discussion of shock transition.

Calculations of EOS in this chapter is focused on the Grüneisen EOS with the Grüneisen law, i.e., $\gamma = \gamma(v)$, and consequently, $C_v = C_v(S)$. According to Fig.2.1, the situation of assumptions corresponds to zone 2, and procedures of estimating physical parameters depend on the models of γ used and also that of C_v used. The number of quantities determined simultaneously by the integration of differential equations depends on the combination of the assumed models for γ without a model for C_v . These situations will be explained later in this chapter.

At shock wave front, the state of material changes very drastically from the uncompressed state to highly compressed state. Thickness of the shock rise is very thin but still has finite value. Structure of shock rise is determined by the balance of steepening and energy dissipation. Steepening arises due to the non-linearity of the mechanical property of matter, while very steep distribution of stress, velocity and temperature causes irreversible flow of several quantities. This is one of the most interesting physics problems in the shock wave science, but we will not discuss this topic in this book in detail. Because the topic requires unknown transport properties of solid materials at high pressures and temperatures as well as the equation of state at high pressure.

Conservation equations at the shock front is common for shock transition in condensed media and in fluids including gases. Let us consider a plane shock wave driven by the piston motion at the origin at time 0. Situation is schematically shown in Fig. 3.1.

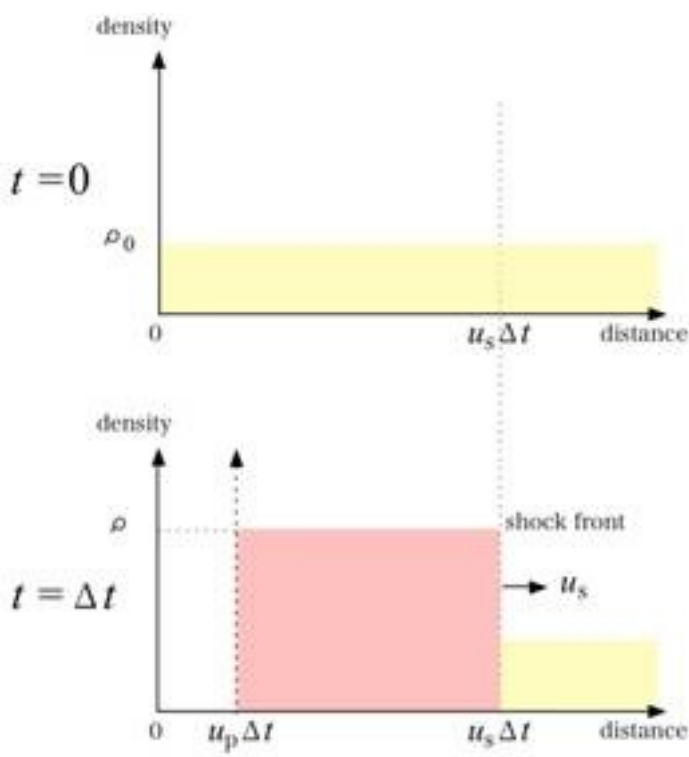


Fig. 3.1 Mass conservation schematic

The upper figure shows the distribution of density just before the piston motion, and the lower figure shows that after Δt time passed. At this time increment, piston compresses the material to the state with the increase in density from ρ_0 to ρ . Higher density region expands as the piston motion, thereby form a shock wave front schematically shown in Fig. 3.1. In this case, material quantity in the compressed region between the shock front and the piston with the density ρ must be equal to that contained in the region between the origin and the shock front of initial density ρ_0 . The resultant expression of mass conservation is written as

$$\rho_0 A u_s \Delta t = \rho A (u_s - u_p) \Delta t \quad (3.1)$$

where A denotes the cross section to the direction of shock propagation. We assume the situation that the wave propagation is plane and also steady, and shock front rise has enough steepness. These constraints, however, for the jump condition to hold is not quite tight. Eq.(3.1) can be rewritten to a simpler form as

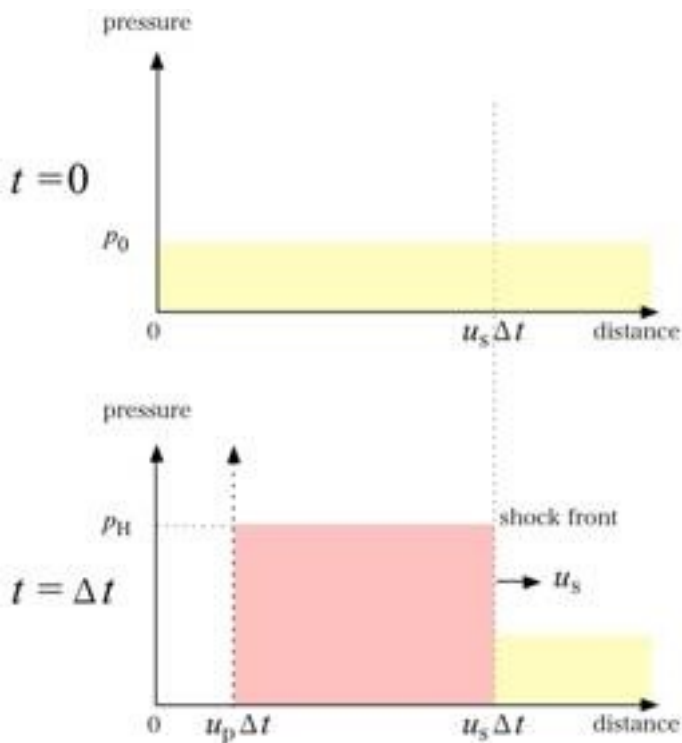


Fig. 3.2 Momentum conservation schematic

$$\rho_0 u_s = \rho (u_s - u_p) \quad (3.2)$$

Similar conservation equations for the momentum and also for energy can be obtained by the similar considerations. For momentum equation, one may consult Fig. 3.2. The momentum of the shock compressed region increases from zero to the value of mass in the region multiplied by the piston velocity. Because this region must move with the velocity just equal to the piston wall. This increment in momentum is supplied by the impulse at shock front, namely,

$$p_H - p_0 = \rho_0 u_s u_p, \quad (3.3)$$

where suffix H denotes the value just after the shock front. Note that shock-compressed state can be expressed by hydrostatic pressure instead of stress tensor. In real materials, they have finite elastic strength, and compressed state should be written by using stress tensor. In this book, descriptions of shock behavior are assumed to be represented by hydrostatic pressure. This assumption is the assumption that elastic strength is negligible at least very high pressure conditions brought about by shock compression. One may consult various bibliographies of shock compression science, if one has interests in strength contributions to shock compression behavior. Elastic-plastic behavior is treated in this book only in chapter 5 in flow problems including high pressure shock propagation.

The third equation of the energy conservation is also obtained by the help of Fig. 3.3. Increment in energy in the shock compressed region can be the sum of the increase in specific internal energy and in kinetic energy per unit mass multiplied by the mass contained in the region. This energy increase is supplied by the mechanical work of piston motion during the time interval Δt . The resultant expression for the energy conservation is given by

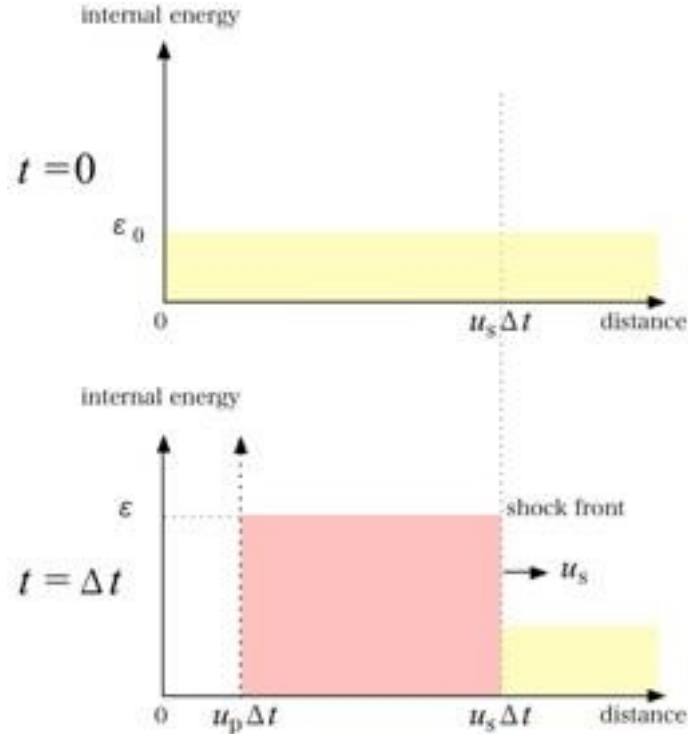


Fig. 3.3 Energy conservation schematic

$$\rho_0 u_s \left[\varepsilon_H - \varepsilon_0 + \frac{1}{2} u_p^2 \right] = p_H u_p \quad (3.4)$$

Now, we have three independent conservation equations at the shock front. These equations include

pressure, density and internal energy at shock front as thermodynamic state variables. We also have parameters for the wave propagation, shock front velocity and piston velocity. From now on, we call u_p the particle velocity because of the real flow velocity of materials in the shock compressed region.

In Eqs.(3.2)-(3.4), the shock jump conditions have parameters of initial state, i.e., initial density, initial pressure and initial internal energy, two of which are independent for the medium in thermodynamic equilibrium. By eliminating flow parameters from Eqs. (3.2)-(3.4), we have an equation connecting three thermodynamic state variables,

$$\varepsilon_H - \varepsilon_0 = \frac{P_H + P_0}{2} (v_0 - v) \quad (3.5)$$

This equation is called Rankine-Hugoniot equation. If one knows the equation of state in the form of $f(p, v, \varepsilon)=0$, one can combine Eq.(3.5) with EOS which results in a curve in EOS surface. This curve is called shock Hugoniot curve, a continuous state succession which can be attained by single shock compression of the substance. The curve is schematically depicted in Fig. 1.1.

One important care must be taken at this point for the non-equilibrium nature of shock compressed states. It is not a clear evidence that the shock compressed state is a thermodynamic equilibrium state. This topic contains various problems such as irreversible transport process occurring inside the shock rise, and the recombination of lattice from the initial crystalline structure to the deformed high density state of the substances. This is still unsolved problem, but empirically, equilibrium description of shock characteristics has been successful at least in the sense of first order approximation. We have to proceed further by assuming that the shocked state can be regarded as a thermodynamic equilibrium state until a clear evidence is found that this approximation is not the case and it has deep effects of the theoretical description.

3.1.2. Shock Hugoniot curve and Rayleigh line

By combining EOS with Rankine-Hugoniot relation, Eq.(3.5), we have the shock Hugoniot compression curve in the form

$$P_H = P_H(v; P_0, \rho_0, \varepsilon_0) \quad (3.6)$$

One may derive shock Hugoniot curve for any two parameters among shock wave parameters with initial state variables. Sometimes, all of these relationships can be called as shock Hugoniot.

As seen in Eq.(3.6), shock Hugoniot curve depends on the initial state variables. On EOS surface of a substance, shock Hugoniot curve starting from some initial state shifts higher temperature direction compared with isentrope centering the same initial state. By altering the initial state by changing any two of three initial state variables, a family of shock Hugoniot curves dually covers the EOS surface. In real materials, however, alteration of the initial states is very difficult and is quite limited. One possible way is the change in initial temperature.

In p-v plane, isotherm, isentrope and shock Hugoniot is schematically shown as in Fig. 3.4. In case of solid substance, one may not access the region lower than 0 K isotherm. Furthermore, we are concerned the shock compression whose attained pressure is much higher than atmospheric pressure, so that the initial pressure p_0 appeared in Eq.(3.1)-(3.6) is neglected. Initial pressure is important only when one may consider reflected shock wave at material interfaces, etc.

Among various experimental method, shock velocity and particle velocity are measured simultaneously to estimate shock Hugoniot states. Successive measurements of these two variables with changing shock loading conditions, it is empirically known that shock velocity and particle velocity satisfies the linear relation

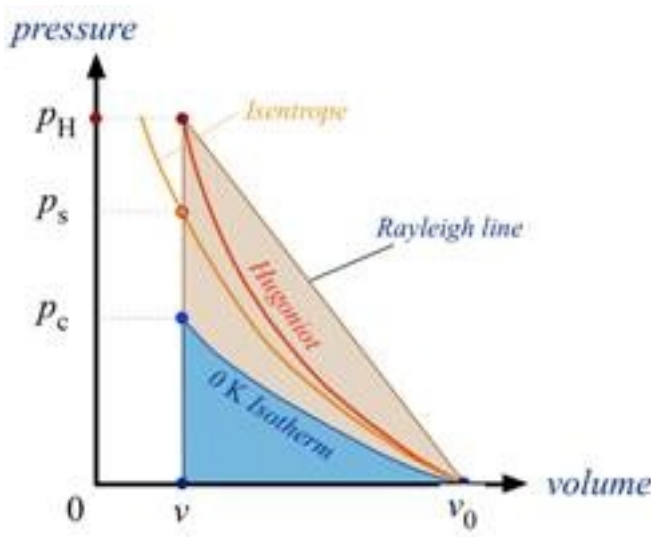


Fig. 3.4 Shock Hugoniot and Rayleigh line

$$u_s = A + Bu_p, \quad (3.7)$$

where A and B are the coefficients of this empirical relationship, and are regarded as material parameters. This relation can also be a shock Hugoniot curve as Eq.(3.6), and then it is used to derive shock Hugoniot curve for other choice of variables, which are, for example,

$$p_H = p_0 + \frac{\rho_0 A^2 \eta}{(1 - B\eta)^2}, \quad (3.8)$$

$$\varepsilon_H = \varepsilon_0 + \frac{A^2}{2} \left[\frac{\eta}{1 - B\eta} \right]^2, \quad (3.9)$$

where degree of compression is defined by

$$\eta = 1 - \frac{v}{v_0}. \quad (3.10)$$

These equations are derived by combining Eq.(3.7) with the conservation equations. From Eq.(3.8) or (3.9), compression curves have an asymptote by approaching the denominator to zero, i.e.,

$$\frac{v_{\lim}}{v} = \frac{B-1}{B}, \text{ or } \frac{\rho_{\lim}}{\rho} = \frac{B}{B-1} \quad (3.11)$$

These equations show shock pressure and therefore shock temperature increases to infinite as shock strength increases. The density limit is determined by the slope of shock-particle velocity Hugoniot. Shock Hugoniot for extremely high pressure region must be discussed by the precise measurement of shock parameters in each material and must be evaluated the shock-particle velocity relationship at that region.

By combining the conservation equations, particle velocity is related to shock velocity as

$$u_p = u_s \frac{\rho - \rho_0}{\rho} = u_s \left[1 - \frac{v}{v_0} \right] = u_s \eta, \quad (3.12)$$

and momentum equation becomes

$$p_H - p_0 = \rho_0 u_s u_p = \rho_0 u_s^2 \eta = \rho_0^2 u_s^2 (v_0 - v) \quad (3.13)$$

This equation is a straight line on p - v plane connecting the initial state and the shock compressed state for given values of shock pressure and volume with fixed shock velocity. The line is called Rayleigh line along which state changes from the initial state to the compressed state. In this explanation, the change of state is inside the very steep shock transition or shock rise, where non-equilibrium transport process proceeds. Since the conservation equations must be valid even between the non-equilibrium states inside shock structure and the initial state. Although we will not discuss the problem of this irreversible transition in this book. We will at least mention that in this non-equilibrium process, pressure must be replaced by the xx -component of stress tensor, where x denotes the coordinate axis parallel to the shock propagation direction.

Figure 3.5 and 3.6 shows the periodicity of the coefficients, A and B of the empirical Hugoniot relation. Figure 3.7 also shows the estimation of density limit for each substance. One may see apparent periodicity for each variable. Negative value of the limiting density ratio should be meaningless. In order to have a positive value of the ratio, parameter B must be larger than unity. We will discuss this periodicity later in this section.

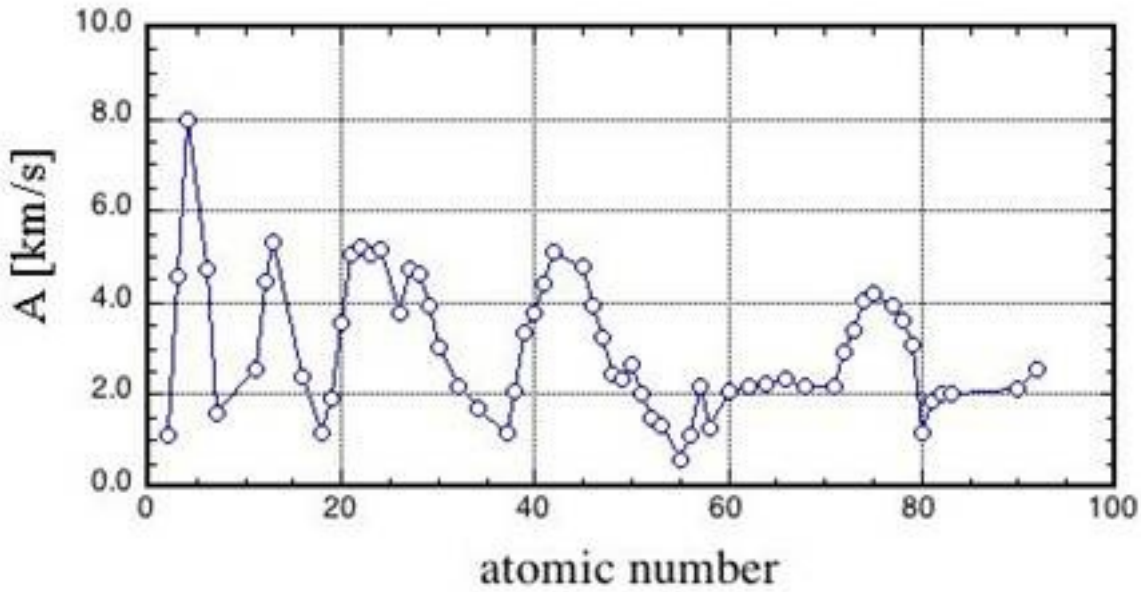


Fig. 3.5 Periodicity of coefficient A in the empirical linear relation.

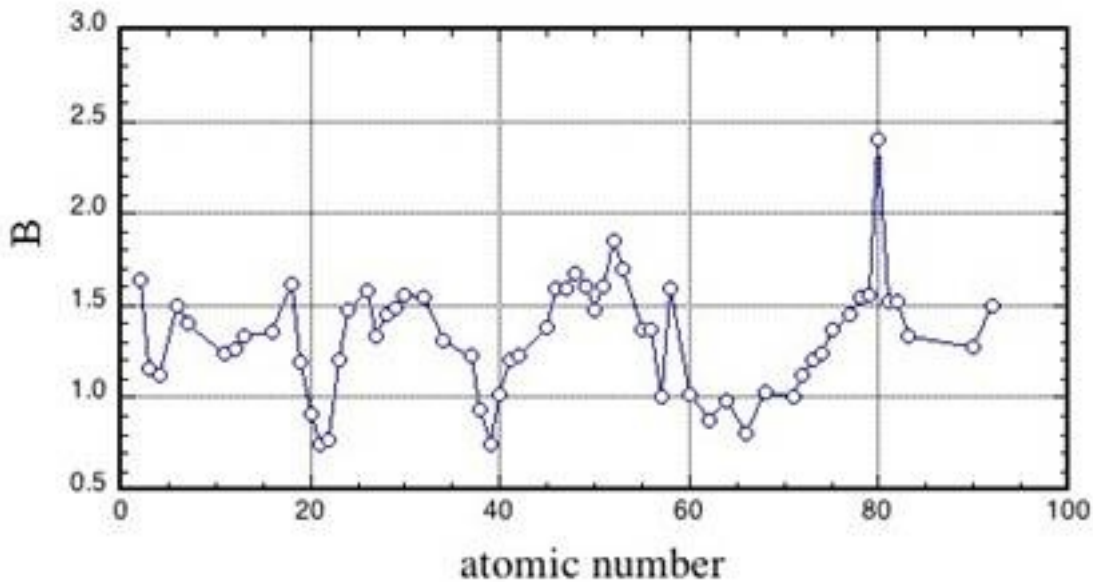


Fig. 3.6 Periodicity of coefficient B in the empirical linear relation.

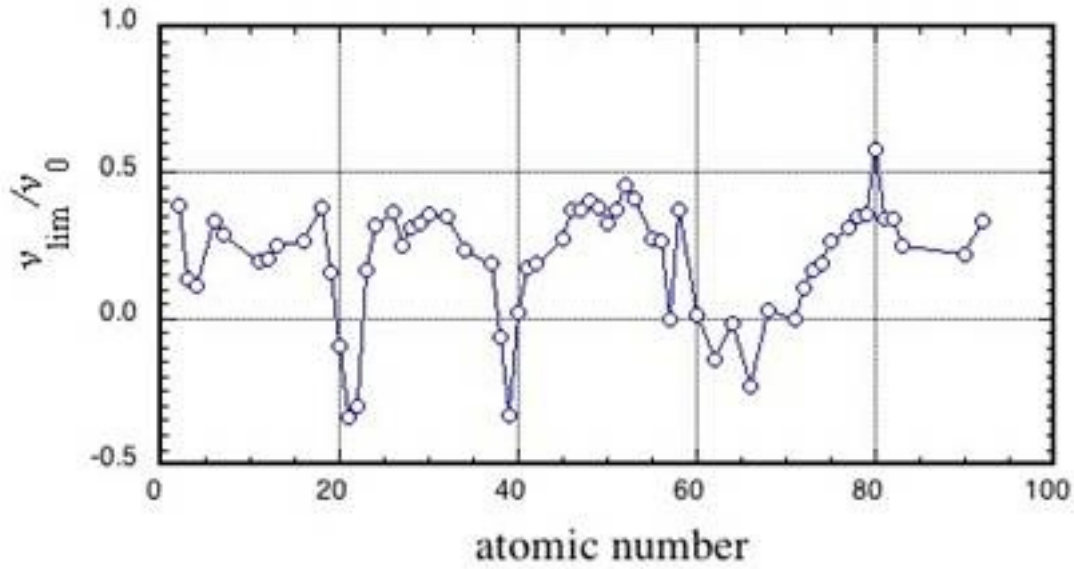


Fig. 3.7 Periodicity of density limit calculated by the empirical linear relation.

3.1.3. Quasi-static thermodynamic process along shock Hugoniot

Because of the high precision of shock measurement, shock Hugoniot compression curve on EOS surface is one of the most reliable information on the form of the state surface of the substance. This is the reason why thermodynamic quantities are calculated along shock Hugoniot curve. Shock Hugoniot curve, however, is not a successive state line along which any thermodynamic process is realized. But if the shock compressed states can be regarded as thermodynamic equilibrium states, one may imagine a quasi-static thermodynamic process along shock Hugoniot curve. In such a process, two states thermodynamically adjacent to each other must satisfy the jump conditions, Eq.(3.2)-(3.4) as well as EOS. Relationships between these states can be calculated by differentiating the jump conditions. First, we start with the mass conservation,

$$\rho_0 du_s = (u_s - u_p) d\rho + \rho (du_s - du_p) \quad (3.14)$$

We will now take the particle velocity u_p as independent variable and all other variables are written as a function of particle velocity. Or at least, we will describe all the variables in terms of shock velocity and particle velocity. For example, Eq.(3.14) can be rewritten as

$$\rho_0 \frac{du_s}{du_p} = (u_s - u_p) \frac{d\rho}{du_p} + \rho \left(\frac{du_s}{du_p} - 1 \right),$$

which will eventually be written to

$$\frac{d\eta}{du_p} = \frac{u_s - u_p \frac{du_s}{du_p}}{u_s^2} \quad (3.15)$$

Other expressions derived from the mass conservation will be

$$\frac{d \ln \rho}{du_p} = \frac{u_s - u_p \frac{du_s}{du_p}}{u_s(u_s - u_p)}, \quad (3.16)$$

or equivalently,

$$\frac{d\rho}{du_p} = \rho_0 \frac{u_s - u_p \frac{du_s}{du_p}}{(u_s - u_p)^2} \quad (3.17)$$

Next formulation is the momentum equation, and it sometimes combines with mass conservation. We have

$$dp_H = \rho_0 \left(u_s du_p + u_p du_s \right) = \rho_0 \left(u_s + u_p \frac{du_s}{du_p} \right) du_p \quad (3.18)$$

or

$$\frac{dp_H}{du_p} = \rho_0 \left(u_s + u_p \frac{du_s}{du_p} \right) \quad (3.19)$$

By combining Eq.(3.19) with Eq.(3.17), we have a slope of Hugoniot in p - v or p - ρ plane as

$$\frac{dp_H}{d\rho} = \frac{dp_H}{du_p} \frac{du_p}{d\rho} = \left(u_s - u_p \right)^2 \frac{u_s + u_p \frac{du_s}{du_p}}{u_s - u_p \frac{du_s}{du_p}} \quad (3.20)$$

Final formulation is the energy equation or the Rankine Hugoniot equation. By using Eq.(3.12), (3.15) and Eq.(3.19), differentiation of Eq.(3.5) gives the following expression for the change in thermal variable

$$\begin{aligned} T_H dS_H &= d\varepsilon_H + p_H dv \\ &= \frac{v_0}{2} \left[\eta dp_H - (p_H - p_0) d\eta \right] \\ &= \frac{u_p^2}{u_s} \frac{du_s}{du_p} du_p \end{aligned} \quad (3.21)$$

Along the shock Hugoniot curve, increase in entropy change is described by the increase in shock strength.

This equation is applied to the thermodynamic identity

$$\begin{aligned}
 dp &= \left(\frac{\partial p}{\partial \rho} \right)_S d\rho + \left(\frac{\partial p}{\partial S} \right)_\rho dS \\
 &= a^2 d\rho + \left(\frac{\partial p}{\partial \epsilon} \right)_v \left(\frac{\partial \epsilon}{\partial S} \right)_v dS \\
 &= a^2 d\rho + \frac{\gamma}{v} T dS
 \end{aligned} \tag{3.22}$$

where we define the local speed of sound in the first term. For the change in these variables along the Hugoniot curve, we have

$$\begin{aligned}
 dp_H &= a_H^2 d\rho + \frac{\gamma}{v} \frac{u_p^2}{u_s} \frac{du_s}{du_p} du_p \\
 &= a_H^2 \rho_0 \frac{u_s - u_p}{(u_s - u_p)^2} \frac{du_s}{du_p} du_p + \frac{\gamma}{v} \frac{u_p^2}{u_s} \frac{du_s}{du_p} du_p
 \end{aligned} \tag{3.23}$$

Formula for the local speed of sound just behind the shock front can be derived by combining Eq.(3.23) with Eqs.(3.19) and (3.20) as

$$\begin{aligned}
 a_H^2 &= \frac{dp_H}{d\rho} - \frac{\gamma}{v} \frac{u_p^2}{u_s} \frac{du_s}{du_p} \frac{du_p}{d\rho} \\
 &= \frac{(u_s - u_p)^2}{u_s - u_p \frac{du_s}{du_p}} \left[u_s + u_p \frac{du_s}{du_p} - \gamma \frac{u_p^2}{u_s - u_p} \frac{du_s}{du_p} \right]
 \end{aligned} \tag{3.24}$$

Sound velocity under compression is then determined by the shock Hugoniot, its slope and Grüneisen parameter. From this equation, it is apparent that measurement of sound velocity under compression may lead to the estimation of the Grüneisen parameter under compression. Several experiments have already reported.

Eq.(3.22) or (3.23) shows that the first term corresponds to the pressure increase by isentropic compression, while the second term corresponds to the pressure change due to entropy change. The entropy change is determined by or proportional to the value of Grüneisen parameter. Value of the entropy term is small for weak shocks due to their small entropy increase, while in very strong compression, very high temperature causes excitation of electrons or anharmonic effects which in turn causes the temperature dependence of Grüneisen parameter as well as volume effects. Eq.(3.24) is equivalent to Eq.(2.70) for $t=0$, i.e., Slater model for the Grüneisen parameter. Since, in this case, q_s is equal to the sound velocity.

In shock experiments, thermal contribution is smaller than cold contribution as schematically depicted in Fig. 3.8. Detailed calculations are shown in later section. We compare the contribution of internal energy, pressure and sound velocity, because they are derivatives along an isentrope in its order. Thermal contribution has relatively large in the shock pressure range of tens of GPa region, while thermal pressure is at most estimated to 10 %, and sound velocity contains thermal effects only around 5% or less. Even so, we need to measure velocity much higher precision than pressure, so that it is necessary to obtain velocity in very high precision in order to discuss the thermal contribution or thermodynamics under shock compression.

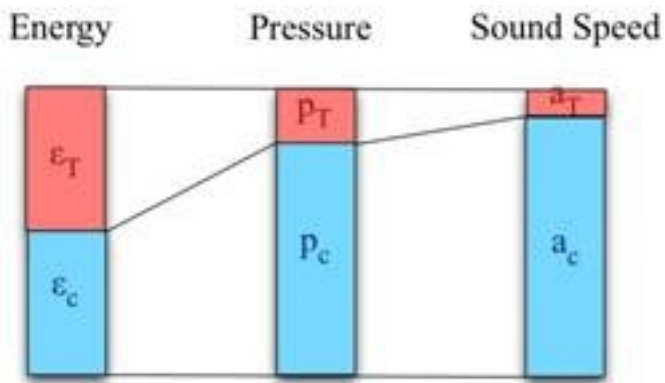


Fig. 3.8 Relative contribution of cold and thermal parts in internal energy, pressure and sound velocity.

Shock thermodynamics formulated so far is not limited to any shock Hugoniot function or any form of the EOS. Formulation is quite general. One may note, however, that application of the empirical linear relationship, Eq.(3.7) to formulae, Eqs.(3.15)-(3.24), leads to simpler formulae, and can be used to estimate various quantities on the shock Hugoniot states.

3.2. Cold Material Functions and New Thermal Variables

3.2.1. Procedure of the calculation of cold compression curves based on several models for the Grüneisen parameter

Due to the relative high precision of measuring pressure by shock compression experiments, many attempts have been made to reduce the shock Hugoniot data to obtain isothermal equation of state. (for example, Chijioke et al 2005) 300-K isotherm or 0-K isotherm (cold compression curve) is preferable in order to compare them with theoretically or experimentally determined isotherms. Our attempts introduced here are also inline with these approaches.

Prior to the display of numerical examples of various material functions and their change along Hugoniot curve, some of the fundamental assumptions used throughout this chapter. They are,

- (i) Grüneisen EOS is adopted for the material description under high pressures and temperatures,
- (ii) Grüneisen law is assumed, so that the Grüneisen parameter is a function of volume and the specific heat at constant volume is a function of entropy.
- (iii) Resultant theories belong to Zone 2 to Zone 4 in the diagram of Fig. 2.1.

It is convenient that a particular compression curve is defined as a reference compression curve. One of the candidates of the reference curves is the zero-Kelvin isotherm, i.e., cold pressure or cold internal energy or an isentrope centering at room temperature, zero pressure state. To obtain such curves, integration of Eq. (2.19) should be performed. In this section, procedure of obtaining such curves is shown. Prior to the integration of Eq.(2.19), boundary conditions of the starting initial states must be calculated. In order to obtain cold functions, it is necessary to have the values of

Hugoniot functions of pressure and internal energy, $p_H(v)$, $\varepsilon_H(v)$,

Initial specific volume or density at zero Kelvin and pressure, v_{00} or ρ_{00} ,

Initial specific internal energy at zero Kelvin and pressure, ε_{00} ,

Volume dependence of Grüneisen parameter, $\gamma(v)$,

where suffix 00 denotes the value at zero Kelvin.

In the following, an example of the calculation procedure for aluminum is shown. For Hugoniot functions, we assumed conventional linear relationship between shock velocity and particle velocity, Eq.(3.7). Shock pressure and specific internal energy are assumed to be described by Eqs.(3.8)-(3.10).

In order to estimate the values of volume and internal energy at zero Kelvin, the Debye model for the specific heat was assumed to evaluate the difference in values of these quantities at zero Kelvin and room temperature. Estimated values for aluminum are given below;

$$\rho_0 = 2.785 \text{ (g/cm}^3\text{)}, \quad v_0 = 0.359 \text{ (cm}^3\text{/g)},$$

$$\rho_{00} = 2.8177 \text{ (g/cm}^3\text{)}, \quad v_{00} = 0.3549 \text{ (cm}^3\text{/g)},$$

$$p_c(v_0) = -0.917 \text{ (GPa)}, \quad p_T(v_0, T_0) = 0.917 \text{ (GPa)},$$

$$p_c(v_{00}) = 0 \text{ (GPa)}$$

$$\varepsilon_c(v_0) = -0.1646 \text{ ((km/s)}^2\text{)}, \quad \varepsilon_T(v_0, T_0) = 0.1646 \text{ ((km/s)}^2\text{)},$$

$$\varepsilon_c(v_{00}) = 0 \text{ ((km/s)}^2\text{)},$$

For the models of the Grüneisen parameter, the following five different assumptions are considered. Most of the computations and comparisons are made by three theoretical models in Zone 3, and sometimes

results of the assumption (iv) in Zone 4 is added to compare them with those by theoretical models.

Zone 3

(i) Slater model, ($t=0$ as in Eq.(2.56)) (3.25)

(ii) Dugdale-MacDonald model, ($t=1$ as in Eq.(2.56)) (3.26)

(iii) Zubarev model, ($t=2$ as in Eq.(2.56)) (3.27)

Zone 4

(iv) $\rho\gamma = \rho_0\gamma_0 = \text{const}$ (3.28)

(v) $\gamma = \gamma_0 = \text{const}$, (3.29)

Three theoretical models used are derived from the close connection between cold specific internal energy and the Grüneisen parameter, and therefore the number of independent material function contained in the Grüneisen EOS must be unity. This means that in the calculations in Zone 3, calculation of the Grüneisen parameter inherently contains the calculations of cold functions such as cold internal energy and cold pressure. According to the introduction of new thermal variables, the calculation in Zone 3 made by this procedure leads to the material function of volume such as

cold internal energy,

cold pressure,

Grüneisen parameter,

Characteristic temperature.

In addition to these, some of the thermal variables such as

thermal internal energy,

thermal pressure,

new thermal variable $C(S)$

can also be calculated for any equilibrium state specified by (p,v) or by (ε,v) without any assumptions on the specific heat at constant volume.

Calculations in Zone 4 by the simple assumption of the behaviors of the Grüneisen parameter, calculation of the cold functions is independent of the Grüneisen parameter behavior, although the assumptions, Eq.(3.28), (3.29) have almost no physical meaning.

Numerical procedures and relationships between the assumptions and obtained quantities are summarized in Fig. 3.9. Since the calculational procedures in Zone 3 and in Zone 4 are different, they are described separately in later sections.

Zone 3 (3 theoretical models)		
$\epsilon_c(v) \Leftrightarrow \gamma(v)$ Differential Equation for $\gamma(v)$ 	Cold functions (O Kelvin isotherm)	
	1. Grüneisen parameter $\gamma(v)$ 2. Cold specific internal energy $\epsilon_c(v)$ 3. Cold pressure $p_c(v)$ 4. Characteristic temperature $\Theta(v)$	
Integration along Hugoniot	Thermal quantities	
	1. New thermal variables $C(S)$ 2. Thermal specific internal energy $\epsilon_T(v,T)$ 3. Thermal pressure $p_T(v,T)$	
Zone 4 (simple γ assumptions)		
$\gamma=\gamma(v) \Rightarrow \text{Char. Temp. } \Theta(v)$ Differential Equation for $\epsilon_c(v)$ 	Cold functions (O Kelvin isotherm)	
	1. Cold specific internal energy $\epsilon_c(v)$ 2. Cold pressure $p_c(v)$	
Integration along Hugoniot	Thermal quantities	
	1. New thermal variables $C(S)$ 2. Thermal specific internal energy $\epsilon_T(v,T)$ 3. Thermal pressure $p_T(v,T)$	

Fig. 3.9 Procedures of calculation and obtainable quantities with various assumptions without any assumptions on the specific heat at constant volume.

Some of the input data for selected materials are summarized in Table 3.1, although further data are cited from the tables in the Appendix. In this table, thermodynamic data is adopted as the value of Grüneisen parameter, but calculations using the theoretical models for the Grüneisen parameter does not use this value.

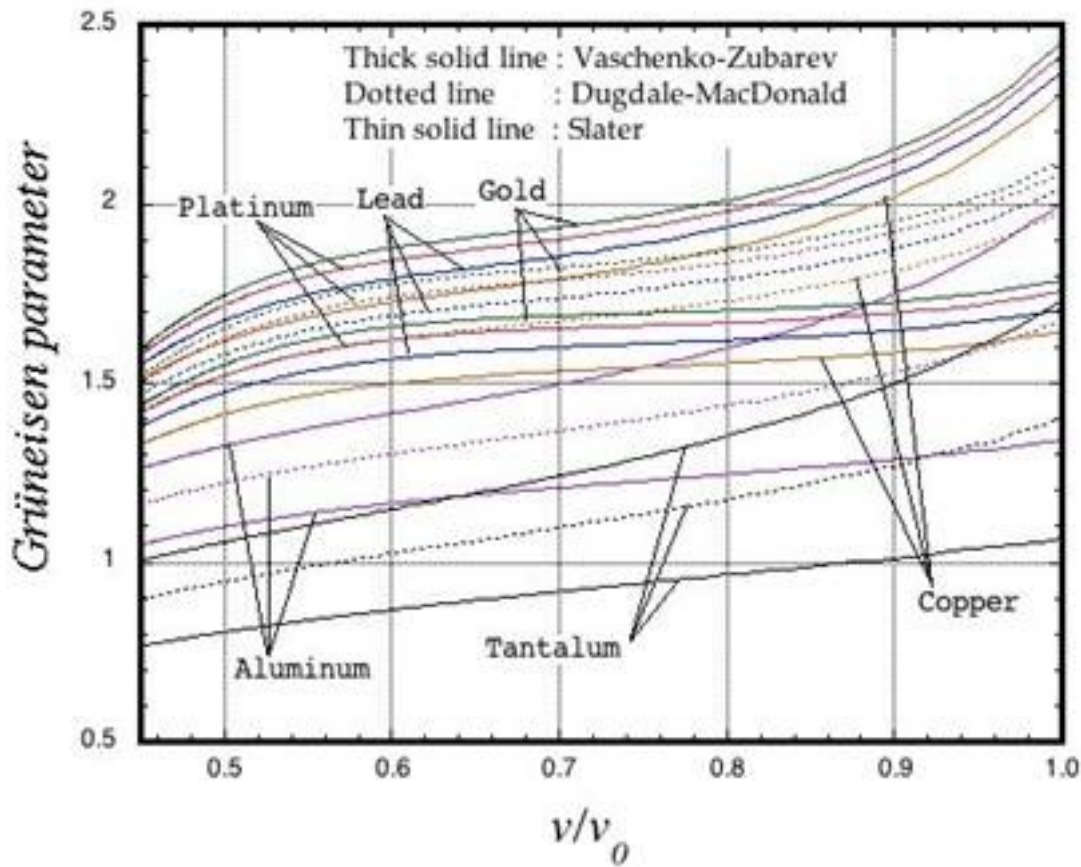
Table 3.1 Input material parameters for the calculation in chapter 3.

material	ρ_0 (g/cm ³)	A (km/s)	B	γ	Θ_D (K)
aluminum	2.785	5.328	1.338	2.0	394
copper	8.93	3.94	1.489	2.02	315
lead	11.34	2.03	1.52	2.74	105
tungsten	19.25	4.029	1.237	1.67	400
gold	19.28	3.080	1.560	2.99	165
platinum	21.47	3.598	1.544	2.74	240
tantalum	16.66	3.414	1.200	1.67	240

Since Hugoniot functions, Eq.(3.8), and (3.9) has an asymptote for definite value of specific volume, Eq. (3.11), numerical integration of Eq.(2.19) can be performed only up to the vicinity of the asymptotic value of specific volume. In the discussion in this chapter, we have no intense care about this limitation, since the states close to the density limit corresponds to extremely high temperature high pressure states, where electronic contribution or further effects prevails. This is out of the scope what we want to treat in this chapter. One may note that pressure volume points above these curves are allowed, since the cold compression curve corresponds to zero-Kelvin isotherm and also to zero-entropy isentropic curve of the material.

3.2.2. Numerical examples of cold functions based on three theoretical models for the Grüneisen parameter (Zone 3)

Figures 3.10 and 3.11 shows the calculated shock compression behaviors of the Grüneisen parameter, the characteristic (Debye) temperature, and cold pressure for several metals in Table 3.1. Plots of some of the Grüneisen parameter for these materials are the reproduction of the results cited in Chapter 2. During the course of the integration of Eq.(2.19), one may also calculate the characteristic temperature by Eq.(2.24). Since the integration is made along the Hugoniot curve, one may also obtain quantities on the Hugoniot such as the value of q_s by Eq.(2.70) and also $C(S_H)$ by the integration of Eq.(2.29) along the Hugoniot curve. This gives the estimate of the thermal part of the specific thermal internal energy ε_T by Eq.(2.23) and thermal pressure p_T by Eq.(2.18). In this procedure of calculation, cold functions, i.e., the specific cold internal energy e_c and the cold pressure p_c are calculated by the subtraction of thermal quantities from the values of specific internal energy and pressure on the shock-compressed states.



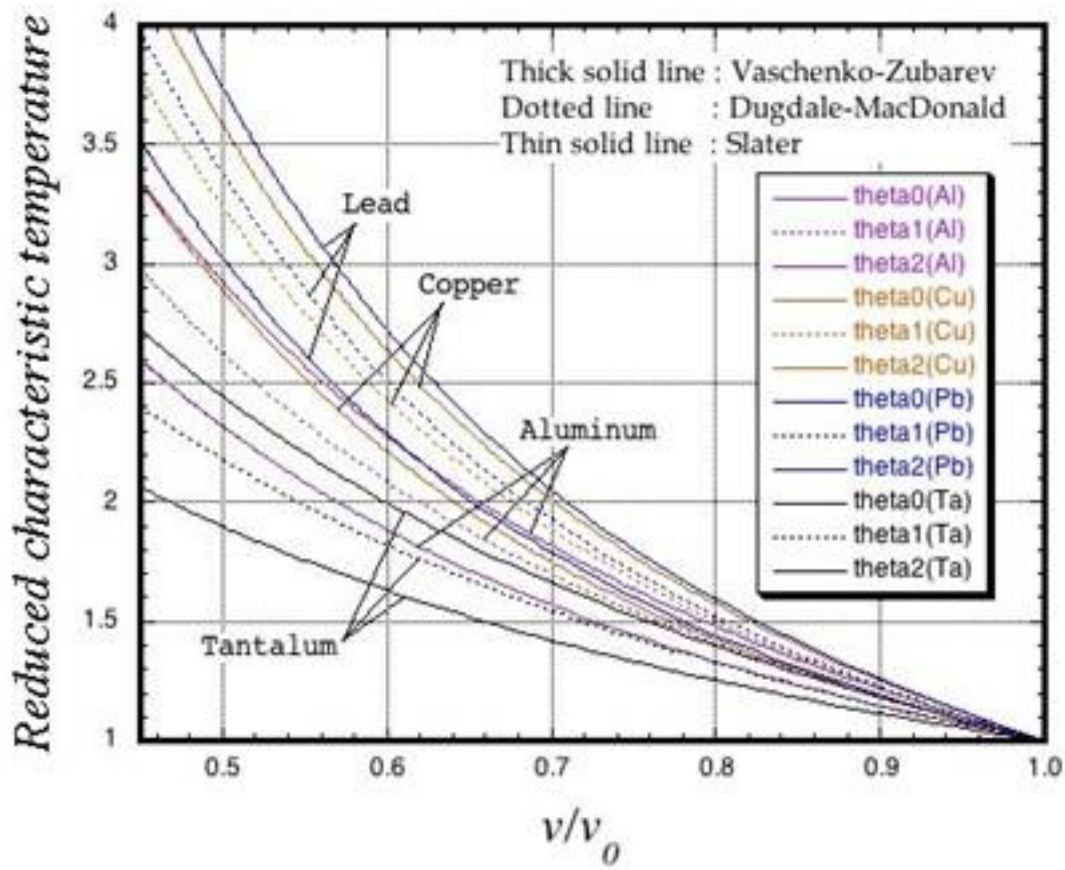


Fig.3.10 Grüneisen parameter and reduced characteristic temperature for several metals based on the three theoretical models for the Grüneisen parameter.

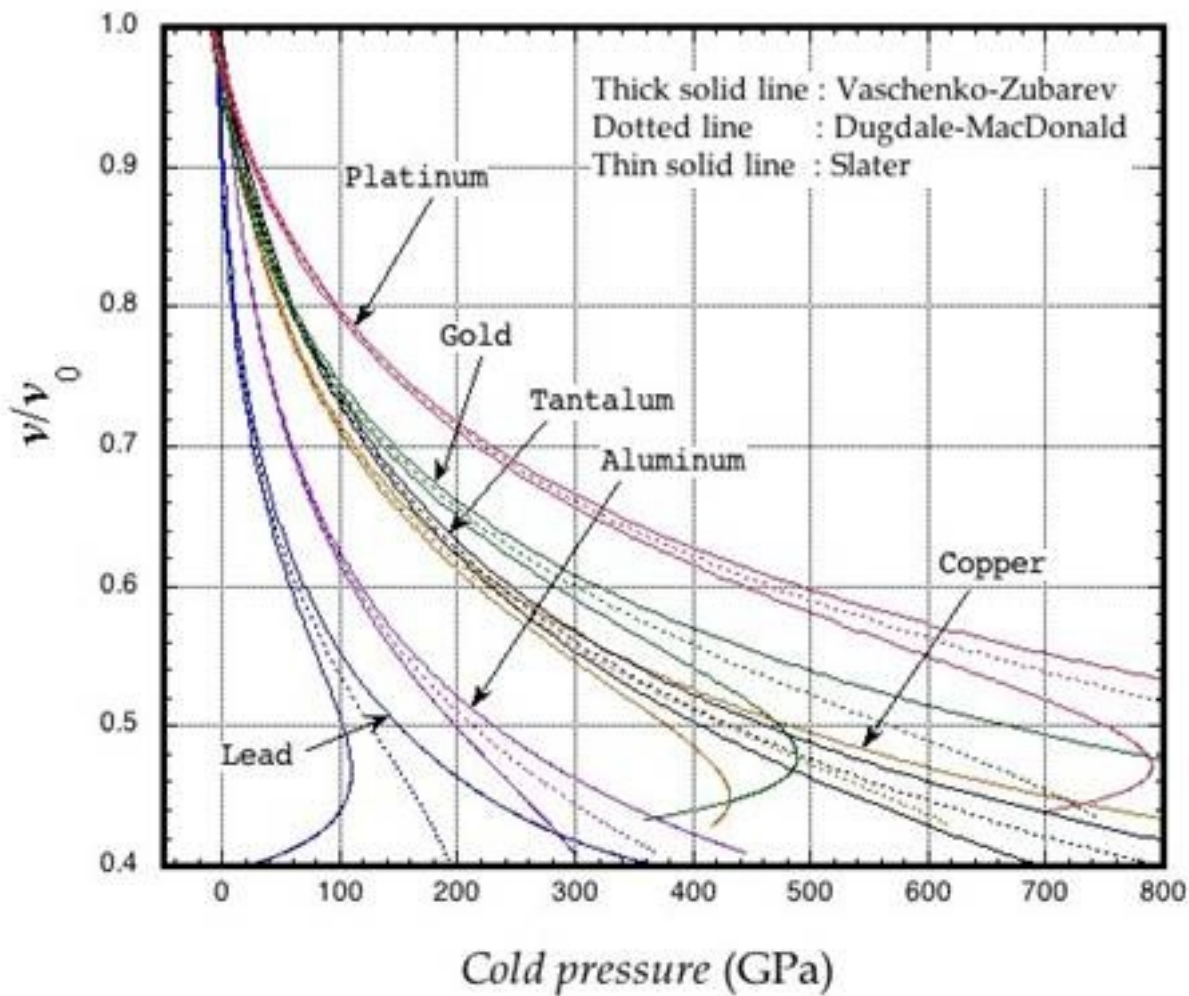


Fig.3.11 Cold pressure function for several metals based on the three theoretical models for the Grüneisen

parameter.

Numerical integration of Eq.(2.19) together with theoretical model for the Grüneisen parameter produces both thermal variables as well as cold variables. One may note that the present calculation completely neglect the electronic contribution which comes into significance in very high temperature region in shock data. We show Figs. 3.10, 3.11 only for the results of cold variables or the material functions assumed they are a function only of volume.

Grüneisen parameter and corresponding characteristic temperature for these materials are seen to depend on theoretical models, and the estimated value decreases from Slater to D-M to V-Z model in this order, or with increasing the parameter t . In this case, Slater model gives the largest value and V-Z model the smallest, and D-M model the intermediate. This order is reversed for the results of cold internal energy and cold pressure. The difference in values by the theoretical models looks quite small. In the comparison of pressure, one may see the difference in compressibility of the material. In the case of cold energy, we compare the specific internal energy. Results clearly show that internal energy per unit volume is larger for light metals.

Figure 3.12 shows the cold energy divided by the square of intercept A in the empirical linear relation of shock Hugoniot. In this figure, this reduced energy is found to quite similar in volume compression characteristics except for lead and tantalum.

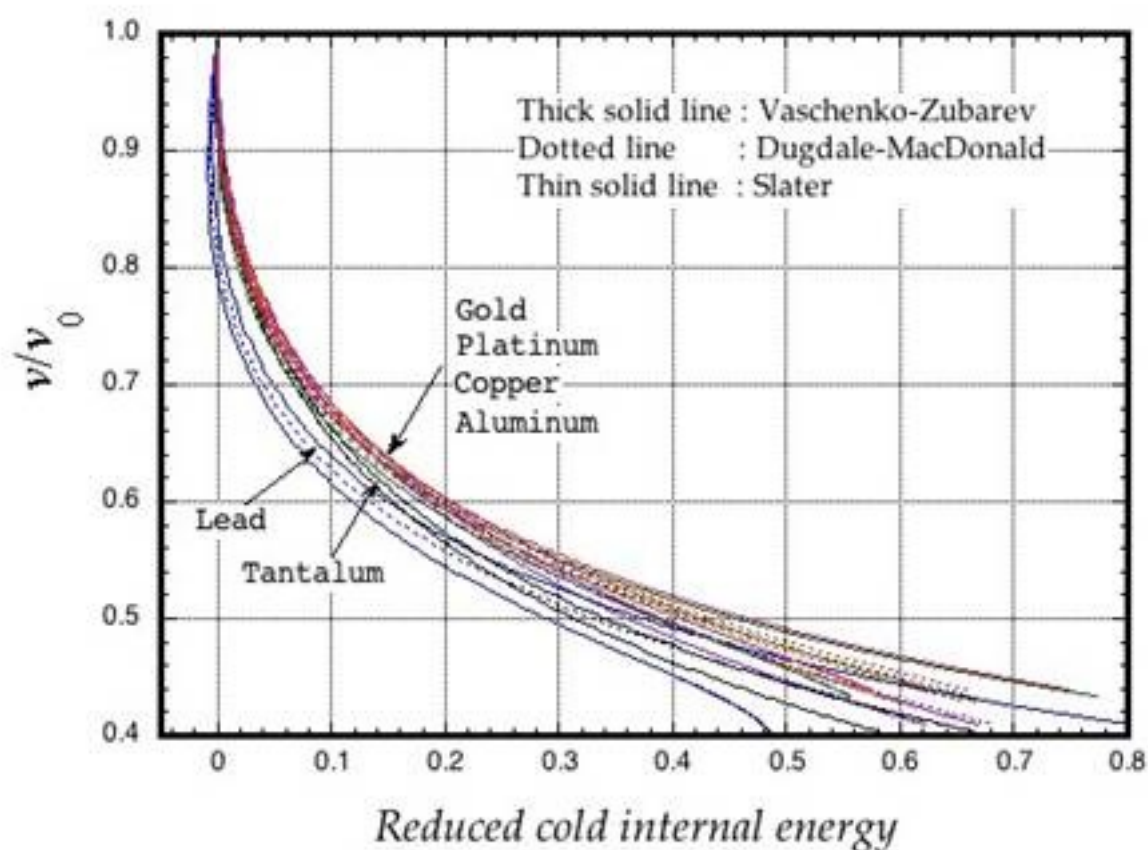


Fig.3.12 Reduced and specific cold internal energy for several metals based on the three theoretical models for the Grüneisen parameter.

3.2.3. Comparisons of cold functions based on three theoretical models for the Grüneisen parameter with theoretical calculations or experimental data (Zone 3)

Although it is still very difficult to measure the value of Grüneisen parameter under strong compression, we now have various theory or data for cold compression curve for various materials. They are, for example, the first principle based theoretical calculations, and high pressure data using diamond anvil cell

(DAC). In this section, results of present calculation are compared with these available data. (Greene et al, 1994, Dewaele et al 2004, Friedli and Ashcroft 1975, Lam and Cohen 1983, Albers et al 1985, Nellis et al 1988, Bercegeay and Bernard 2005) DAC data is based on the ruby pressure scale. This scale is compared with the data reduced from the shock wave data and also with the first-principle calculations. Although there is still a discussion on the reliability of the pressure scale used in DAC data, we will compare our calculations by three theoretical models with DAC data and the first principle based theoretical calculations.

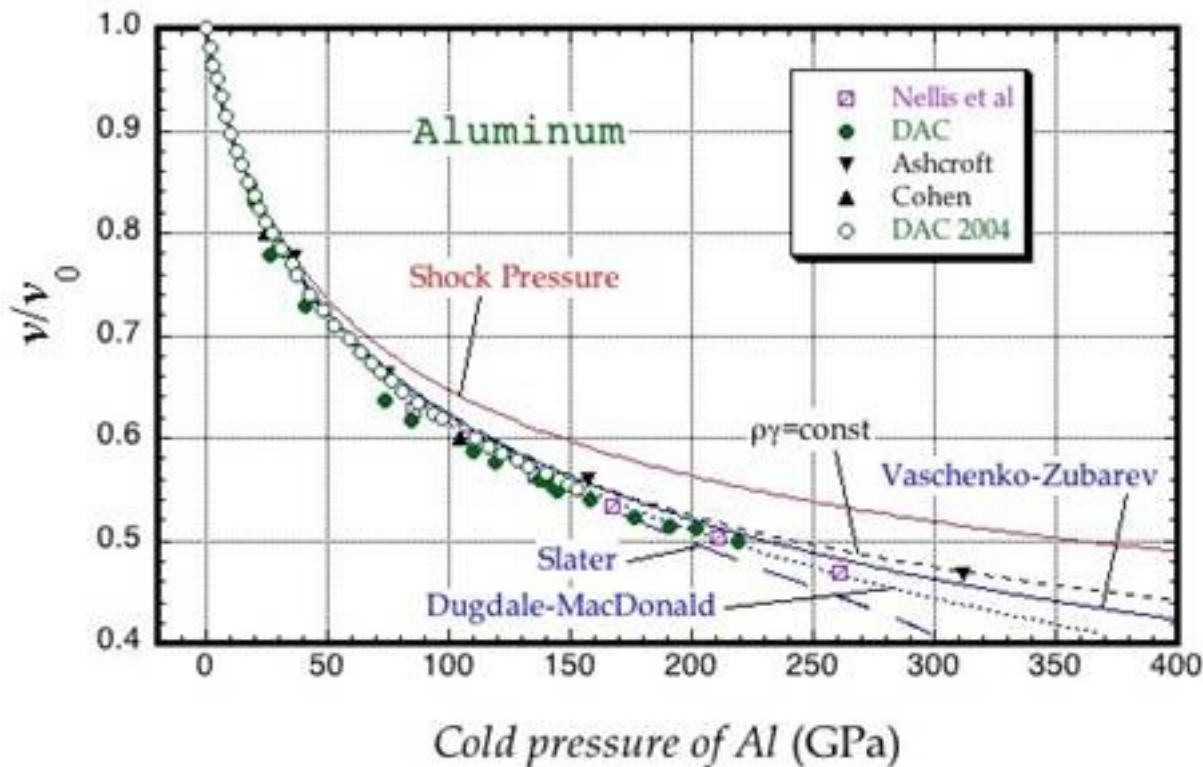
Figures 3.13, 3.14, 3.15 and 3.16 show cold pressure function for aluminum, copper, lead and tungsten with DAC data or first principle calculation. For all figures, in addition to the plot of wide pressure range, the same plot up to less than 200 GPa is shown in order to examine the lower pressure region, where DAC data is available. For reference, we add the calculation with $\rho\gamma=\text{const}$, and also the shock pressure in all the figures.

In Fig. 3.13, we compare the present calculation for aluminum with two DAC data obtained by different group, and also with theoretical predictions by several authors. Two kinds of DAC data for aluminum exhibit apparent discrepancy between them, and DAC data 2004 (Dewaele et al 2004) seems to be in harmony with the other theoretical predictions and present calculation. In case of aluminum, Slater model gives appropriate description at least in lower pressure region, while Dugdale-MacDonald model gives better explanation in higher pressure region. At least for cold pressure, $\rho\gamma=\text{const}$ assumption also gives no bad representation to the compression behavior. As shown in this figure, from Slater to Dugdale-MacDonald model with increasing pressure is only preferable in case of aluminum. The other examples of these comparison reveals that favorite model changes from Dugdale-MacDonald to Vaschenko-Zubarev model with increasing pressure.

In case of copper as you see in Fig. 3.14, calculated cold pressure curve as well as DAC data is best approximated by Vaschenko-Zubarev model rather than other theoretical models. In lower pressure region, difference between the results by three theoretical models or other calculations is quite small, and it is difficult to say which is better approximates the DAC data and other calculations. In this case, $\rho\gamma=\text{const}$ assumption also gives good approximation to DAC and theoretical results. Slater model, on the contrary, deviate drastically especially in very high pressure region.

Results of lead as in Fig. 3.15 give unique feature by its high compressibility. Theoretical calculations by Nellis et al (Nellis et al 1988) best coincide again with Vaschenko-Zubarev model and $\rho\gamma=\text{const}$ assumption.

For materials with little compressibility such as tungsten shown in Fig. 3.16, difference in results between each model is very small. It is therefore quite difficult to say which model or assumption is better than others by the comparison with experimental data.



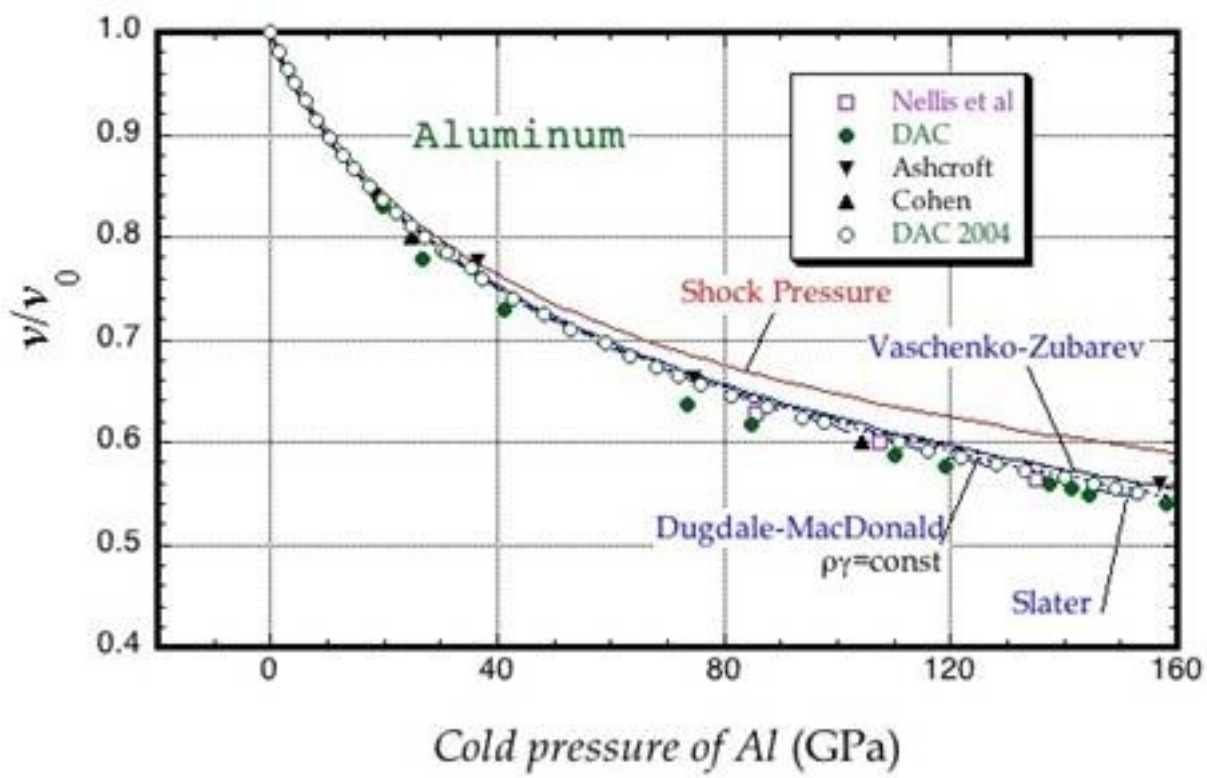
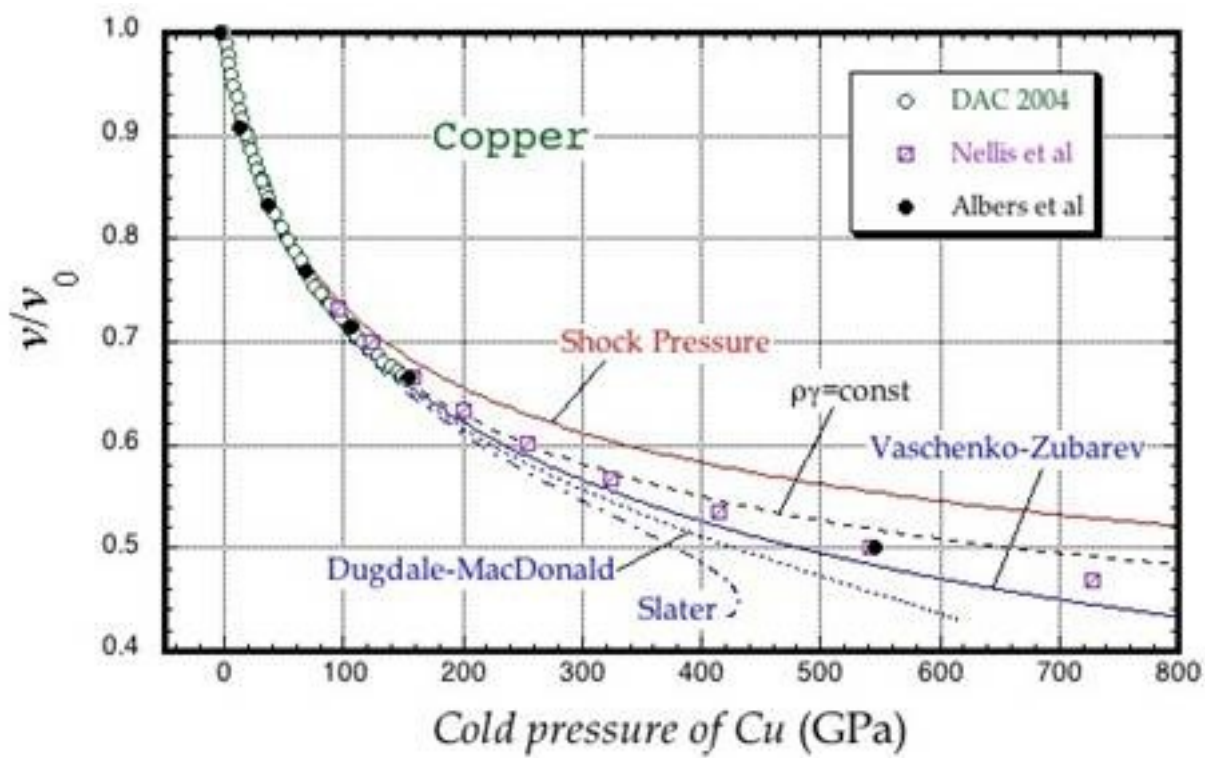


Fig. 3.13 Comparison of cold pressure function from theoretical gamma model with DAC experiment or first principle calculation for aluminum. Upper and lower figure contain same data for different pressure area.



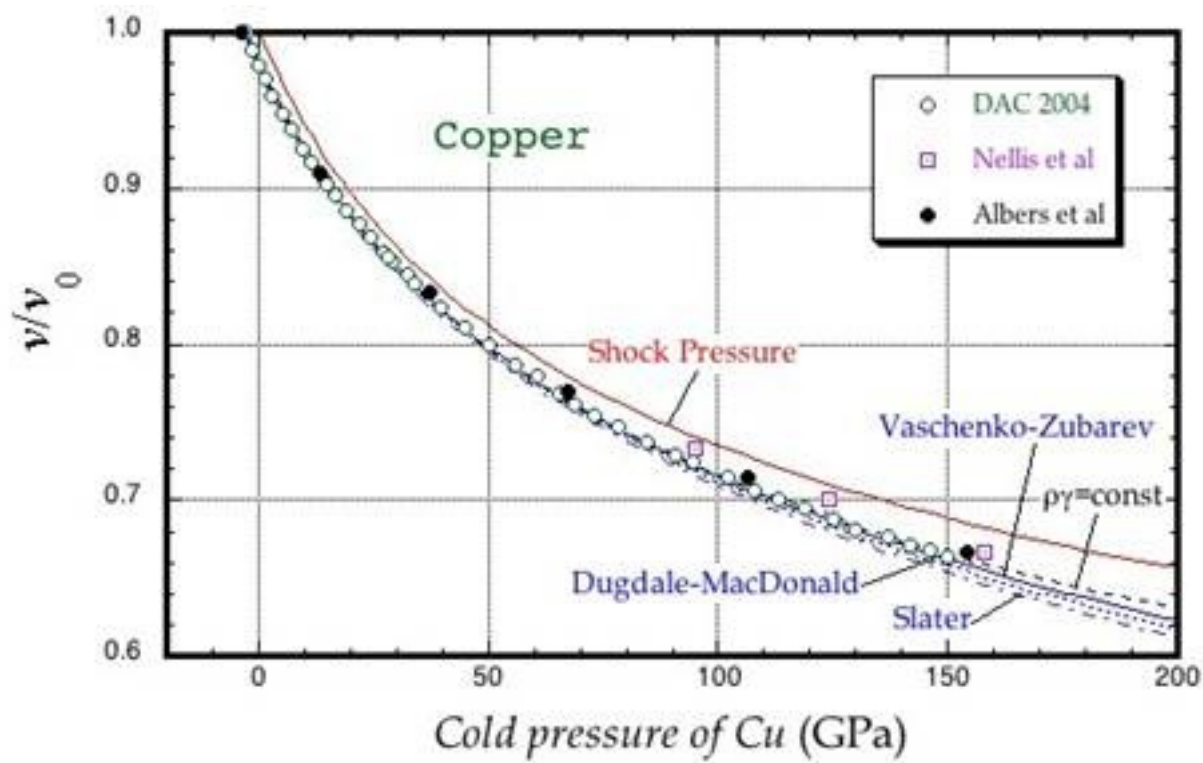
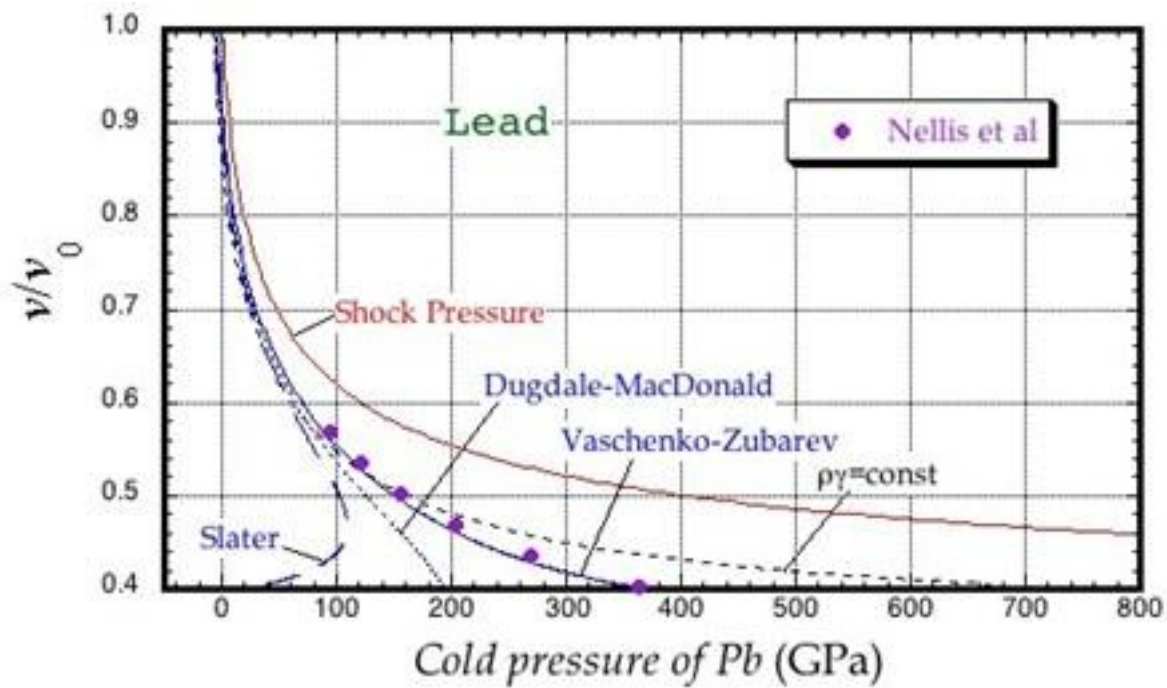


Fig. 3.14 Comparison of cold pressure function from theoretical gamma model with DAC experiment or first principle calculation for copper. Upper and lower figure contain same data for different pressure area.



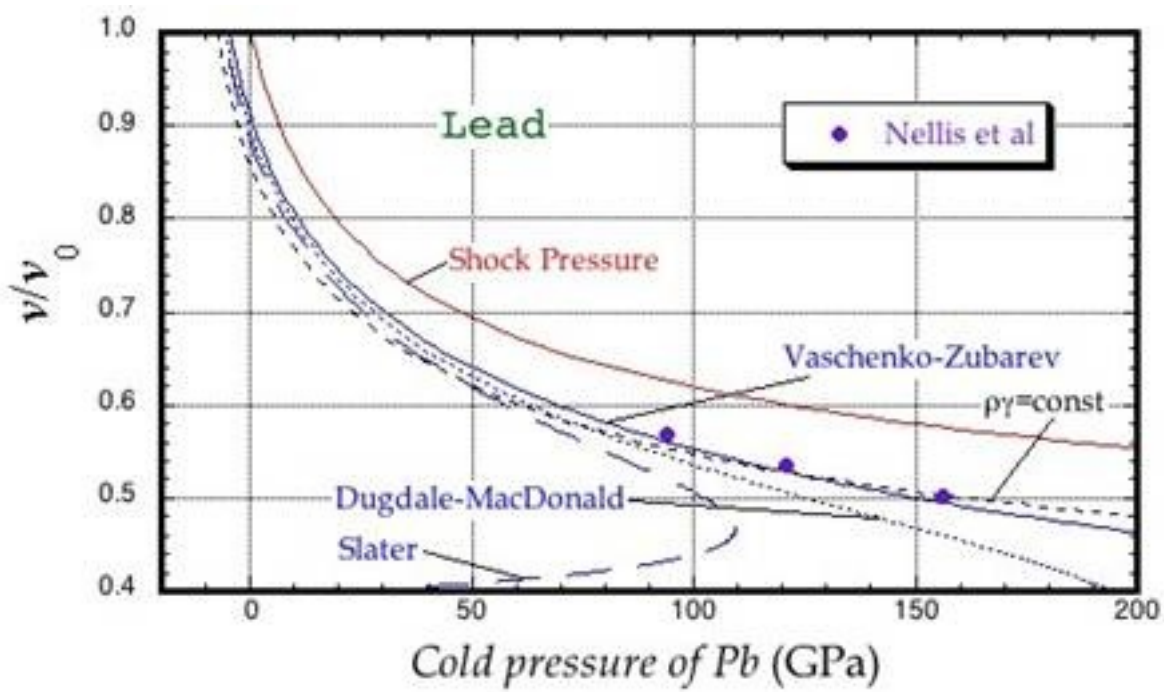


Fig. 3.15 Comparison of cold pressure function from theoretical gamma model with first principle calculation for lead. Upper and lower figure contain same data for different pressure area.

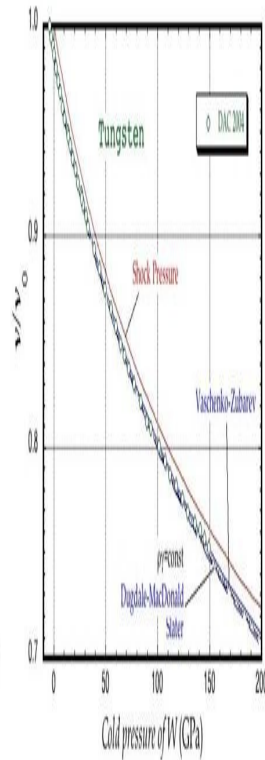
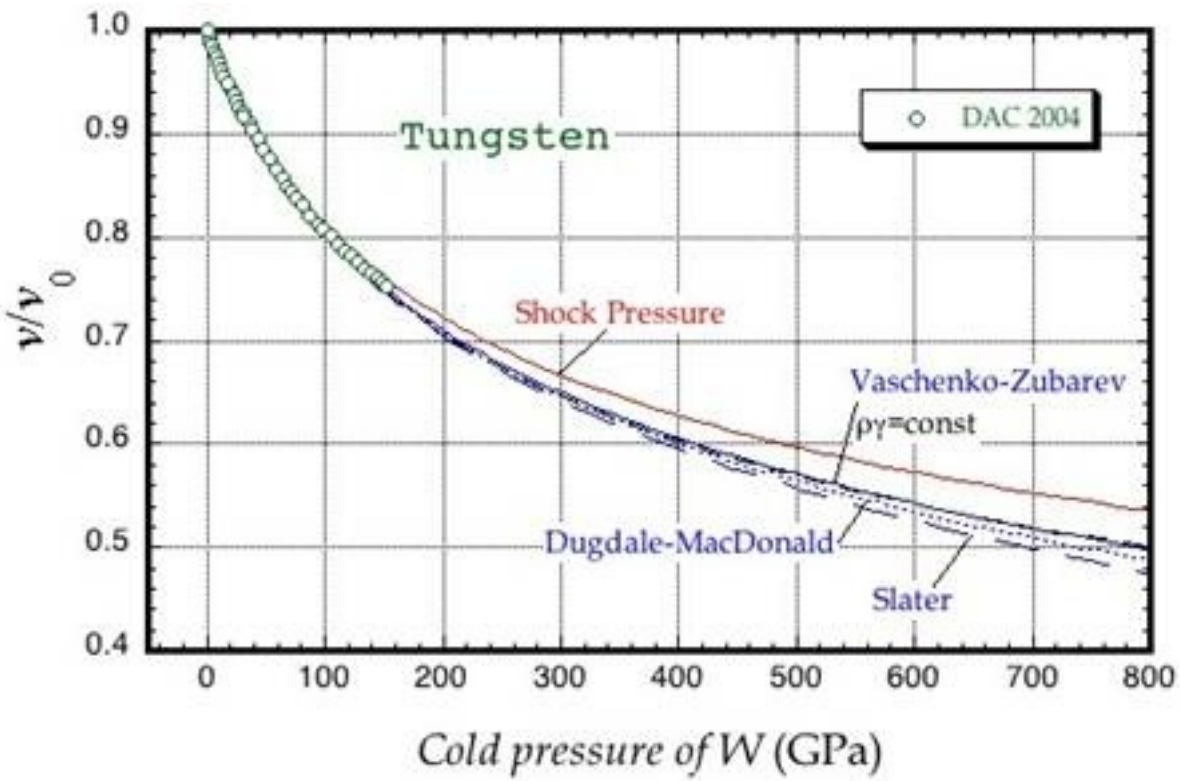


Fig. 3.16 Comparison of cold pressure function from theoretical gamma model with DAC data for tungsten. Upper and lower figure contain same data for different pressure area.

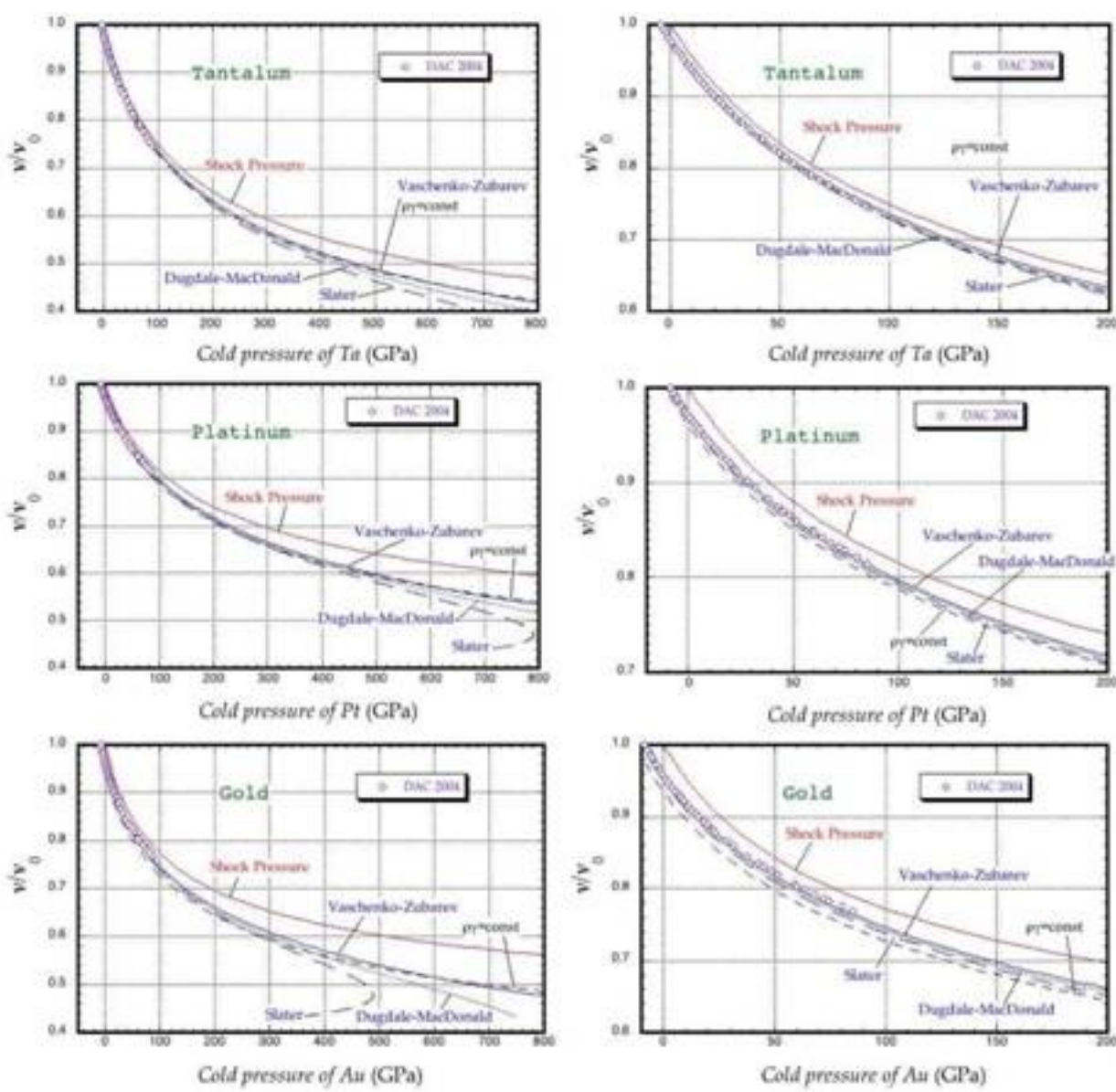


Fig. 3.17 Comparison of cold pressure function from theoretical gamma model with DAC data for tantalum, gold and platinum. Two figures for each material contain same data for different pressure area.

Comparisons for other materials shown in Fig. 3.17 show almost similar conclusions, i.e., Vaschenko-Zubarev model gives best explanation to DAC data. Although $p\gamma=\text{constant}$ assumption has no definite physical background, it also gives good approximation at least to cold pressure function in many metals. Cold pressure in low and very low pressure region, other theoretical models, Dugdale-MacDonald or Slater model are sometimes preferable to Vaschenko-Zubarev model.

3.2.4. Definition of shock Mach number and Numerical examples of thermal functions based on three theoretical models for the Grüneisen parameter but without models for the specific heat (Zone 3)

One may note again that present procedure of calculating the Grüneisen parameter and cold functions can estimate thermal state variables such as (i) thermal internal energy, (ii) thermal pressure, and (iii) new thermal variable $C(S)$, if the thermodynamic equilibrium state is specified as pressure-volume or energy-volume point. We have already calculated various state variables on shock Hugoniot starting from the initial state with room temperature and zero pressure.

Temperature and entropy are the exceptions. Prediction of their value at any state requires a model for the specific heat at constant volume. In this sense, calculation of high pressure isotherms is quite different from that of isentropes. In this section, isentrope centering any thermodynamic states can easily be calculated

by using new thermal variable $C(S)$ without any assumptions on the specific heat at constant volume.

One may also note that cold variables are also an isotherm and also an isentrope starting from zero Kelvin and zero pressure. In this section, we will discuss about isentropes centering zero pressure other than zero Kelvin.

It is an easy and straightforward task to calculate isentropes other than zero entropy. One may use Eq. (2.25) for internal energy and Eq. (2.26) for pressure to calculate isentropes. In this section, we start to give definition of shock Mach number and formulate how to calculate the value of thermal variable C as a function of Mach number. Then we will develop the formulation of calculating high pressure isentropes starting various Hugoniot states down to zero pressure, i.e., release isentropes.

Definition of shock Mach number is given by

$$M = \frac{u_s}{A} \quad (3.30)$$

In this definition, we have used the bulk sound velocity A instead of real speed of sound. As a unique measure of velocity, it will be presented that parameter A can be a very suitable choice.

In this section, attention is focused to solids whose shock Hugoniot is given by the linear empirical law, Eq. (3.7), although the extension of the discussion to non-linear Hugoniot is possible. Combining this definition with Eq. (3.7) and the jump conditions at the shock front, the other shock wave parameters can be given by

$$u_p = \frac{A}{B} [M - 1] \quad (3.31)$$

$$p_H = \frac{\rho_0 A^2}{B} M [M - 1] \quad (3.32)$$

$$\varepsilon_H = \varepsilon_0 + \frac{A^2}{2B^2} [M - 1]^2 \quad (3.33)$$

$$\eta_B = B \frac{v_0 - v}{v_0} \frac{M - 1}{M} \quad (3.34)$$

These expressions indicate that the following variables should be defined to have the universal Hugoniot function of the variable in terms of the shock Mach number.

$$\tilde{u}_p = \frac{B u_p}{A} = M - 1 \quad (3.35)$$

$$\tilde{p}_H = \frac{p_H}{\frac{\rho_0 A^2}{B}} = M [M - 1] \quad (3.36)$$

$$\tilde{\varepsilon}_H = \frac{\varepsilon_H}{A^2} = \tilde{\varepsilon}_0 + [M - 1]^2 \quad (3.37)$$

One may see that all three expressions are considered universal, since they do not include any material parameters. Among these mechanical variables, density cannot be expressed as the universal function free of material parameters. The universal quantity related to compression is the degree of compression divided by the parameter B . This way of defining non-dimensional variables seems to be inconsistent, since the variables with the same dimension cannot be reduced by the same parameter. In fact, by defining Mach number, shock velocity is divided by A , whereas defining non-dimensional velocity, the particle velocity should be divided by A/B . It should be emphasized, however, that the appropriate choice of variables leads to the universal form of Hugoniot function for the variable. This is possible, only in the case of using shock Mach number. Similar discussion has been made by Renero and Prieto. (Renero and Prieto 1998) Some of the physical meanings of the quantities appeared in the above expressions has been already discussed by Rodean. (Rodean 1977)

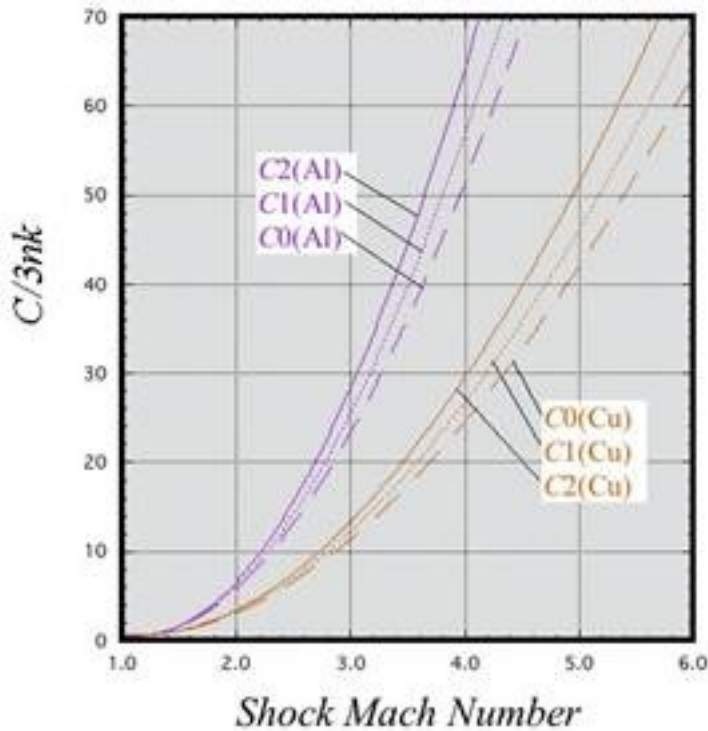


Fig.3.18 New thermal variable C as a function of shock Mach number based on the three theoretical models for the Grüneisen parameter.

Figure 3.18 shows the plot of increase in C as a function of M in three metals based on three theoretical models for the Grüneisen parameter. It is apparent that sensitive change in shock Mach number will take place for the material with large non-linear mechanical properties. In other words, for material with large value of Hugoniot slope B , Mach number changes appreciably with increasing particle velocity or volume compression. Among three metals in this calculation, copper has the largest value of B , so that Mach number change is the largest as in Fig. 3.18. In this sense, relationship $C(M)$ is not a universal function, but a material function with a material parameter of B .

The quantity q_s along shock Hugoniot curve is also calculated and is shown in Fig. 3.19. It is noteworthy that this quantity depends strongly on the theoretical models. For example, q_s is equal to the square of sound velocity behind shocked state as in the Slater model. Measurement of the value may give serious check of the feasibility of the Slater models to predict state variables on shock Hugoniot.

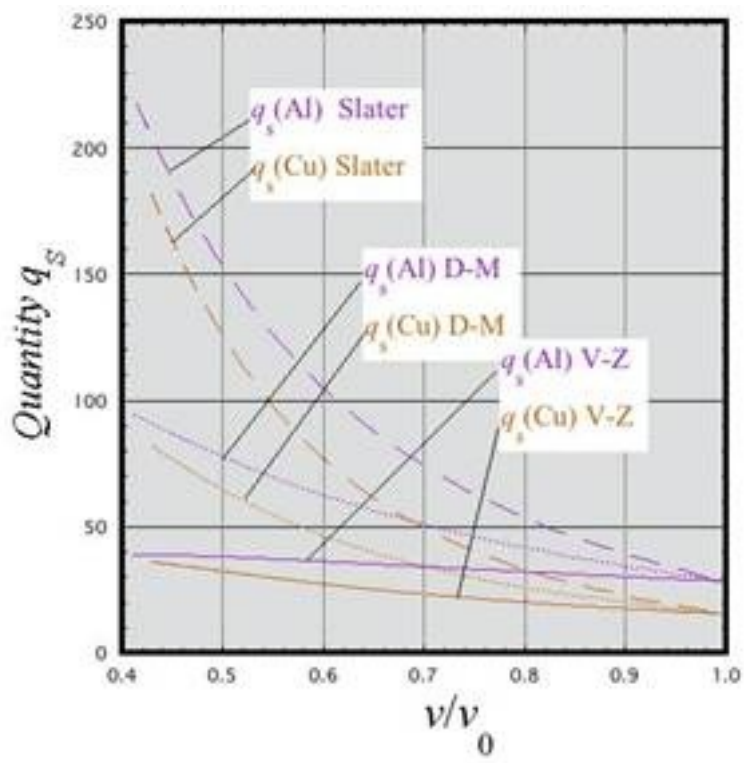


Fig.3.19 Quantity q_s for three materials along shock compression curve based on the three theoretical models for the Grüneisen parameter.

3.3. High Pressure Isentropes

3.3.1. High pressure isentropes centering various Hugoniot states

As explained earlier, isentropes and isotherms are quite different in treatment in the realm of the Grüneisen EOS due to the combination of thermodynamic state variables. They are inherently suitable for the material flow phenomena and it contains full information on the isentropic change of state of the materials.

In order to see this, we will show how simple to calculate isentropes by the present formulation of the EOS. For this purpose, we adopted three shock pressure points of aluminum for three models for the Grüneisen parameter as a starting point of calculating isentropes. Table 3.2 shows some of the values of state variables at these points. Parameter t indicates the model used in the calculations defined in Chapter 2. Values of the characteristic temperature and C are known at these points indicating the value of entropy is also given. In the present analysis, value of entropy is not necessary, we have to know only the value of C which is a unique function of entropy for the given material.

Table 3.2 Three Hugoniot points of Aluminum for the starting point of high pressure isentrope

t	p_H (GPa)	v (cm ³ /g)	$\Delta\epsilon_H$ ((km/s) ²)	$\Theta(v)$ (K)	$C/3nk$	γ
0	300	0.186	25.9	975	19.2	1.35
1	300	0.186	25.9	879	20.9	1.24
2	300	0.186	25.9	779	23.1	1.12
0	200	0.202	15.7	871	11.6	1.39
1	200	0.202	15.7	792	12.5	1.28
2	200	0.202	15.7	710	13.7	1.15
0	100	0.233	6.30	714	4.61	1.45
1	100	0.233	6.30	660	4.89	1.34
2	100	0.233	6.30	603	5.22	1.19

As for the isentropes passing through the Hugoniot state characterized by the parameters, $(p_H, v_H, \epsilon_H; u_s, u_p)$, one may calculate the isentropic function as follows;

$$\epsilon(v, S_H) = \epsilon(v, C(S_H)) = \epsilon_c(v) + C(S_H)\Theta(v) \quad (3.38)$$

$$p(v, S_H) = p(v, C(S_H)) = p_c(v) + \frac{\gamma(v)}{v} C(S_H)\Theta(v) \quad (3.39)$$

$$\begin{aligned}
\left(\frac{\partial p}{\partial v}\right)_{S_H}(v, S_H) &= \frac{dp_c(v)}{dv} + \frac{\gamma(v)}{v} C(S_H) \frac{d\Theta(v)}{dv} \\
&+ C(S) \Theta(v) \frac{d}{dv} \left(\frac{\gamma(v)}{v} \right) \\
&= \frac{dp_c(v)}{dv} + C(S) \Theta(v) \left[- \left(\frac{\gamma(v)}{v} \right)^2 + \frac{d}{dv} \left(\frac{\gamma(v)}{v} \right) \right] \quad (3.40)
\end{aligned}$$

These equations give estimation of energy, pressure and its derivative at any value of volume.

Figure 3.15 shows calculated isentropes in pressure-volume plane passing through selected three high pressure states on the shock Hugoniot of aluminum tabulated in Table 3.2. Hugoniot points and continuous lower pressure states are called release isentropes. One may see very small differences of release isentropes by the difference in theoretical models. Values of the pressure at the same volume points are greater for Slater, D-M and V-Z models in the cited order.

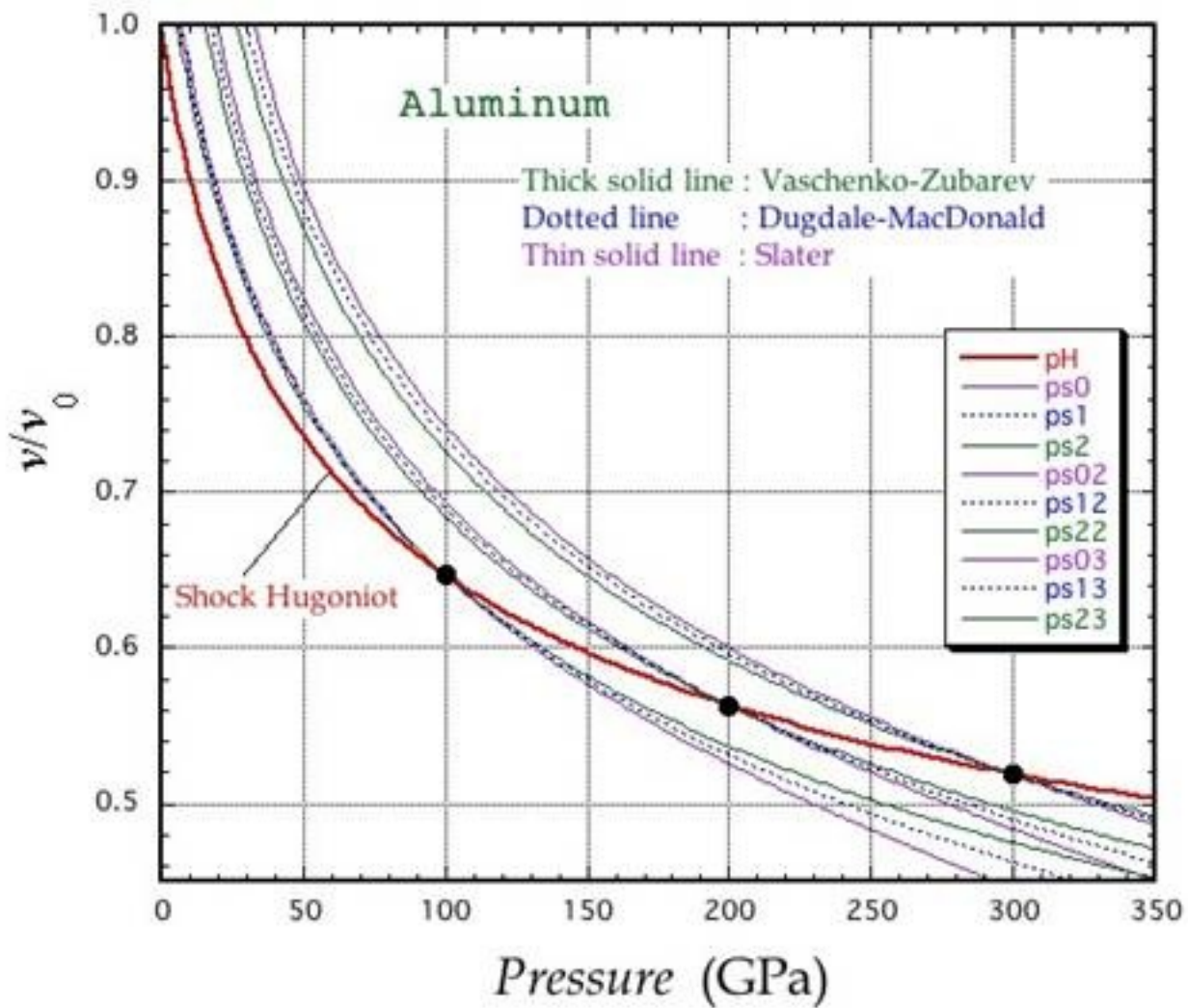


Fig. 3.20 High pressure isentropes for aluminum centering the Hugoniot states of 100, 200 and 300 GPa pressure.

Arbitrary isentropes centering the high pressure states off the Hugoniot states can also be given easily in the following way. When the high pressure state is described by (p, v) , the values of the volume functions, $\gamma(v)$, $\Theta(v)$ and $p_c(v)$ are given, and the new variable $C(S)$ is calculated by the relation,

$$C(S) = \frac{v}{\gamma(v)} \frac{p - p_c(v)}{\Theta(v)}, \quad (3.41)$$

thus, the isentrope centering the state, (p, v) , is represented as

$$p = p_c(v) + \frac{\gamma(v)}{v} C(S) \Theta(v), \quad (3.42)$$

which is a function of a curve on p - v plane with $C(S)=\text{constant}$. For a state described by (e, v) , the values of the volume functions, $\gamma(v)$, $\Theta(v)$ and $\varepsilon_c(v)$ are given, the new variable $C(S)$ is calculated by the relation,

$$C(S) = \frac{\varepsilon - \varepsilon_c(v)}{\Theta(v)}, \quad (3.43)$$

thus, the isentrope centering the state, (ε, v) , is represented as

$$\varepsilon = \varepsilon_c(v) + C(S) \Theta(v), \quad (3.44)$$

which is a function of a curve on e - v plane with $C(S)=\text{constant}$. In a similar way, for arbitrary combination of variables, which can be described by the characteristic temperature and a new variable, it is always possible to represent isentropes by using these variables.

In various numerical simulations of flow problems including shock wave propagation, thermodynamic state variables are described by two extensive parameters, (ε, v) , procedures given by Eqs.(3.43) and (3.44) can be applied to evaluate isentropes in these calculations.

One of natural intuitive questions is that how different are the cold internal energy and characteristic function. This topic will be covered in Chapter 5, since close connection of two material functions is sometimes conveniently used in solving flow problems including shock propagation.

3.3.2. Release states from Hugoniot states

After a shock wave propagates over the slab of a material, an unloading or release wave propagates back in the slab which brings the state of the material from a shock Hugoniot state to zero-pressure state. Change of states in this unloading or release wave is isentropic and these isentropes are called release isentropes. Here, we will consider one interesting state with the initial volume, which is reached along a release isentrope down from a shock Hugoniot state but before reaching zero-pressure. The internal energy and pressure at the point are given by

$$\begin{aligned} \varepsilon(v_0, S_H) &= \varepsilon(v_0, C(S_H)) = \varepsilon_c(v) + C(S_H) \Theta(v_0) \\ &= \varepsilon_0 + [C(S_H) - C(S_0)] \Theta(v_0) \end{aligned} \quad (3.45)$$

$$\begin{aligned} p(v_0, S_H) &= p(v_0, C(S_H)) = p_c(v_0) + \frac{\gamma_0}{v_0} C(S_H) \Theta(v_0) \\ &= \frac{\gamma_0}{v_0} [C(S_H) - C(S_0)] \Theta(v_0) \end{aligned} \quad (3.46)$$

At this state, derivative of pressure along this isentrope is estimated by

$$\left(\frac{\partial p}{\partial v}\right)_s(v_0, S_H) = \frac{dp_c(v)}{dv} \Big|_{v_0} + C(S_H)\Theta(v_0) \left[-\left(\frac{\gamma_0}{v_0}\right)^2 + \frac{d}{dv} \left(\frac{\gamma(v)}{v} \right) \Big|_{v_0} \right] \quad (3.47)$$

By using these equations, the real release state at $p=0$ can then be evaluated.

Along an isentrope, temperature and volume has simpler relationship, which is derived by Eq.(2.1).

$$\frac{dT}{T} = -\frac{\gamma}{v} dv, \quad \text{along } dS = 0 \quad (3.48)$$

which gives

$$\frac{T}{\Theta(v)} = \frac{T_H}{\Theta(v_H)} \quad (3.49)$$

Referring to Fig.3.10 for the characteristic temperature, estimated release temperature is a significant function of the theoretical models.

3.4. High Pressure Isotherms and Shock Temperature Calculation

3.4.1. Temperature Calculation with the Debye model for the specific heat at constant volume

In this section, we will discuss the method of calculating temperature and entropy by the Grüneisen EOS and its applications to the shock temperature calculation and to isotherms with several values of temperature. Temperature is given in terms of volume and entropy by the equation,

$$T = \Theta(v) \frac{dC(S)}{dS} \quad (3.50)$$

which is derived in Chapter 2 by the introduction of new thermal variables. In order to obtain temperature, we need to specify the material functions, i.e., the Grüneisen parameter and the derivative of a new thermal variable $C(S)$ as a function of entropy. It is not possible only by the knowledge of the Grüneisen EOS, but requires the model for the specific heat. The situation is also seen in the thermodynamic identity,

$$\frac{dT}{T} = -\frac{d\Theta(v)}{\Theta(v)} + \frac{\frac{d^2 C(S)}{dS^2}}{\frac{dC(S)}{dS}} dS = -\frac{\gamma(v)}{v} dv + \frac{1}{C_v(S)} dS \quad (3.51)$$

where one may note that with the knowledge of the specific heat, it is possible to calculate temperature by the integration of Eq.(3.51) along any thermodynamic path.

For this purpose, we adopt the Debye model for the specific heat at constant volume. It is adopted simply by the following reason,

(i) Debye model is fully compatible with the volume-dependent Grüneisen parameter, since specific heat by Debye model is a function only of entropy.

(ii) Even for solids with non-crystalline or with Density Of States different from that of Debye model, it gives an appropriate description of thermal properties of substance, i.e., specific heat, and thermal energy.

(iii) As explained later, it can be handled rather simple by the use of polynomial formulae.

3.4.2. Calculational procedure of thermal variables

We already used the Debye model for the specific heat in the previous chapter only for the purpose of imagining the concrete functional form of the relationship between the new variable C as a function of entropy S , although the introduction of new variable does not need the model for the specific heat. In this chapter, we will have more positive use of the Debye model in order to estimate temperature.

As cited in chapter 2, the Debye model uses a non-dimensional parameter $x=\Theta_D(v)/T$, given by Eq. (2.47). The model shows that the specific heat, C_v , the entropy, S and the new variable C are a function of x only. They are given by Eq.(2.51), (2.50) and (2.49), but they contain a function of x represented by an integral of an analytical function.

A new procedure of temperature calculation in the present scheme is based on the use of the relationships by Eq.(2.51), (2.50) and (2.49). If the high pressure state is described by $(C(S), \Theta(v))$, the value of x is given by the function

$$x = x(C(S)), \quad (3.52)$$

which is an inverse function of that by Eq.(2.49). Since the Debye temperature or the characteristic temperature is known, temperature T is calculated by

$$T = \frac{\Theta_D(v)}{x} \quad (3.53)$$

This is the strategy of calculating the temperature in the present formulation. In this way, the new variable formulation is simply coupled with the Debye model in order to estimate thermal variables, T and S from the new variable set, $(C(S), \Theta(v))$.

Here is the summary of the strategy of estimating thermal variables:

- (i) Estimate the new variables, $C(S)$ and $\Theta(v)$ from the given set of thermodynamic state variables, say, (ϵ, v) ,
- (ii) Calculate the value of x given by Eq.(3.52), the reciprocal function of that by Eq.(2.49), and finally,
- (iii) Calculate the temperature T by using Eq.(3.53). If the value of entropy S and the specific heat C_v are necessary, you may use Eq.(2.50) and Eq.(2.51).

In later section, we will give polynomial expressions of the Debye functions for the convenience of calculation.

Figures 3.21 and 3.22 shows the shock temperature and the new variable C and entropy along shock Hugoniot curve based on the three theoretical models for the Grüneisen parameter. Procedure of calculating these variables is the one explained in the previous section.

It is quite impressive from Fig.3.21 that shock temperature is a very insensitive function of the theoretical models adopted here. Range in variation of temperature is the largest of all the variables calculated, so that it is plotted in logarithmic scale. This masks the slight change in values for respective models, but even so, the change is seen to be quite small.

In Fig. 3.22, it is apparent that rate of change in variable C and entropy S on Hugoniot is quite different as is expected by the relationship given by Fig. 2.2 in Chapter 2. But the change of them by theoretical models is found to be very small.

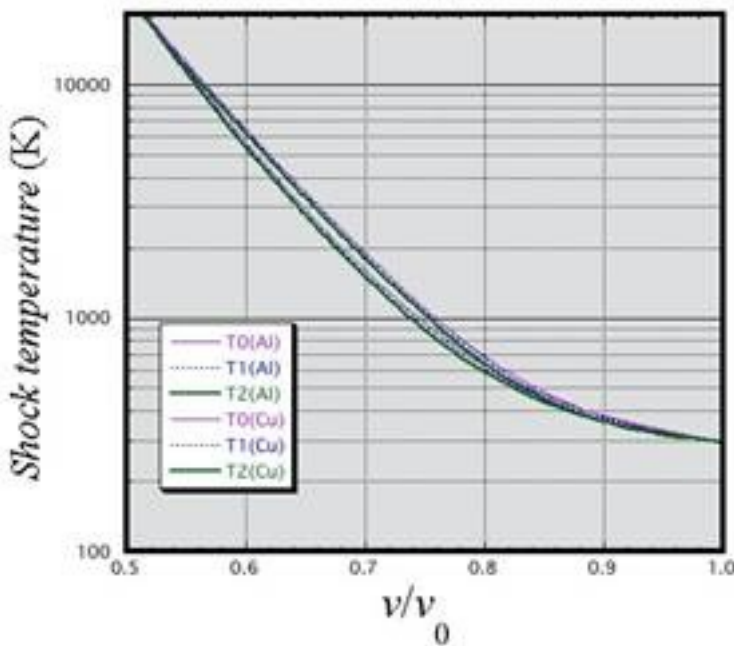


Fig.3.21 Shock temperature for three materials along shock compression curve based on the three theoretical models for the Grüneisen parameter. Notations used in the legend such as T0, T1, and T2 indicate the value of Grüneisen parameter by Slater, D-M and V-Z models, respectively.

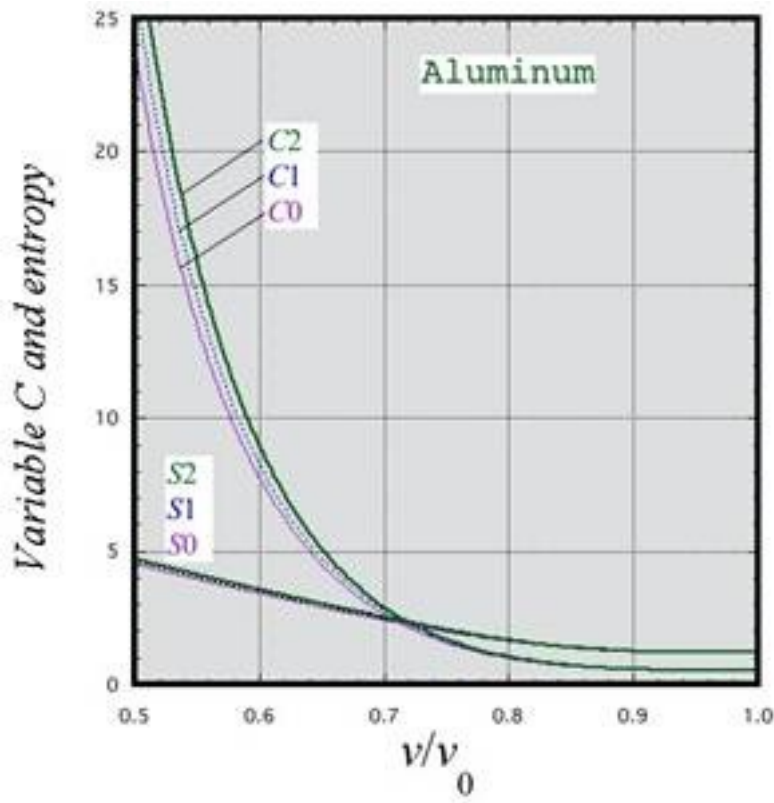


Fig.3.22 New thermal variable C and entropy for aluminum along shock compression curve based on the three theoretical models for the Grüneisen parameter.

3.4.3. Calculation of High pressure isotherms

Calculation of isotherm through some high pressure state can also be performed in the following way. One may choose any thermodynamic state given by $(C(S), \Theta(v))$. Temperature of the state, T can be given by the procedure explained in the previous section. Or you can start with the other state variable combination including temperature as one of the state variables. By changing the specific volume with the fixed value of temperature T , calculate the characteristic temperature, $\Theta(v)$, and then $x = \Theta_D(v)/T$. For the new value of x , one may calculate the value of $C(S)$ through the formula given by Eq.(2.49). Then you may calculate any thermodynamic state variables by the new set of parameters, $(C(S), \Theta(v))$.

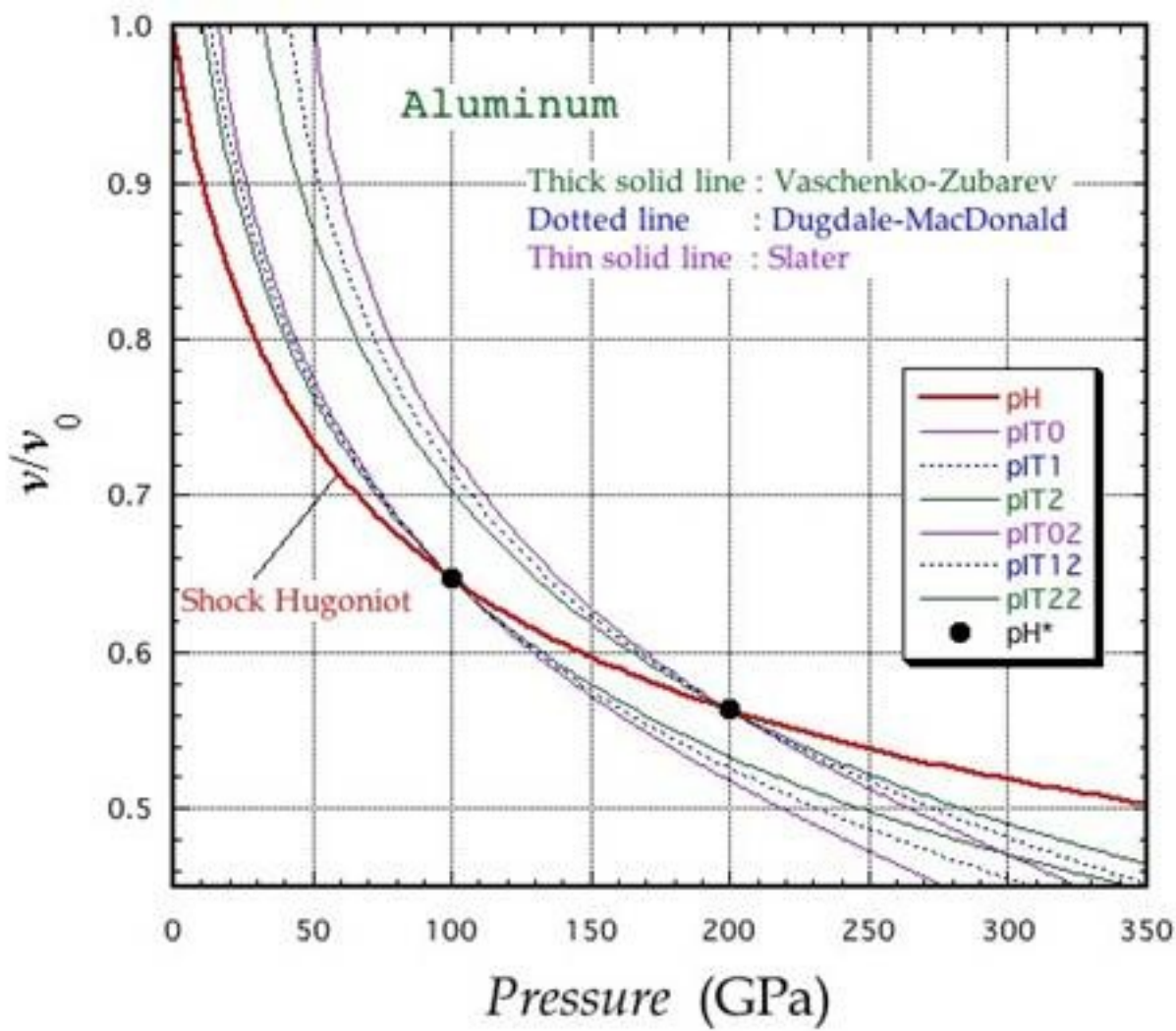


Fig.3.23 High pressure isotherm of aluminum passing through the Hugoniot point of 200 GPa and 100 GPa based on the theoretical models for the Grüneisen parameter combined with the Debye model for the specific heat.

Figure 3.23 shows two high pressure isotherms passing through two Hugoniot points, 200 GPa and 100 GPa of aluminum as represented in Table 3.2. Temperature of these two isentropes is around 10^4 K for 200 GPa Hugoniot point and around 3500 K for 100 GPa Hugoniot point, respectively.

Discrepancy of isothermal curves for three models is larger than that of isentropes as seen in Fig. 3.23. Slope of isotherms on p - v plane for three models is largest for Slater model, then D-M model and V-Z model in this order.

Importance of temperature arises appreciably in the case of discussing high pressure phase transformations or various chemical reactions expected at high pressure. In the shock propagation without such a transformation, temperature plays little role for the entire process.

Temperature calculation in this section is based on the theoretical models for the Grüneisen parameter and Debye model. Precision of the theory must be evaluated by the reliable temperature measurement under high pressures and temperatures, which are supposed to be a tough task to perform.

3.4.4. Very simple calculational procedure of thermal variables based on the simple assumption of the volume dependence of Grüneisen parameter

In this section, we especially focus our attention on the following simple assumption for the Grüneisen parameter,

$$\rho\gamma = \rho_0\gamma_0 = \text{const} \quad (3.54)$$

This assumption is seen to be quite convenient in various situation, simply because this product appears

in many formulae. However, this assumption has no physical background. Very small excuse for the adoption of this assumption is that theoretically the Grüneisen parameter of most materials decreases upon compression indicating increase in bulk modulus with compression.

The introduction of this assumption leads to the gross simplification of various calculations. Some of the formulae will be replaced by the polynomial expressions.

In this section, we focus the calculation of shock temperature based on the assumption, Eq.(3.54).

Unlike the conventional methods, most of the calculation can be replaced by the approximate polynomial expressions. The present method includes no numerical integration. Within the framework of Debye model, thermal variables can be calculated almost instantaneously.

Under the assumption of Eq.(3.54), characteristic temperature or the Debye temperature is given in terms of shock Mach number as

$$\Theta(v) = \Theta(v_0) \exp \left[-\frac{\gamma_0}{v_0} (v - v_0) \right] = \Theta_0 \exp \left[-\frac{\gamma_0}{B} \frac{M-1}{M} \right] \quad (3.55)$$

As a numerical example, the values of $C(S)$ along the Hugoniot curve under this assumption have also been calculated. For the present calculation, it is also required to represent the behavior of the Grüneisen parameter as a function of shock Mach number.

To do so, by combining Eq.(2.29) with Eq.(3.21), we have

$$\begin{aligned} dC(S_H) &= \frac{T_H dS_H}{\Theta(v)} = \frac{d\varepsilon_H + p_H dv}{\Theta(v)} = \frac{1}{\Theta(v)} \frac{u_p^2}{u_s} du_s \\ &= \frac{A^2}{\Theta_0 B^2} \exp \left[-\frac{\gamma_0}{B} \frac{M-1}{M} \right] \frac{(M-1)^2}{M} dM \end{aligned} \quad (3.56)$$

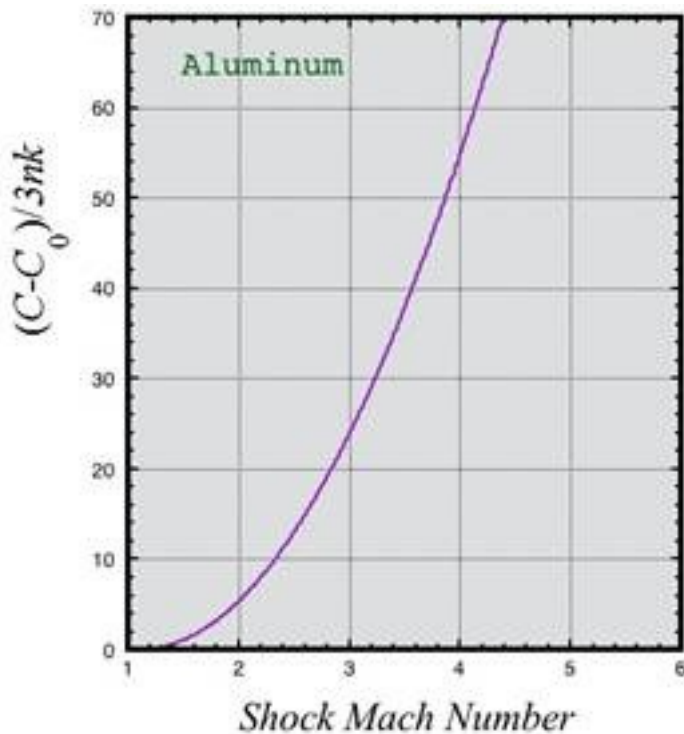


Fig. 3.24 New variable C as a function of shock Mach number M . Material parameters are chosen to represent aluminum.

Integration of this equation gives

$$C(M) = C(1) + \frac{A^2}{\Theta_0 B^2} \int_1^M \exp \left[-\frac{\gamma_0}{B} \frac{M-1}{M} \right] \frac{(M-1)^2}{M} dM, \quad (3.57)$$

where $C(1)$ is the initial value of C at the uncompressed state. Furthermore, this equation states that there are only two independent material parameters, which are $(A/B)^2/\Theta_0$ and γ_0/B .

Figure 3.24 shows the calculated results of C for aluminum as a function of Mach number under the assumption of Eq.(3.54). As the value of Θ_0 , the Debye temperature has been used. In this case, the quantity C has the dimension of entropy. In Fig.3.24, the increment in C , i.e., $C(M)-C(1)$ is plotted. The functional relationship, $C(M)$ is not universal, since it contains two material parameters.

One may compare Fig.3.24 with Fig.3.18 for $C(M)$ behaviors with different γ models. Assumption Eq. (3.54) gives similar results as by the three theoretical models, and the function by Eq.(3.54) lay between that by Slater and D-M model.

In the present chapter, the state variable $C(S)$ can be expressed in terms of shock wave data and also of Debye function. If these two ways of representing $C(S)$ are combined, a new method of calculating the shock temperature can be constructed.

We propose a new and much simpler method, calculating the state variable $C(S)$, instead of calculating the heat capacity as in the conventional method. The procedure is the same as was already explained in the previous section, but this time, further simplification is realized.

New method consists of four stages:

- (1) Calculate the value of C at the initial state, $C(S_0)$ (or $C|_{M=1}=C(1)$) by the Debye function, i.e., as a function of $x=\Theta_D/T$,
- (2) Calculate the increment in C from $C(1)$, $\Delta C=C(M)-C(1)$ for the shock strength M , by Eq.(3.57).
- (3) Calculate the corresponding value of x to the value of $C(M)$, by using the inverse function, i.e., $x=x(C(M))$.
- (4) Calculate the Debye temperature $\Theta(M)$ by Eq.(3.55), then use it with the value of x to obtain the temperature T .

The most striking feature of this procedure of shock temperature calculation is that calculation step using Debye model and that using Grüneisen assumption is completely independent.

Inspecting this procedure more precisely, it is revealed that independent material parameters appearing in the formulae are only three, which are $(A/B)^2/3nk\Theta_0$, γ_0/B and $C(1)$. Naturally, however, the number depends on the assumptions used.

Debye model says that heat capacity or entropy depends only on the non-dimensional parameter x , and the relationship contains no material parameters. In other words, this relationship can be regarded as one of the law of corresponding states. Therefore, the calculation in the Step (1) and (3) needs no material parameters.

We have tried to simplify the calculation of each step by replacing the numerical integration by the polynomial approximation.

3.4.5. Universal polynomial for thermal variables by Debye model

Function $C(x)$ has been calculated by numerically integrating Debye function. For a wide possible range of the variable x , the value of C also ranges several orders of magnitude. We have approximated the relationship also by the polynomial expression. Sufficient precision has been obtained only when the functional relationship has been represented in the plane of $(\ln C)-(\ln x)$.

It is required to calculate C from x in Step (1), and also to calculate x from C in Step (3). For this purpose, it is necessary to have two approximate formulae. By introducing the variables,

$$\varsigma = \ln C, \quad \xi = \ln x, \quad (3.58)$$

then by writing the polynomial formulae in the following form,

$$\begin{aligned} \varsigma &= Q_0 + Q_1\xi + Q_2\xi^2 + Q_3\xi^3 + Q_4\xi^4 + Q_5\xi^5 + Q_6\xi^6 + Q_7\xi^7 + Q_8\xi^8 + Q_9\xi^9, \\ \xi &= QQ_0 + QQ_1\varsigma + QQ_2\varsigma^2 + QQ_3\varsigma^3 + QQ_4\varsigma^4 + QQ_5\varsigma^5 + QQ_6\varsigma^6 + QQ_7\varsigma^7 + QQ_8\varsigma^8, \end{aligned} \quad (3.59)$$

the coefficients of the expansion has been obtained by method of least square fits, and are given by

$$\begin{aligned} Q_0 &= -0.39390925583 & QQ_0 &= -0.29108336532 \\ Q_1 &= -1.4112049057 & QQ_1 &= -0.76850728989 \\ Q_2 &= -0.22105029892 & QQ_2 &= -0.072627595071 \\ Q_3 &= -0.08187302888 & QQ_3 &= 0.0068279735108 \\ Q_4 &= -0.022886680929 & QQ_4 &= 0.0018993280418 \\ Q_5 &= -0.0046986746487 & QQ_5 &= -0.0004445271904 \\ Q_6 &= -0.00059581949858 & QQ_6 &= -0.000060342849602 \\ Q_7 &= -0.000018701254466 & QQ_7 &= 0.000028720614136 \\ Q_8 &= 0.0000057170796191 & QQ_8 &= -0.0000026118858428 \\ Q_9 &= 0.00000058720648417 & & \end{aligned} \quad (3.60)$$

These formulae can reproduce the numerical results within the precision of at least more than 3 digits over the change in variables of two or three orders of magnitude.

3.4.6. Shock temperature calculation under the assumption of $\rho\gamma=\text{constant}$

Integration in Eq.(3.57) cannot be expressed as the elementary functions. We have expanded the exponential term in Eq.(3.57), and integrated over M , term by term. The convergence of this expansion becomes better for weaker shock waves. Since the shock Hugoniot data for solids has been obtained up to or less than $M=2$ for most material, the shock wave is not said to be very strong, as long as the shock strength is measured in Mach number. By this reason, we have truncated the infinite series to 6 - 8 terms as

$$\begin{aligned}
& \int_1^M \exp\left[-\frac{\gamma_0}{B} \frac{M-1}{M}\right] \frac{(M-1)^2}{M} dM \\
&= \left[\frac{M^2}{2} - 2M + \ln M + \frac{3}{2} \right] \\
&\quad - \frac{\gamma_0}{B} \left[\frac{M^2}{2} - 3M + 3\ln M + \frac{1}{M} + \frac{3}{2} \right] \\
&\quad + \frac{1}{2} \left(\frac{\gamma_0}{B} \right)^2 \left[\frac{M^2}{2} - 4M + 6\ln M + \frac{4}{M} - \frac{1}{2M^2} \right] \\
&\quad - \frac{1}{3!} \left(\frac{\gamma_0}{B} \right)^3 \left[\frac{M^2}{2} - 5M + 10\ln M + \frac{10}{M} - \frac{5}{2M^2} + \frac{1}{3M^3} - \frac{10}{3} \right] \\
&\quad + \frac{1}{4!} \left(\frac{\gamma_0}{B} \right)^4 \left[\frac{M^2}{2} - 6M + 15\ln M + \frac{20}{M} - \frac{15}{2M^2} + \frac{2}{M^3} - \frac{1}{4M^4} - \frac{35}{4} \right] \\
&\quad - \frac{1}{5!} \left(\frac{\gamma_0}{B} \right)^5 \left[\frac{M^2}{2} - 7M + 21\ln M + \frac{35}{M} - \frac{35}{2M^2} + \frac{7}{M^3} - \frac{7}{4M^4} + \frac{1}{5M^5} - \frac{329}{20} \right] \\
&\quad + \dots \tag{3.61}
\end{aligned}$$

This expansion approximates Eq.(3.57) at least up to $M=5$ within the precision of more than 3 orders of magnitude. This approximation is found to be better than the power series of $(M-1)$. In case of very weak shock, i.e., $M \approx 1$, each term in Eq.(3.61) is a very small quantity proportional to $(M-1)^3$, $(M-1)^4$, $(M-1)^5$, $(M-1)^6$, ... Therefore, this calculation should be performed in double precision.

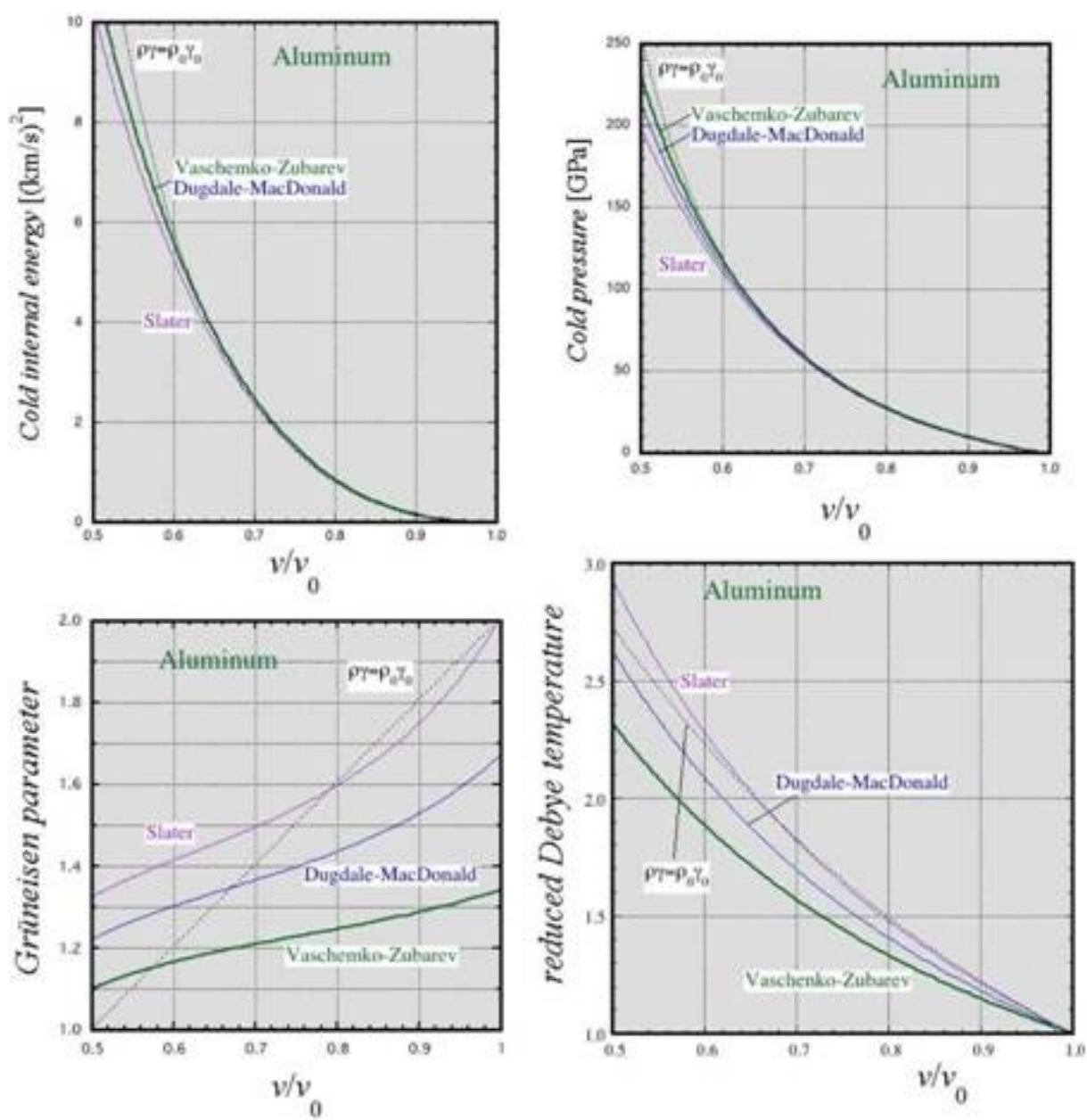


Fig. 3.25 Comparison of material functions for aluminum with three theoretical models for the Grüneisen parameter and $\rho\gamma = \text{constant}$ assumption.

Before computing shock temperature, various material functions under the assumption of $\rho\gamma = \text{constant}$ were performed in order to compare them with those by theoretical models. Figure 3.25 shows some of these plots. In this figure, one may apparently recognize the difference in the behavior of the Grüneisen parameter. Most functions depicted in these plots resemble each other and $\rho\gamma = \text{constant}$ assumption leads to the functions lay close to some of the theoretical models. As shown here, the Debye temperature behavior by $\rho\gamma = \text{constant}$ gives similar function in between Slater and D-M models. While cold internal energy and cold pressure function by $\rho\gamma = \text{constant}$ gives slightly larger values than those 3 models.

Computation has been performed by using the present procedure to calculate the shock temperature for metals already tabulated elsewhere. Since the code contains no numerical integration, calculation is almost immediate. About precision, we have checked that the result completely reproduces the published results.

Figure 3.26 shows the calculated shock temperature and new variable C by $\rho\gamma = \text{constant}$ assumption. It is striking that assumption gives very close values of these variables to those by theoretical models for the Grüneisen parameter.

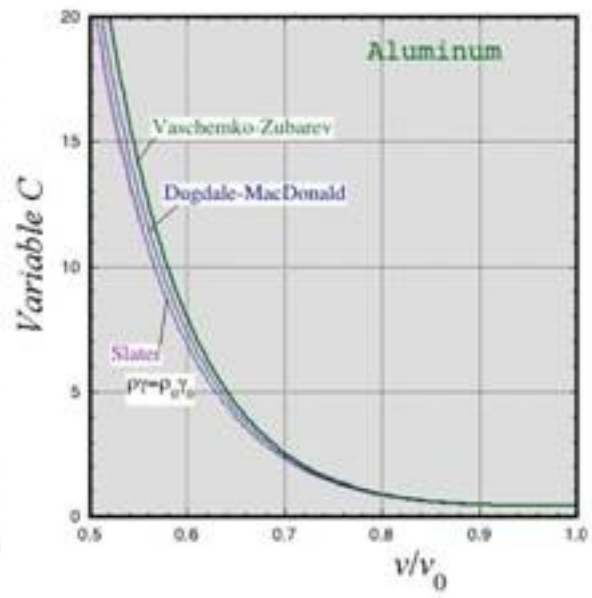
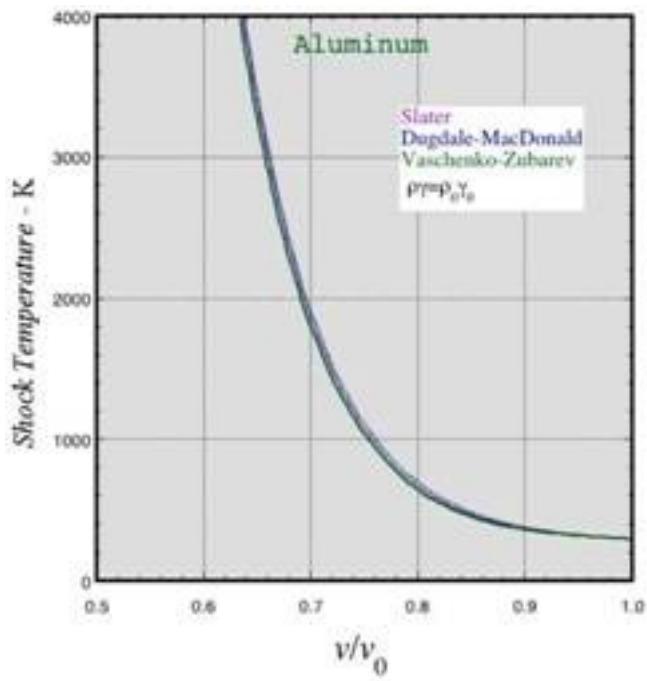


Fig. 3.26 Shock temperature and new variable C comparison for aluminum calculated by 3 theoretical models and by $\rho/\rho_0 = \gamma_0$.

3.5. Irreversible Heating by Shock Compression

3.5.1. Definition of irreversible heating by shock compression

Strong shock compression of substance yields entropy increase, although the process is considered to be adiabatic. Increase in entropy, therefore, is attributed to the irreversible process which is taking place at the shock front structure. The energy dissipation mechanisms responsible for such irreversible process in gases are, for example, the viscosity, the mass diffusion, thermal conduction, chemical reaction, etc. In case of shock compression of condensed substance, however, these dissipation mechanisms are almost unknown especially for extremely high strain rates realized in shock rise in condensed media. Microscopic standpoint might be required to reveal what kind of elementary processes are important to compete with the nonlinearities to steepen the front.

Entropy increase by shock compression of solids is one of the keys to understand what material parameters could affect the energy dissipation. The estimation of the entropy change caused by shock compression, however, requires two (or precisely speaking, three) theoretical models for condensed media. One of it is the assumption of the type of the equation of state at high pressures and temperatures. Normally, the Grüneisen type equation of state is assumed. The second one is the assumption on the concrete functional dependence of the Grüneisen parameter upon compression. This might give complexity on the accuracy of the estimated thermal variables at high pressure. The third one is the so-called Debye model for the specific heat. All of the assumptions cited here may have some effects on the reliability of the estimated values. Even so, the values of these variables at various shock Hugoniot states have some help to understand the irreversible processes upon shock front.

Wallace have described the extended thermodynamic theory of irreversible processes for shock compression of solids, but it may be limited to the case of weak shock compression regime. (Wallace 1980, 1980a, 1980b) No reliable theory for the irreversible processes within strong shock compression of solids has been established yet. The elementary processes responsible for the shock front structure might be imagined to be viscous or mechanical dissipation as well as the thermal energy dissipation, and more. These topics might be made clear by Molecular Dynamics simulations or non-equilibrium statistical mechanics, or from the experimental data of shock compression combined with continuum translation.

In this section, another thermal variable to represent the effects of irreversible processes is proposed. The variable is found to be relatively insensitive to the models used for the calculations. Instead of estimating temperature or entropy based on the previously cited three assumptions, the presently proposed variable might have a simpler alternative for the more reliable key to understand the irreversible processes in the shock propagation in condensed media. The procedure of calculating the thermal energy increase caused by the irreversible heating of solids will be proposed. The estimation is based on the Grüneisen assumption, and needs some assumption on the behavior of Grüneisen parameter, but no need of the Debye model. Some numerical examples have been presented to show how thermal energy by the irreversible processes increases with the increase in the total internal energy.

Driving energy to induce high-pressure shock wave in condensed media is imparted equally into the increase in the kinetic energy, $u_p^2/2$, and into the increase in the specific internal energy of the substance, $\Delta\epsilon_H$. The increase in specific internal energy can then be decomposed into the increase in cold compression energy and into the increase in thermal energy.

We will have more interest in the increase in the internal energy at the shock Hugoniot state, $\epsilon(S_H(v), v)$, from the internal energy of the state of the same volume, but on an isentrope centering the initial state, $\epsilon(S_0, v)$. We call this difference, the irreversible heating, q_{irrev} , since this denotes the quantity of heat acquired by the irreversible heating through the various irreversible and non-equilibrium processes occurring within the shock wave front. The irreversible heating, q_{irrev} will approach to the thermal internal energy, since most of the thermal energy acquired by shock compression will be those by the entropy-increasing irreversible processes in the limit of strong shock compression. In this sense, the calculation of q_{irrev} will be useful as a rough estimation of the thermal energy increase. Since this quantity can be estimated without assuming physical assumption of specific heat, the quantity described above is a much more reliable measure of the

irreversibility of the substance subjected to strong shock compression.

By using the definition of the shock Mach number and empirical linear relationship between shock and particle velocity, Eq.(3.7), Eq.(3.21) can be rewritten as

$$T_H dS_H = \frac{u_p^2}{u_s} \frac{du_s}{du_p} du_p = \frac{A^2}{B^2} \frac{(M-1)^2}{M} dM \quad (3.62)$$

Integrating this equation along shock Hugoniot, we obtain

$$\int_H T dS = \frac{A^2}{2B^2} [M^2 - 4M + 3 + 2 \ln M] \quad (3.63)$$

where the suffix H in this equation denotes that the integration should be made along Hugoniot. In Eq. (3.62), and (3.63), the included material parameters are A and B , and they are figured outside of the function of Mach number. In this sense, the resultant formula is a universal one in nature.

Thermodynamically, the quantity TdS is not a good quantity in the sense that it is not a state variable, and the integrated value of it along some state path depends on the path itself. We have formulated such an integrated quantity along the material Hugoniot, and it can be a universal nature in their form. Even so, the quantity expressed by Eq.(3.21) or (3.63) may have a very close connection to the irreversible heating of solids by shock compression. They will be the result of the irreversible processes at the shock wave front responsible for the front structure determined by the competition of these processes with the non-linearity of the material properties to steepen the wave front.

Figure 3.27 shows the schematic illustration of shock Hugoniot, isentrope centering the initial state, and zero Kelvin isotherm, and their change by small increment in shock strength on p - v plane. In this figure, gray area corresponds to the addition of irreversible heating by small increment in shock strength, dp_H .

It is proved here that the irreversible heating of solids by shock compression of the substance, q_{irrev} is always greater than the above-defined quantity, $\int_H TdS$. The quantity, q_{irrev} can be defined in the following way

$$\begin{aligned} q_{\text{irrev}} &= \varepsilon(S_H(v), v) - \varepsilon(S_0, v) \\ &= \Delta \varepsilon_H(v) + \int_{v_0}^v p(S_0, v') dv' \\ &= \int_H TdS - \int_H p dv + \int_{v_0}^v p(S_0, v') dv' \\ &= \int_H TdS - \int_{v_0}^v [p_H(v') - p_{S_0}(v')] dv' \end{aligned} \quad (3.64)$$

The last expression is an abbreviated form of the second last expression of Eq.(3.64). The second term of the last expression of Eq.(3.64) revealed always positive, since the integrand is always positive for any values of the volume.

The irreversible heating of solids by shock compression of the substance, q_{irrev} is a good variable in the thermodynamic sense, since it is a difference in the value of specific internal energy at two specific equilibrium states. As it will be shown later, the second term of the last expression of Eq.(3.64) cannot be expressed as the universal formula. It is, therefore, interesting to know which of the two terms in Eq.(3.64) is greater and how.

Figure 3.28 shows the geometrical representation of various quantities defined previously. The cold compression curve, the isentrope centering the initial state, the shock Hugoniot curve, are shown in the figure. Increment in the total internal energy is given by the triangular area limited by the zero pressure line, the isochoric at $v=v$, and the Rayleigh line.

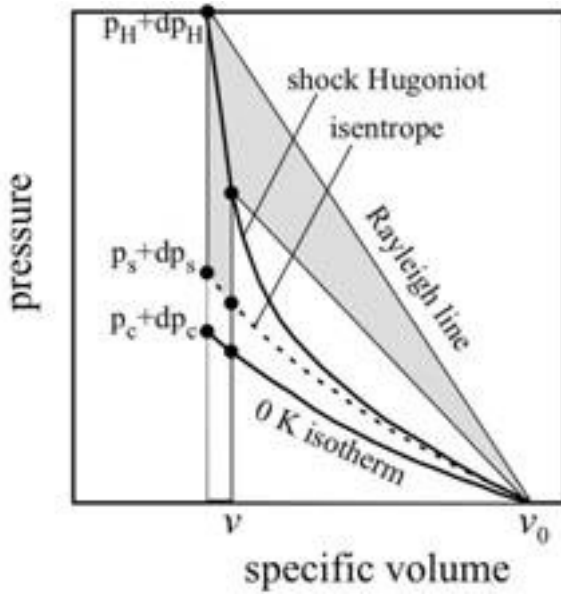


Fig. 3.27 Schematic illustration of the increase in the irreversible heating by the small increment in shock strength.

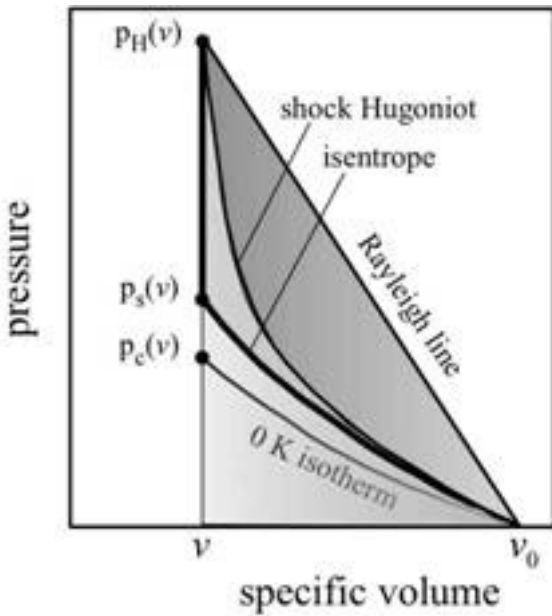


Fig. 3.28 Schematic illustration of some of the defined quantities in this section including irreversible heat by shock compression.

The area limited by the Hugoniot curve and the Rayleigh line (hatched top-right to bottom-left) corresponds to the value of $\int_H T dS$. Secondly, the area limited by the Hugoniot curve and the isentrope centering the initial state corresponds to the value of the second term of the last expression of Eq.(3.64). The sum of areas of two differently grayed areas, therefore, corresponds to q_{irrev} , i.e., the irreversible heating of solids by shock compression.

It is again noted that the value of one of the gray region is not a good thermodynamic variable, while sum of these two areas becomes a good variable. As calculated in Eq.(3.63), one of the areas can be easily given by the available shock Hugoniot data. The ratio of these two gray areas is, therefore, important. As shown later, the hatched lower-pressure region is found to be smaller than $\int_H T dS$, i.e., typically about 10 percent of $\int_H T dS$. Roughly speaking, the value of $\int_H T dS$ is a good measure of irreversible heating by shock compression. This indicates that the irreversible heating can be estimated very simply not by assuming physical models of the equation of state for the substances at high pressures and temperatures.

3.5.2. Irreversible Heat of the Grüneisen Solids

By using Eq.(2.26) with Eq.(3.63), we obtain

$$\begin{aligned}
 q_{irrev} &= \int_H TdS - \int_{v_0}^v [p_H(v') - p_{S_0}(v')] dv' \\
 &= \int_H TdS - \int_{v_0}^v \frac{\gamma(v')}{v'} [C(S_H(v')) - C(S_0)] \Theta(v') dv' \\
 &= \int_H TdS + \int_{\Theta_0}^{\Theta(v)} [C(S_H(\Theta')) - C(S_0)] d\Theta'
 \end{aligned} \tag{3.65}$$

where the change in the new variable $C(S)$ can be estimated by

$$\begin{aligned}
 dC(S_H) &= \frac{T_H dS_H}{\Theta(v)} = \frac{1}{\Theta(v)} \frac{u_p^2}{u_s} du_s \\
 &= \frac{1}{\Theta(M)} \frac{A^2}{B^2} \frac{(M-1)^2}{M} dM
 \end{aligned} \tag{3.66}$$

One may use any assumptions on the characteristic temperature other than the assumption, Eq.(3.54).

One of the fundamental parameter of the irreversibility may be the ratio of the irreversible heating to the total energy increase by shock compression,

$\Delta\epsilon_H(v)=u_p^2=A^2/B^2(M-1)^2/2$. By combining Eqs.(3.63), (3.65), (3.66), we have an expression of this reduced irreversible heating for the Grüneisen solid

$$\tilde{q}_{irrev} = \frac{q_{irrev}}{\Delta\epsilon_H} = \frac{M^2 - 4M + 3 + 2\ln M}{(M-1)^2} + \frac{2}{(M-1)^2} \int_{\Theta(1)}^{\Theta(M)} \int_1^{M'} \frac{(x-1)^2}{\Theta(x)x} dx d\Theta(M') \tag{3.67}$$

In this expression, the first term has no material dependence, if the expression is given in terms of Mach number, while the second term contains material properties in that the compression behavior of the characteristic temperature function $\Theta(v)$ will affect the integrated values. We will show from now, that the material dependent term provides smaller contribution to the irreversible heating than the dominant Mach number function term.

In order to investigate the contribution of the first and second terms of the above expression, we will make an approximation of weak shock limit of the above expression. The first term, $\int_H TdS$ can be written as a power series of $(M-1)$,

$$\frac{\int_H TdS}{\Delta\epsilon_H} = \frac{2}{3}(M-1) - \frac{1}{2}(M-1)^2 + \frac{2}{5}(M-1)^3 \dots \tag{3.68}$$

while the second term can be expanded as

$$\frac{\int_{\Theta_0}^{\Theta} [C(S_H(\Theta')) - C(S_0)]}{\Delta\epsilon_H} = \frac{\gamma_0}{6B} (M-1)^2 \tag{3.69}$$

Combining, we have the expression for q_{irrev} as

$$\tilde{q}_{irrev} = \frac{q_{irrev}}{\Delta \epsilon_H} = \frac{2}{3}(M-1) - \frac{1}{2} \left[1 - \frac{\gamma_0}{3B} \right] (M-1)^2 \dots \quad (3.70)$$

From Eq.(3.69), the contribution of the second term is smaller than the first one at least in weak shock regime. And the first term may be responsible for the entropy production at the wave front structure. At least up to the second order of $(M-1)^2$ in the above equation, no definite theory for the Grüneisen parameter is needed, but requires only the value at the initial state of the material. For most substances whose shock Hugoniot data is available, sign of the bold parenthesis of the second order term is shown to be positive, so that the sign of the second term is positive as a whole.

In order to examine how is the contribution of the second term of Eq.(3.65) on the value of non-dim. q_{irrev} , we have performed the numerical integration of Eq.(3.65) for aluminum. Figure 3.29 shows the calculated irreversible heat of aluminum upon compression. Figures 3.30 shows the calculational results of the increase of non-dim. q_{irrev} upon shock strength and upon volume compression. In these calculations, the behavior of the Grüneisen parameter is assumed to be given by three theoretical models.

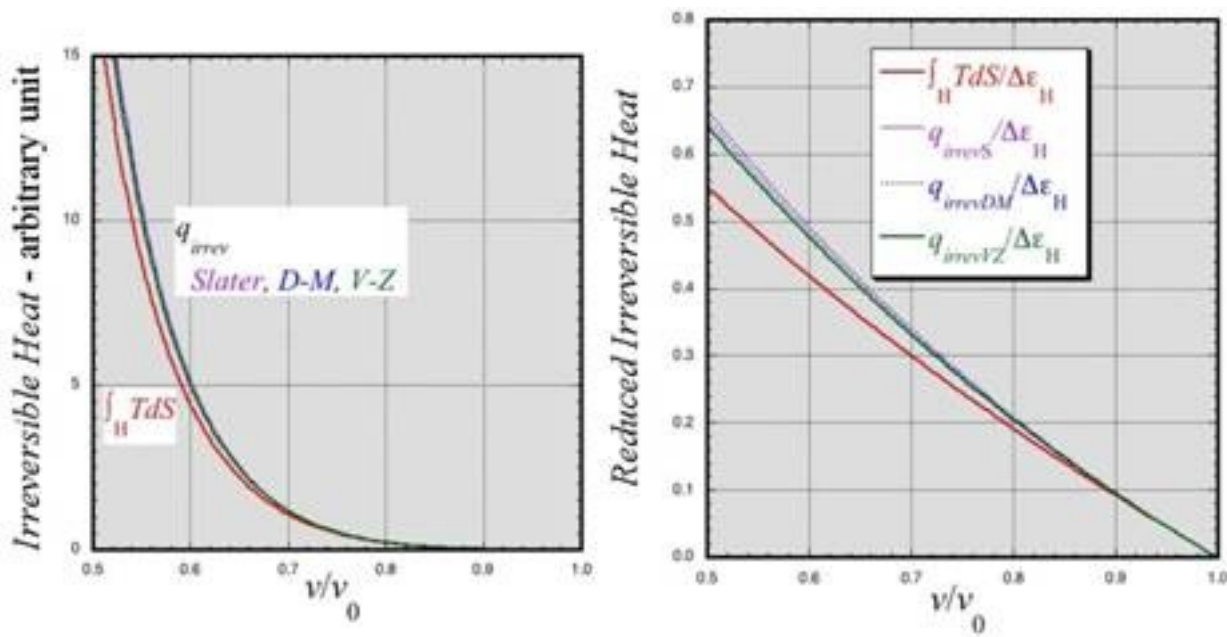


Fig. 3.29 Estimated irreversible heat by shock compression of aluminum. Lower plot shows the irreversible heat divided by increase of internal energy by shock compression, non-dim. q_{irrev} .

It is seen from Figs. 3.29 and 3.30 that the term, $\int_H TdS$ is always the dominant portion of the irreversible heat of aluminum. It has been evidenced that this tendency is common for the various metals covered in the present calculation. It is also seen that in the weak shock regime, the term, $\int_H TdS$ gives almost complete description of the irreversible heating, as is predicted by Eq.(3.70).

With no assumptions on the specific heat for solids, it is found that the irreversible heating of condensed media can roughly be estimated by using the available shock Hugoniot data. More accurate estimation of it can be made by calculating the increase in the thermal internal energy caused by the irreversible processes taking place at the shock front structure. For this purpose, we have to assume the compression behavior of the Grüneisen parameter.

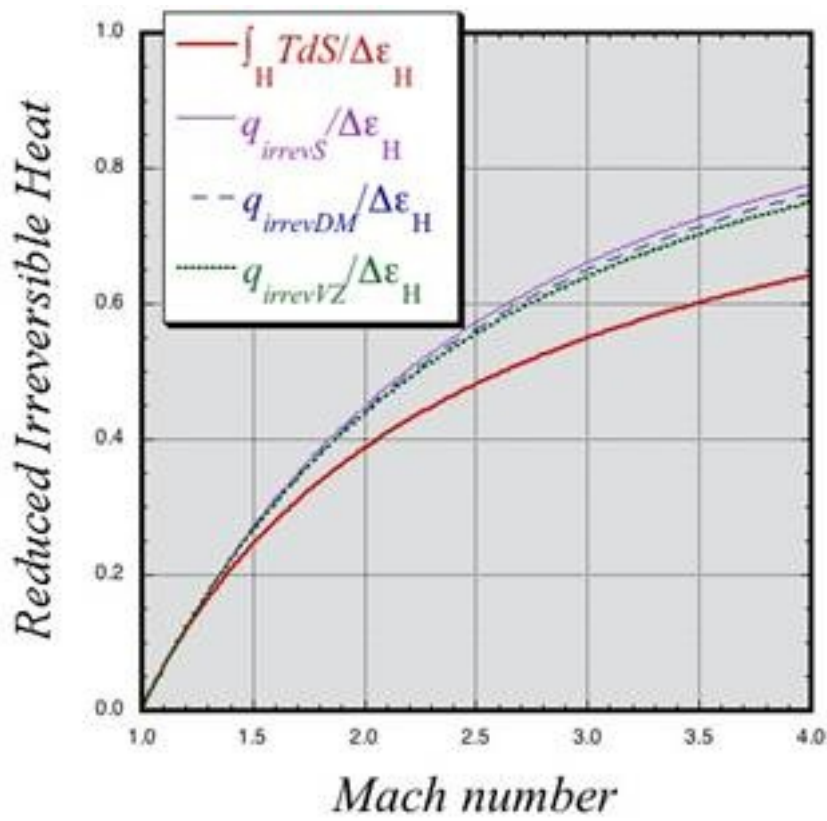


Fig. 3.30 Estimated reduced irreversible heat, non-dim. q_{irrev} against shock Mach number.

From these discussions, it is shown that

The irreversible heating, q_{irrev} , which denotes the quantity of heat acquired by the irreversible heating through the various irreversible and non-equilibrium processes occurring within the shock wave front is found to be calculated by the available shock wave data combined with the Grüneisen assumption with no physical models for the specific heat.

The irreversible heating, q_{irrev} , can be approximated by $\int_H TdS$, and the quantity divided by internal energy increase by shock compression is given by a function only of the shock Mach number.

The detailed calculation based on the theoretical models for the Grüneisen parameter showed that the results are found to be insensitive to the assumptions on the behavior of the Grüneisen parameter.

Chapter 4 Detonation of Condensed Phase High Explosives

Detonation waves in condensed high explosive or high energetic materials are a kind of shock wave associated with a very fast chemical reaction at the front. The most significant difference between high pressure shock waves in inert materials and detonation waves is that the detonation wave is a self-sustained wave backed up by the constant energy supply through detonation chemical reaction. In order to understand the detonation phenomena of condensed phase high explosives, enormous amount of experimental data and theoretical calculations have been published. (for example, Fickett and Davis 1979, Gibbs and Popolato 1980, Mader et al 1982) Equation of state (EOS) for the detonation product gases is one of the important research topics, which attracts many researchers. (Fickett and Davis 1979, Mader 1998, Zukas and Walters 1997, Cheret 1993) Theoretical calculations based on the first principle, chemical kinetics calculations, quantum mechanical calculations, etc have made to aim at the collection of information on the basic features of the phenomena. (Shaw 1989, Shaw 1998, Ree et al 1998, Pastine 1998) Although the experimental data set may not be so precise to evaluate the theories.

Another strategy of research of EOS might be to provide convenient tool to use in a computer code for the numerical simulation of the detonation phenomena. (Mader et al 1982) Many authors have already published extensive works in this direction. (Shaw 1989, Miller and Alexander 1989, Davis 1998) There still need a comprehensive and closed form EOS function, which is proved to be valid within tolerable accuracy. For example, to simulate the shock to detonation transition (SDT) process, EOSes of the detonation gases and unreacted material, and a physical model of shock-induced reaction onset are required. None of these have known precisely for any kind of energetic materials. Among these issues, information of the EOS of the detonation gases may be the most reliable than the other two issues.

In this chapter, at first, a general thermodynamic analysis of detonation behavior by the change in the initial state parameters is given. We will then present new alternative way of determining the usable EOS function based on the minimum set of experimental data on the detonation velocity and some others, explained later. The present method gives an EOS, which is fully compatible with the experimental measurement within the experimental error. Based on the close examination of the Jones-Stanyukovich-Manson relation the role of the Grüneisen parameter is discussed. After a possible error analysis of using this equation together with the experimental data for the detonation velocity, a simplified method to calculate the Grüneisen type EOS for the detonation gas is given. Present method can be used mathematically consistent with the data set of different quantities. In the course of this process, very simple approximation to the C-J states is formulated. Then the error contained in the estimated functional form of EOS is again discussed.

Then we will discuss the outcome from the temperature dependence of detonation velocity. Finally, we will discuss also the equation of state for unreacted high explosive substance with stressing special density of states characteristics of these materials.

4.1. EOS for the Detonation Product Gas

As the traditional classical theories such as Chapman-Jouguet theory (C-J theory) or the Zel'dovich-Neumann-Döring theory (ZND theory) shows, the same shock jump conditions hold at the shock front. (Fickett and Davis 1979) In this case, shock jump followed by the reaction zone can be regarded as shock front structure, and the shock jump conditions are valid inside and up to the steady equilibrium state after the completion of reaction. Equilibrium state which drives the detonation wave must be thermal and also chemical equilibrium state, if one considers the fully developed steady detonation wave. These two hypotheses are a 1-d theory which approximates the behavior of so-called high explosives. Gaseous detonation suggests, however, that detonation wave front may have 3-d structure schematically depicted as in Fig. 4.1. (bottom right picture). Furthermore, many industrial explosives have revealed not to be understood by such ideal detonation theories.

Various modifications to this ideal situation are found to be taken place. Some of these are (i) no complete 1-d steady detonation wave does not exist, rather shock front structure is believed to be inherently 3-d, (ii) detonation wave velocity is known to be temporally oscillatory, and (iii) detonation front in many industrial explosives is inherently considered to have finite thickness. The situation is schematically shown in Fig. 4.1.

Even so, major conventional explosives still are well approximated as an ideal 1-d detonation wave. In this chapter, therefore, we will focus our interests in the steady 1-d detonation wave.

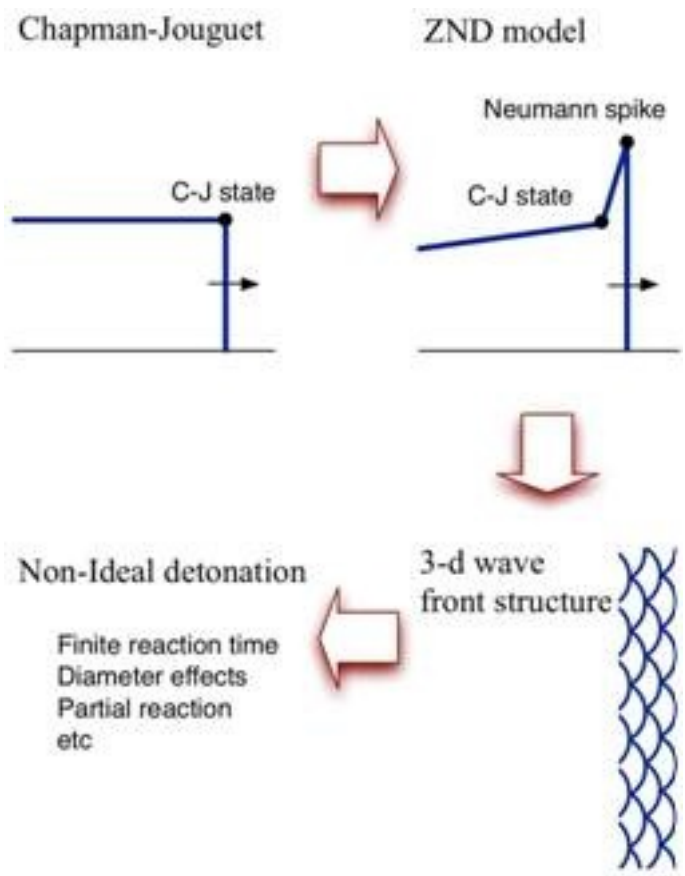


Fig. 4.1 Schematic illustration of hypotheses in detonation theory.

As stated previously, at any points in the region inside shock rise, reaction zone after passing through von Neumann spike to the C-J state, shock jump conditions can be applied. If the C-J state can be regarded as chemically as well as thermally equilibrium state, not only C-J state variables but detonation velocity D and particle velocity u_p can also be assumed to be a sort of state variable determined by the C-J state.

In this way, parameters representing detonation behavior are a function of two initial state variables such as the simple shock wave in materials. As a natural choice of these two state variables, one may choose initial specific volume, v_0 (or initial density ρ_0) and specific internal energy, ε_0 , since both appears in the shock jump conditions.

In fact, detonation velocity is given by

$$D = D(v_0, \varepsilon_0). \quad (4.1)$$

Freedom of the choice of initial state parameters, however, is quite limited for most of the energetic materials except for the powdered medium. In this chapter, we will focus on change in the detonation properties of these materials based on the Jones-Stanyukovich-Manson relation (J-S-M relation).

Detonation parameters or C-J parameters depend on the initial state of the explosive. It is necessary to be careful of the fact that powdery state of solid substance does not correspond to thermal equilibrium state in its strict sense. Even so, appreciable change in the bulk initial density can be altered by changing the porosity of the medium. On the other hand, the change in the specific internal energy is realized by changing the initial temperature. Although temperature change of the energetic materials is quite limited due to the relatively low critical temperature for onset of decomposition.

We will start with the shock jump condition for the detonation wave front connecting the C-J state with the initial state

$$\rho_0 D = \rho [D - u_p] \quad (4.2)$$

$$p_{CJ} - p_0 = \rho_0 D u_p \quad (4.3)$$

$$\varepsilon_{CJ} - \varepsilon_0 = \frac{p_{CJ} + p_0}{2} (v_0 - v) \quad (4.4)$$

where shock velocity is replaced by the detonation velocity, D . Equation of state for the substance before reaction and that after reaction are apparently different. It is assumed here that chemical equilibrium is reached at C-J point irrespective of the initial state. As seen in Eq.(4.2)-(4.4), three thermodynamic state parameters for the initial state description are used. They are the initial density (or initial specific volume), initial pressure and initial specific internal energy. It is apparent that two of these three parameters are independent in case of thermodynamic equilibrium state.

Initial state and the C-J state must be on the equation of state surface of unreacted and also on that of reacted explosive. The situation is schematically shown in Fig. 4.2. Rayleigh line as this 3-d representation is not a straight line but a curved line connecting unreacted and reacted surfaces. If one shifts the initial state gradually, the Rayleigh line will also shift correspondingly reaching a successive C-J points on the reacted EOS surface. In other words, successive C-J states reached by the different initial states gives information on the state surface of the reacted gas. In later sections in this chapter, the Grüneisen type equation of state for the detonation products is formulated based on the initial density or temperature dependence of the detonation velocity.

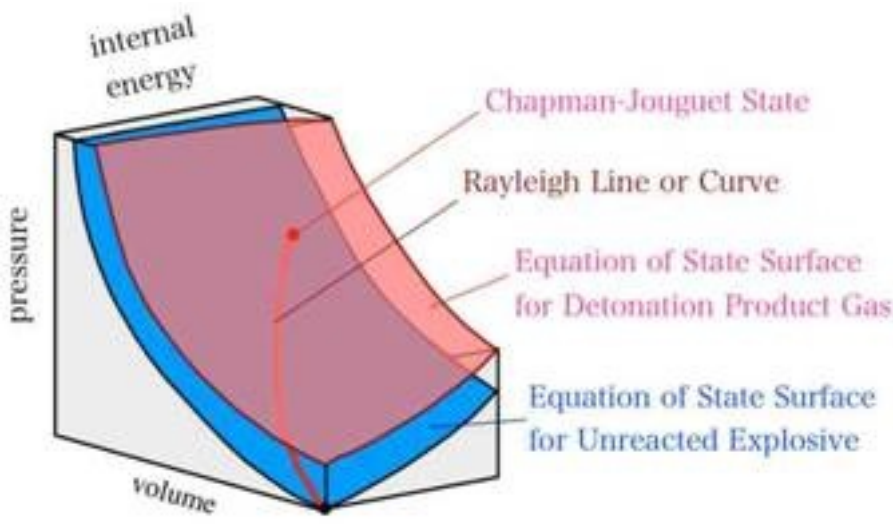


Fig. 4.2 Equation of state surface for unreacted and reacted energetic material on p - v - ϵ space. Rayleigh line or curve connects the unreacted and reacted Chapman-Jouguet state.

For this purpose, we will follow the thermodynamic discussion due to Wood-Fickett. (Wood and Fickett 1963) The change in the detonation velocity due to the change in the initial state is formally represented as

$$\frac{dD}{D} = -A \frac{dv_0}{v_0} + B \frac{d\epsilon_0}{D^2} - C \frac{dp_0}{\rho_0 D^2}, \quad (4.5)$$

where

$$A = \frac{\Gamma - 1 - \alpha}{\alpha + 2}, \quad (4.6)$$

$$B = \frac{\alpha(\Gamma + 1)^2}{\alpha + 2}, \quad (4.7)$$

$$C = \frac{\Gamma + 1}{\alpha + 2}. \quad (4.8)$$

Parameters defined in Eqs.(4.6)-(4.8) are as follows:

$$\alpha = p \left(\frac{\partial v}{\partial \epsilon} \right)_p \quad (4.9)$$

$$\Gamma = -\frac{v}{p} \left(\frac{\partial p}{\partial v} \right)_s = -\left(\frac{\partial \ln p}{\partial \ln v} \right)_s \quad (4.10)$$

Normally, parameter Γ is used as the Grüneisen parameter in detonation physics, but in this book it is defined as an exponent of the isentrope centering the C-J state or any other defined state. The Grüneisen

parameter γ is defined and related to these parameters as

$$\gamma = v \left(\frac{\partial p}{\partial \varepsilon} \right)_v = \frac{\alpha \Gamma}{\alpha + 1}. \quad (4.11)$$

These equations could be a basis of analyzing the detonation characteristics under various initial density and initial temperature. Since it is not always an easy task to estimate the parameters appeared in these equations, further considerations or formulations must be necessary.

4.2. Envelope Approximations

4.2.1. Envelope of Rayleigh lines for different initial density explosives

Among various parameters specifying the detonated thermodynamic state, i.e., the C-J state, the detonation velocity is the parameter that can be measured most reliably. Although even in the measurement of the detonation velocity, there exists some ambiguity. Empirically, the detonation velocity D is found to be an increasing function of loading density ρ_0 , namely,

$$D = j + k\rho_0, \quad (4.12)$$

where j and k denote material parameters determined for an explosive and for an interval of the initial density. (Mader et al 1982, Dobratz 1985, Zukas and Walters 1997) Parameters j and k are determined for each explosive and for a definite range in initial density. In case of PETN, for example, the value of them are

$j = 2.14, k = 2.84$	$\rho_0 < 0.37,$
$j = 1.82, k = 3.7$	$0.37 < \rho_0 < 1.65,$
$j = 2.89, k = 3.05$	$1.65 < \rho_0,$

although the ranges in the initial density of lowest and highest are small. Kerley has pointed out that at least the deflection at $\rho_0 = 1.65 \text{ g/cm}^3$ might be explained by the production of HCOOH , but the influence is gradual and has no sharp jump in the slope. (Kerley 1989) Deflection at the lower side may have some problems of measurements and scatter of the data due to the measurement method. It may have a plausible possibility that the relationship between detonation velocity and initial density is almost linear but very complicated. (Kerley 1989) As shown later, the slope k of the relationship plays an important role for the formulation of EOS, and due to the reason explained above, there is no rigid physical reason to adopt a three segment linear relationship given above. Rather we can show that the break in the slope k gives a break in some physical variables, like the detonation pressure or the Grüneisen parameter. This seems to be non-physical in this case. We will adopt the following one simple linear relation in the following analysis,

$$j=1.8482, k=3.6511. \quad (4.13)$$

Parameters used here are close to the widest range of the density above. Figure 4.3 shows the D - ρ_0 relationship described by the parameters in Eq.(4.12) and several of experimental data.

Detonation velocity is a parameter which can be measured most easily among various other parameters involved in the detonation phenomena, and is found to be the most insensitive parameter of the phenomena. If one knows the value of the initial density of the high explosive and the corresponding detonation velocity, one can plot the so-called Rayleigh line in the p - v plane. The C-J state should be on this line. Rayleigh line in p - v plane is described as

$$p_{CJ} = p_0 - Z^2(\rho_0, \varepsilon_0)[v - v_0], \quad (4.14)$$

where p , v , and ε denote the pressure, the specific volume and the specific internal energy, respectively, and the suffix 0 denotes the value at the initial state. Shock impedance $Z(\rho_0, \varepsilon_0)$ is defined as

$$Z(\rho_0, \varepsilon_0) = \rho_0 D(\rho_0, \varepsilon_0) = \frac{D(v_0, \varepsilon_0)}{v_0} \quad (4.15)$$

where the detonation velocity $D(\rho_0, \varepsilon_0)$ is realized by the initial state specified by the initial density and specific internal energy, (ρ_0, ε_0) or the initial specific volume and specific internal energy, (ρ_0, ε_0) . From now on, the initial specific volume v_0 or the initial density ρ_0 is used as an equivalent parameters. According to the C-J hypothesis, Rayleigh line touches the Hugoniot compression curve at the C-J point, and the slope of the Hugoniot curve at the C-J point is equal to that of an isentrope centering the C-J point. If we have a collection of data on the detonation velocity as a function of initial volume or initial density, it is a collection of Rayleigh lines, which covers the accessible thermodynamic states in p - v plane. Since the thermodynamic states on each Rayleigh line has a physical meaning especially on the C-J state, a collection of Rayleigh lines corresponds to a collection of isentropes, which is meaningful only in a narrow region near the C-J states.

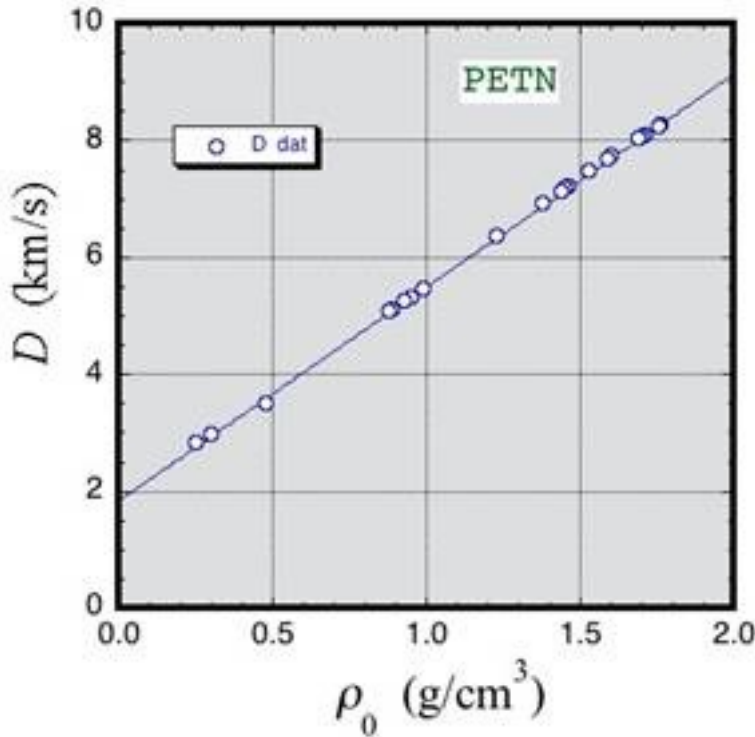


Fig. 4.3 Initial density dependence of detonation velocity for PETN. Open circles show data with additional data of C-J pressure.

Figure 4.4 shows the collection of Rayleigh lines on p - v plane drawn by using the experimental values of detonation velocities for PETN. C-J pressure data points given by Hornig et al are also shown in the same plot. (Hornig et al 1970) As is seen clearly, experimental pressure volume points are naturally on their Rayleigh line, and they seem to be on a curve of the envelope of the collection of Rayleigh lines. This looks a very good approximation for this data. We checked other explosive data and found that the envelope function of Rayleigh lines on p - v plane gives an excellent approximation to the C-J states on the plane.

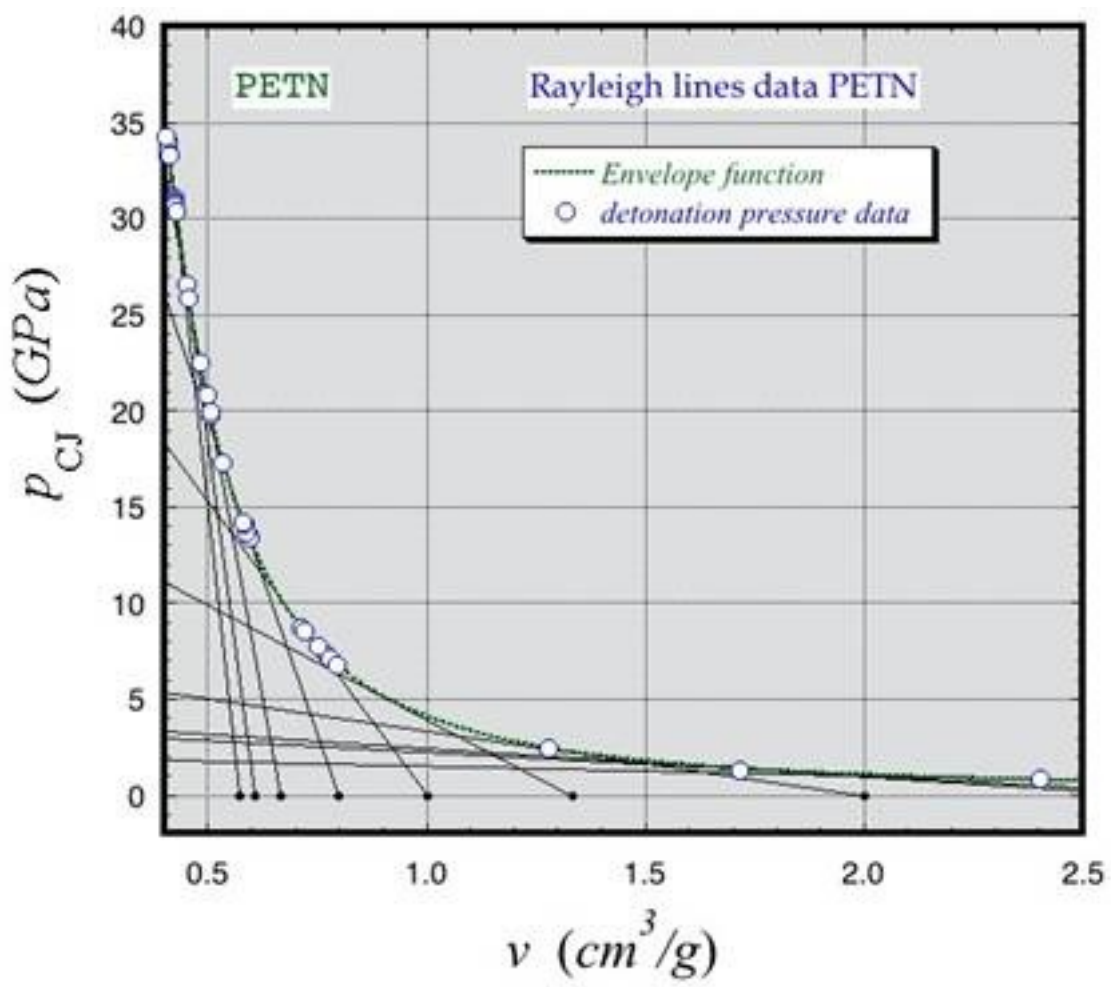


Fig. 4.4 Collection of Rayleigh lines starting from different initial volume points, and the envelope function for PETN. Open circles on each Rayleigh line are estimated C-J states.

Mathematical functional form of the envelope function of Rayleigh lines can be derived easily as

$$v = v_0 - \frac{v_0}{2(1+\varphi)} \quad (4.16)$$

$$p_{CJ} = p_0 + \frac{\rho_0 D^2}{2(1+\varphi)} \quad (4.17)$$

where the non-dimensional parameter φ is defined as

$$\varphi = \left(\frac{\partial \ln D}{\partial \ln \rho_0} \right)_{\varepsilon_0} = - \left(\frac{\partial \ln D}{\partial \ln v_0} \right)_{\varepsilon_0} \quad (4.18)$$

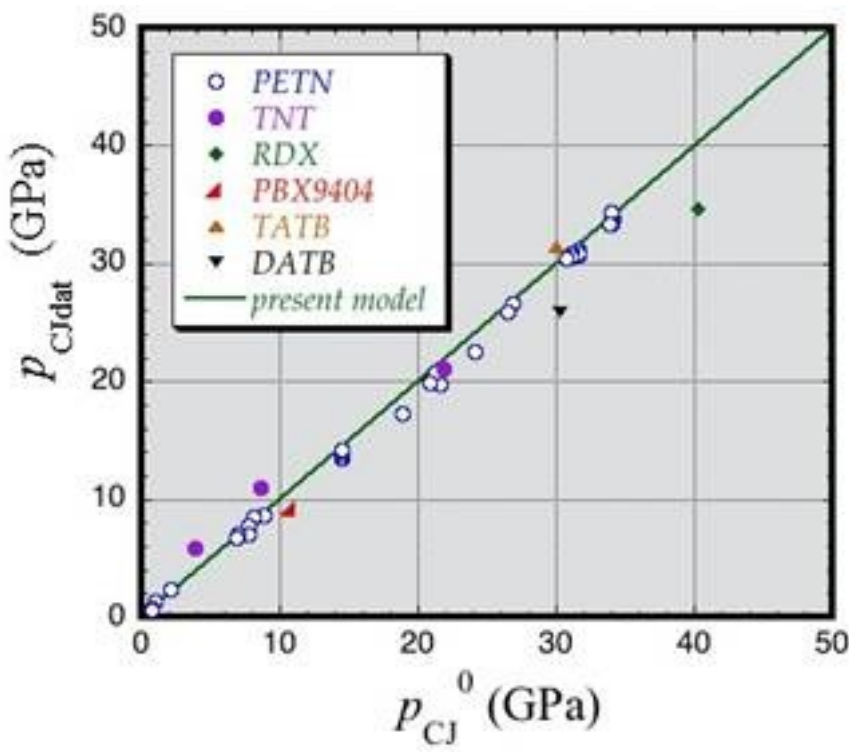


Fig. 4.5 Evaluation of the present approximation by the comparison with the measured data.

Other parameters on the C-J state can be obtained through the jump conditions for the detonation wave front, which then gives relationships between other variables on C-J state. Comparison of these functions with the experimental data shows systematic deviation of several to ten percent of their values. The agreement, however, is extremely good only on the p - v plane.

Figure 4.5 shows the comparison of the measured C-J pressure with the present approximation for various condensed explosives. Most of the measured pressure is somewhat lower than the predicted value as seen in Fig. 4.5. Later consideration shows that some data larger than the prediction can be understood in one of following three possibilities. One is that C-J assumption is violated in the sense that the state at the wave front reaches no complete thermodynamic equilibrium. The other possibility is that chemical reaction does not finished at the front. Experimental error contained in the data is within the difference in the pressure value. In other words, larger data is physically prohibited for C-J states. Precision of the present approximation will be discussed in more detail in a later section.

4.2.2. Jones-Stanyukovich-Manson (J-S-M) relation and the Grüneisen parameter

In Fig. 4.4, a narrow region on a Rayleigh line can be regraded as states on an isentrope centering the C-J state reached by the initial state, (v_0, ε_0) . Thermodynamic states within this narrow range may also be approximated by a state on the Hugoniot curve, which should be determined by combining the EOS surface of the detonation product with the Rankine-Hugoniot relationship,

$$\varepsilon - \varepsilon_0 = \frac{P + P_0}{2} (v_0 - v) \quad (4.19)$$

Since the present formulation can also be applied to the explosive substance of any phase, we include the initial pressure in Eqs. (4.14) and (4.19). We will omit p_0 from now on to proceed to the discussion of the detonation of condensed high explosives. Note that a couple of equations, Eqs.(4.14) and (4.19) gives a complete set of thermodynamic description of the ε - p - v equation of state, if one adds an assumption that each equation describes an isentrope around the C-J state point. In other words, if we give the value of two of three variables, ε , p , or v , we can calculate the other variable and also the derivative at the point by using these two equations. Most important point in the present discussion is that now we know the complete set of EOS

equations, which is valid within the range of thermodynamic state near the C-J point. It is always possible to consider a state slightly off a C-J state, which should be on another Rayleigh line, which we know the slope and the initial volume point. It is stressed again that it is possible only when we know the initial density dependence of the detonation velocity.

These analysis lead to the so-called Jones-Stanyukovich-Manson (J-S-M) relation, (Lee and Hornig 1969, Jones 1949)

$$\gamma = \frac{\Gamma(\Gamma - 1 - 2\varphi)}{\Gamma - \varphi} \quad (4.20)$$

where the parameters appeared in Eq.(4.20) are already defined in an earlier section.

Parameter Γ in Eq.(4.20) is defined as a value pertinent to the C-J state,

$$\Gamma = -\frac{v}{p_{CJ}} \left(\frac{\partial p_{CJ}}{\partial v} \right)_s \quad (4.21)$$

where suffix CJ denotes the value at the C-J state in order to stress that the pressure is assigned at the C-J state. All of the parameters, Γ , γ , and φ are state variables, and a function of initial density ρ_0 or volume v_0 .

The envelope approximation developed in the previous section is proved to be the approximation that the value of the Grüneisen gamma γ is equal to zero at C-J state. This assumption is then proved to be equivalent to the assumption that the slope of the adjacent C-J states with different initial volume is equal to that of an isentrope passing through the state. The difference of the C-J pressure data and that of envelope approximation for PETN can be seen in Fig. 4.6.

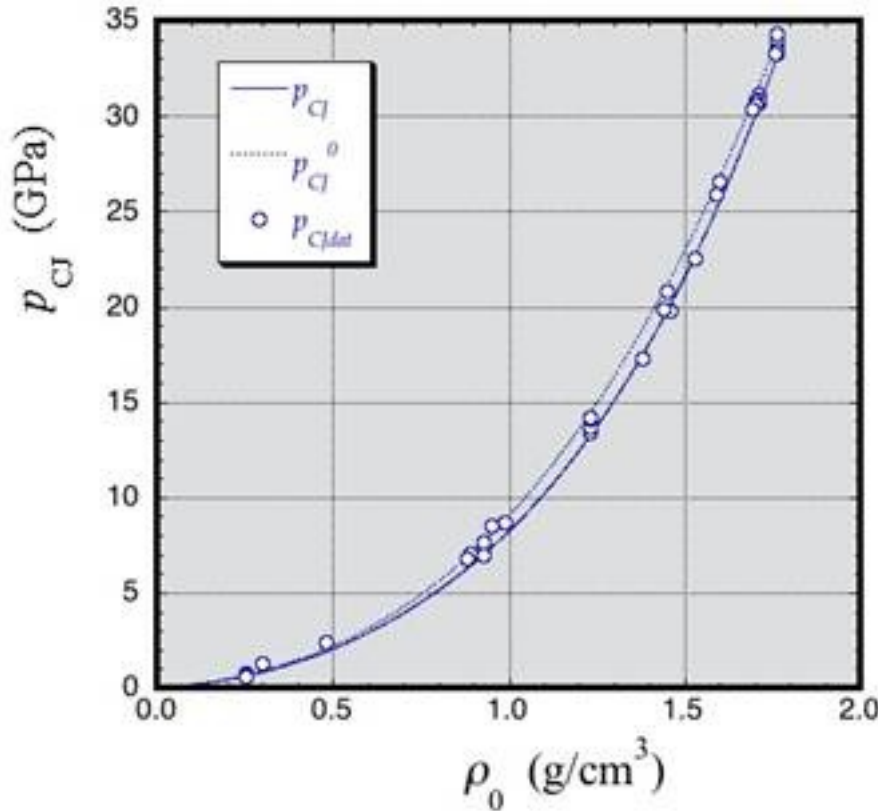


Fig. 4.6 C-J pressure vs initial density relationship for PETN. Dotted line is an envelope ($\gamma=0$) approximation.

The formulae of Eqs.(4.16) and (4.17) can be derived by putting $\gamma=0$ in the J-S-M relationship, i.e,

$$\Gamma_0 = 1 + 2\varphi \quad (4.22)$$

The other possibility from Eq.(4.20) is abandoned by the physical consideration. Since this equation contains a parameter φ which is determined only by the measurement of the detonation velocity. In this sense, this value can basically be evaluated rather in high precision compared with other parameters. Even so, we will examine the error contained in obtaining φ as

$$\frac{d\Gamma}{\Gamma} = \frac{2d\varphi}{1+2\varphi} \quad (4.23)$$

In case of PETN, we have two kinds of expression for Eq.(4.12) with different parameter set. Since the value of parameters used in this calculation is very similar to those of the second segment relation in the previous section, the difference in the value of Γ stems from that in the value of k . Resulting difference in the value of Γ is 0.008. This value is negligibly small and one may consider that the estimated approximate pressure value is valid within the precision of the assumptions.

Solid line in Fig. 4.6 is the calculated C-J pressure explained in the later section. These two C-J pressure can be compared, and the difference may be attributed to the contribution from the Grüneisen gamma. The Grüneisen gamma contribution can be estimated by the J-S-M formula as

$$\Gamma = 1 + 2\varphi + \frac{\Gamma - \varphi}{\Gamma} \gamma \quad (4.24)$$

Since C-J pressure p_{CJ} is derived by the expression

$$p_{CJ} = \frac{\rho_0 D^2}{1 + \Gamma} \quad (4.25)$$

contribution of Grüneisen gamma can be seen by comparing the value of γ with or without the third term in Eq.(4.24). Figure 4.7 shows the ratio of γ_0/γ to evaluate the contribution of Grüneisen gamma. Details of the calculation of γ will be presented in a later section. Discrepancies of the value of Γ is almost 10 % or less over a wide range of initial density. All the theoretical and experimental efforts are to fill this gap. (Steinberg 1985, Brown and Braithwaite 1989) One may note, however, that only a very accurate measurement of variables other than detonation velocity or a reliable theoretical calculation with the precision higher than several % can contribute to reach further knowledge of the detonation physics.

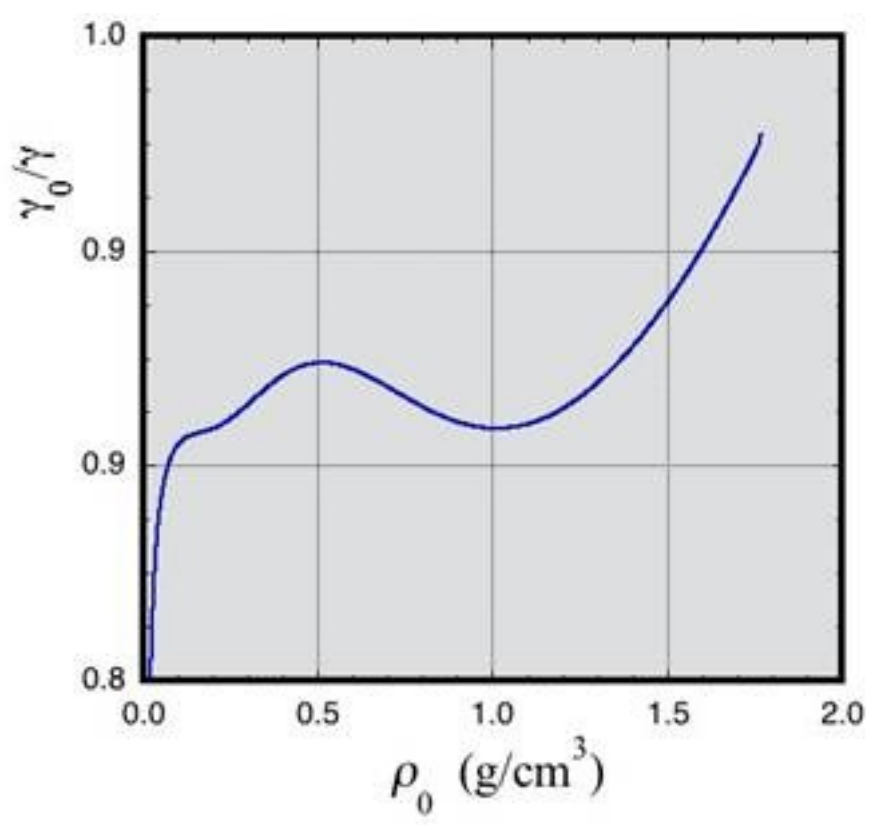


Fig. 4.7 Evaluated contribution of Grüneisen gamma to the adiabatic index of PETN.

4.3. Grüneisen EOS for Detonation Product Gas

4.3.1. Volume dependent Grüneisen parameter of detonation product gases

In this chapter, the Grüneisen type equation of state for the medium other than crystalline solids is discussed. In this case, cold compression curve may have no role in the determination of the Grüneisen parameter and material function $f(v)$. Under the assumption of the Grüneisen parameter as a function of volume only, $\gamma=\gamma(v)$, together with the thermodynamic definition, one may again arrive at Eq.(2.9) by integrating Eq.(1.4) along an isochoric. Instead of cold compression curve, one may choose any succession of states on the state surface. The most reasonable choice of a compression curve must be an isentrope centering an appropriate thermodynamic state described in terms of volume, pressure or internal energy. In this case, we have the relation,

$$p_s(v) = f(v) + \frac{\gamma(v)}{v} \varepsilon_s(v) \quad (4.26)$$

where $p_s(v)$ and $\varepsilon_s(v)$ denote an isentropic compression curve. One may also choose, however, any compression curve on a state surface of the medium in question. The Grüneisen equation of state expressed by Eq.(4.26) has an important property such that arbitrary compression curve $p_a(v)$ and its corresponding internal energy function $\varepsilon_a(v)$ must satisfy the condition

$$p_a(v) - \frac{\gamma(v)}{v} \varepsilon_a(v) = f(v) \quad (4.27)$$

This relationship has no physical constraint on the choice of compression curve on the state surface. This is the fundamental property of the Grüneisen equation of state except for the assumption of $\gamma=\gamma(v)$.

To obtain a functional form of the equation of state for the detonation product gases, it is necessary to have further data set in addition to the D - ρ_0 data. Other data cannot be the approximate C-J pressure data, but the precision C-J pressure data with different initial density, or an isentropic curve deduced from the cylinder expansion experiment, etc. As is seen in Fig. 4.6, C-J pressure measurement has not enough precision to calculate the Grüneisen parameter at that volume. Although there still have problems for the cylinder expansion experiments, we will choose here to adopt to use one isentropic curve determined by the cylinder expansion data to calculate the Grüneisen parameter.

We further assume that the Grüneisen parameter defined by Eq.(4.11) is a function of volume, and no dependence on temperature. Precision of this assumption will be discussed later. Lee and Hornig (Lee and Hornig 1969) have calculated the Grüneisen parameter of PETN in almost the same situation. They assumed a test function for the Grüneisen parameter to fit the experimental data for the detonation velocity. Their method is quite tedious to fulfill the high precision result, and furthermore their calculation seems not to be very accurate.

Here we present much more direct and accurate method of obtaining the Grüneisen type equation of state of the form,

$$p = p_s(v) + \frac{\gamma(v)}{v} [\varepsilon - \varepsilon_s(v)] \quad (4.28)$$

which can reproduce the detonation velocity data as well as the cylinder expansion data completely. In Eq.(4.28), material functions, $p_s(v)$, $\varepsilon_s(v)$ and $\gamma(v)$ should be determined. If we can obtain an isentrope, for example, from the cylinder experiment, we now know the isentropic functions as $p_s(v)$ and $\varepsilon_s(v)$.

Fundamental assumptions or procedures to obtain $\gamma(v)$ to have a closed form Grüneisen EOS, are :

- (1) C-J hypothesis is valid,
- (2) D - ρ_0 data available,
- (3) full use of J-S-M relationship for calculation,
- (4) C-J state variables data at crystal density detonation,
- (5) an isentrope through a C-J state at crystal density detonation.

After a tedious but straightforward calculation, we have a differential equation along the C-J states as

$$\frac{dv}{d\rho_0} = \frac{F_1}{F_2} \quad (4.29)$$

$$F_1 = \frac{\Gamma(\Gamma + 1)}{\rho_0(\Gamma - \varphi)^2} (3\varphi^2 - 2\varphi\Gamma + \Gamma^2) \quad (4.30)$$

$$F_2 = \frac{\gamma(\gamma + 1)}{v} - \gamma \frac{\frac{dp_s}{dv} + \rho_0^2 D^2}{p_{CJ} - p_s} - \frac{\rho_0(\Gamma + 1)^2}{(\Gamma - \varphi)^2} \times (3\varphi^2 - 2\varphi\Gamma + \Gamma^2 + \varphi) \quad (4.31)$$

where the change in the Grüneisen parameter is determined as

$$\frac{d\gamma}{dv} = \frac{\gamma(\gamma + 1)}{v} - \gamma \frac{\frac{dp_s}{dv} + \rho_0^2 D^2}{p_{CJ} - p_s} \quad (4.32)$$

Eqs.(4.28)-(4.31) together with E.(4.32) form a closed set of equations, which can be integrated along the C-J state curve. We can choose the C-J state reached from the initial density of explosive or crystal density as a starting point of calculation, although that point is a singular point of the differential equation. One may derive the limiting relationship near the singular point to start the integration. As the information on the isentrope needed to the calculation, we adopt the Jones-Wilkins-Lee (JWL) parameters for the PETN at the C-J point against the crystal density. (Kury et al 1965, Zukas and Walters 1997, Kuhl 2010) JWL parameters we use in the present calculation are (Mader et al 1982)

$$A = 617.0 \text{ [GPa]}$$

$$B = 16.93 \text{ [GPa]}$$

$$C = 0.6312327 \text{ [GPa]}$$

$$R_1 = 4.40$$

$$R_2 = 1.20$$

$$w = 0.25$$

Meaning of the parameters is of a standard one.

The result of the calculation is already shown in Figs. 4.6 and 4.7. The Grüneisen parameter γ , adiabatic index Γ , detonation parameter φ for PETN as a function of initial density and of specific volume are depicted in Figs. 4.8 and 4.9.

Among these three parameters, the value of ϕ is determined only by the measurement of detonation velocities, and precision of it is very high. Dependence of ϕ on the initial density and on the specific volume is smooth, but the other parameters, Γ and γ has a maximum at some value of initial density or of volume. This result is once explained by the theoretical reason due to the shape of the molecular potential function, but it might be attributed to the properties of the JWL functions to express the cylinder expansion data. (Yoo, et al 1998, Kury et al 1965)

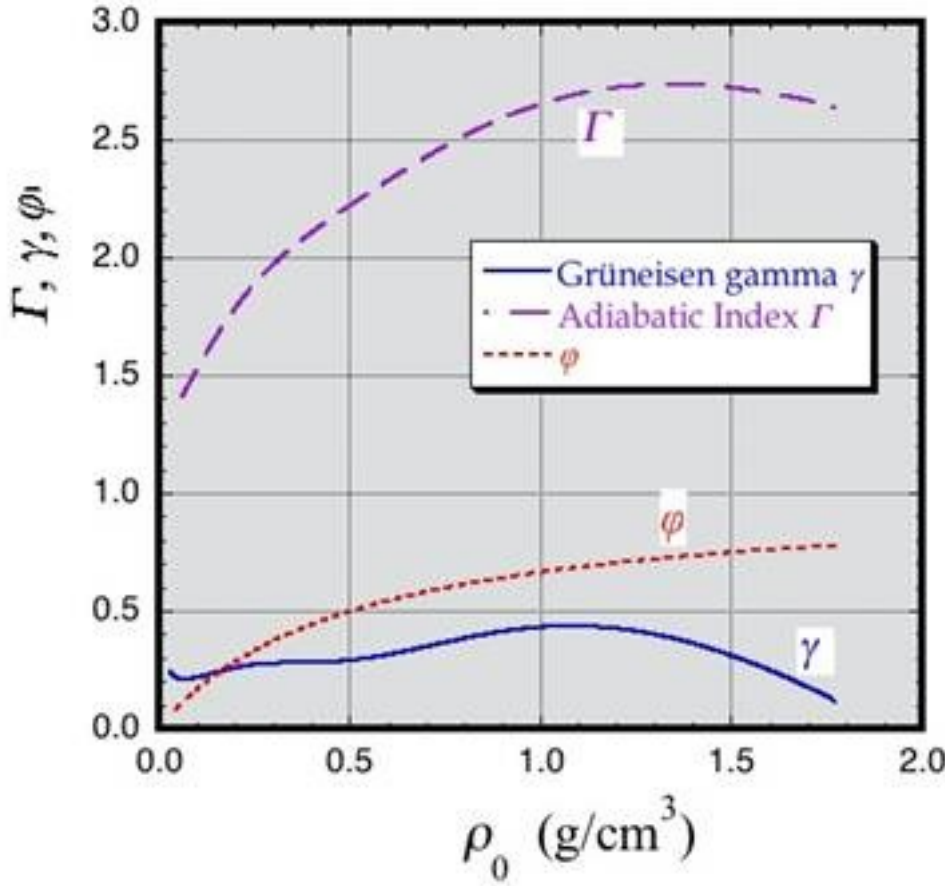


Fig. 4.8 Grüneisen parameter, adiabatic index and detonation parameter as a function of initial density.

4.3.2. Comparison of release isentropes centering several C-J states reached by detonation of PETN with different initial densities

For PETN, other three different cylinder expansion data are available with different initial densities. (Zukas and Walters 1997) To examine the plausibility of the obtained EOS for the detonation gas of PETN, isentropes corresponding to the experimental data of cylinder expansion are calculated and compared. Isentropes other than $p_s(v)$ or $\varepsilon_s(v)$ are calculated by integrating the differential equation

$$\frac{dp}{dv} = \frac{dp}{dv} + \left[\frac{d \ln \gamma(v)}{d \ln v} - \gamma(v) - 1 \right] \frac{p - p_s(v)}{v} \quad (4.33)$$

Figure 4.10 shows the calculated isentropes. To examine the compatibility of the calculated isentropes with the measured isentropes using the published JWL parameters by cylinder expansion, isentropic pressure volume relationships starting from three different C-J states of PETN are compared in Fig. 4.11. Ratio of the value of pressure is plotted in the figure. Since the estimated value in this work of C-J state parameters other than that for the theoretical maximum initial density is slightly different from the published isentropic data, the values of the state is adjusted as a starting point of numerical integration of Eq.(4.33).

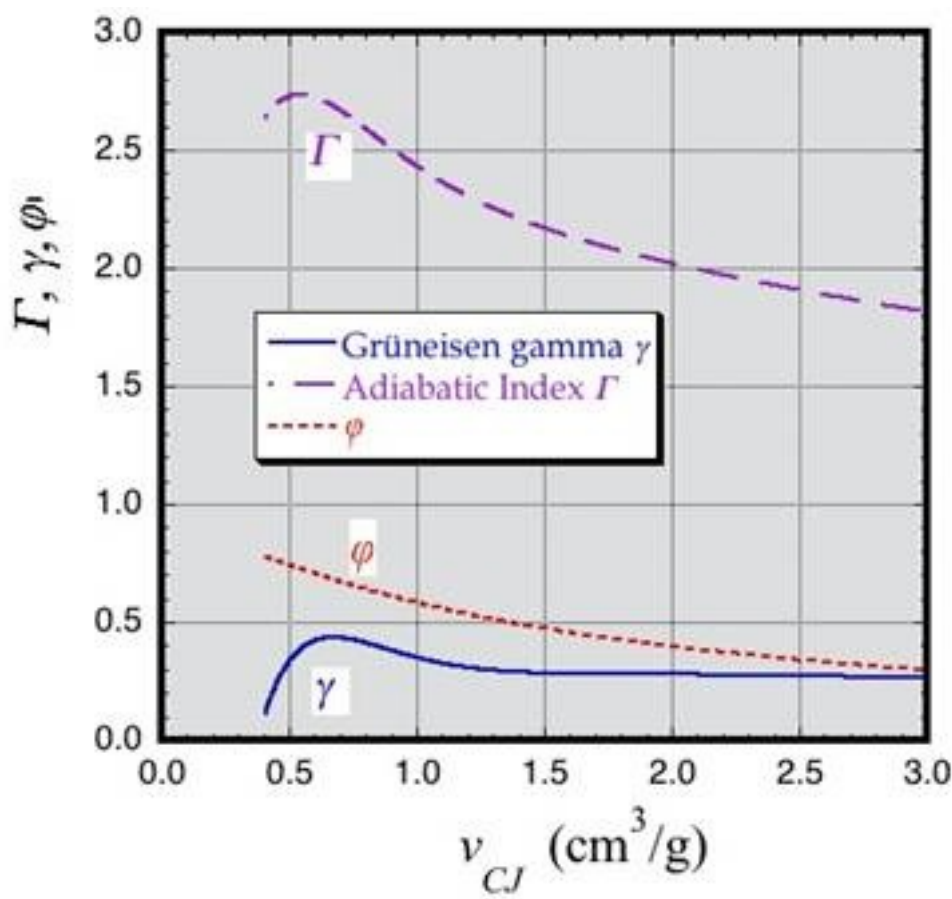


Fig. 4.9 Grüneisen parameter, adiabatic index and detonation parameter as a function of specific volume at C-J states.

From Fig. 4.11, estimated error in the isentropic pressure is found to be within 3% over wide range of pressures less than 1 GPa. This accuracy is supposed to an acceptable level. It is suggested by the physical consideration that the temperature dependence of the Grüneisen parameter may be one of the possibilities to explain the difference between these two pressure values. Rather we can safely say that temperature dependence of Grüneisen parameter is not very large to appear in the pressure volume relationship centering rather different pressure-temperature states.

This study strongly suggests that the Grüneisen type EOS with the volume-dependent Grüneisen parameter together with the available detonation velocity data gives a sufficient description of the EOS which can explain isentropes centering the C-J states reached with different initial density detonation as well as the detonation velocity data.

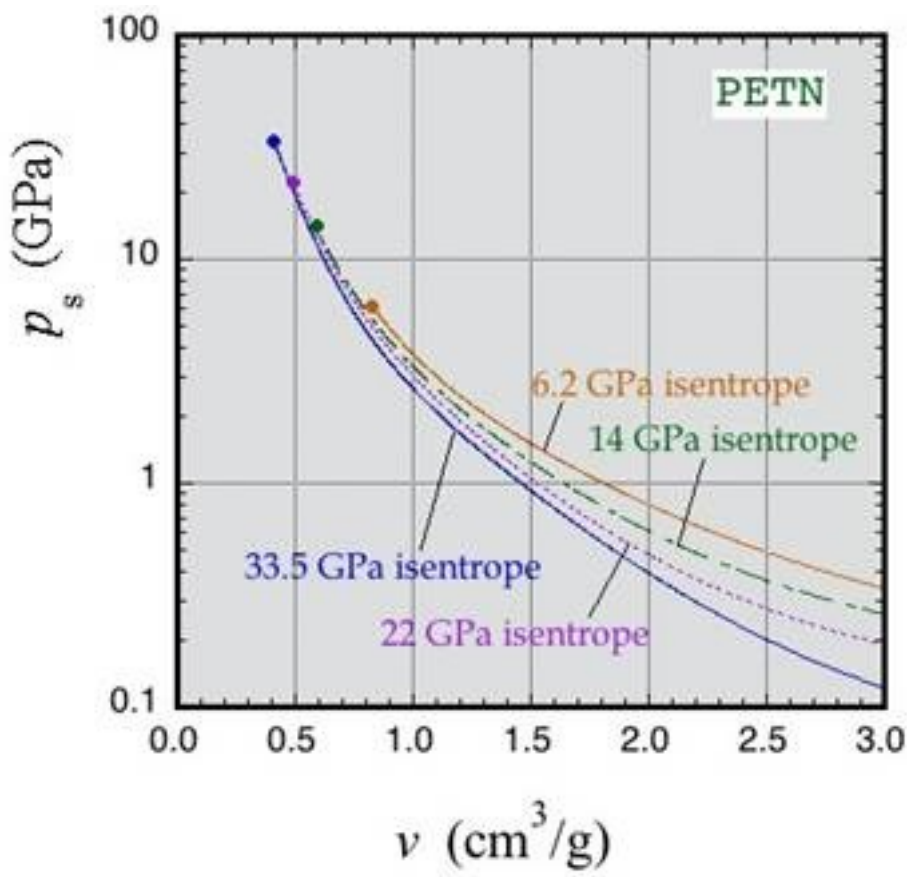


Fig. 4.10 Calculated isentropes. Case (a), (b), (c) and (d) are an isentrope through $p_{CJ} = 33.5$ GPa, 22.0 GPa, 14.0 GPa and 6.2 GPa, respectively; All of lines are calculated by integrating EOS using Eq.(4.21).

We have developed a simple approximation for the C-J state variables based on the detonation velocity measurement with different initial density. The present model is found to be an approximation of Grüneisen gamma equal to zero. Contribution of the Grüneisen parameter is discussed to be several to ten %. Integration method is established to calculate Grüneisen type EOS for the detonation products, and the numerical calculation has been made for the PETN explosive. Results have been compared with the isentropes derived from the cylinder expansion experiments. This rather global description of the detonation of different density but same explosive substance naturally leads us to the description of shock to detonation transition by one global Grüneisen EOS. This work is under way. (Kubota et al 2010)

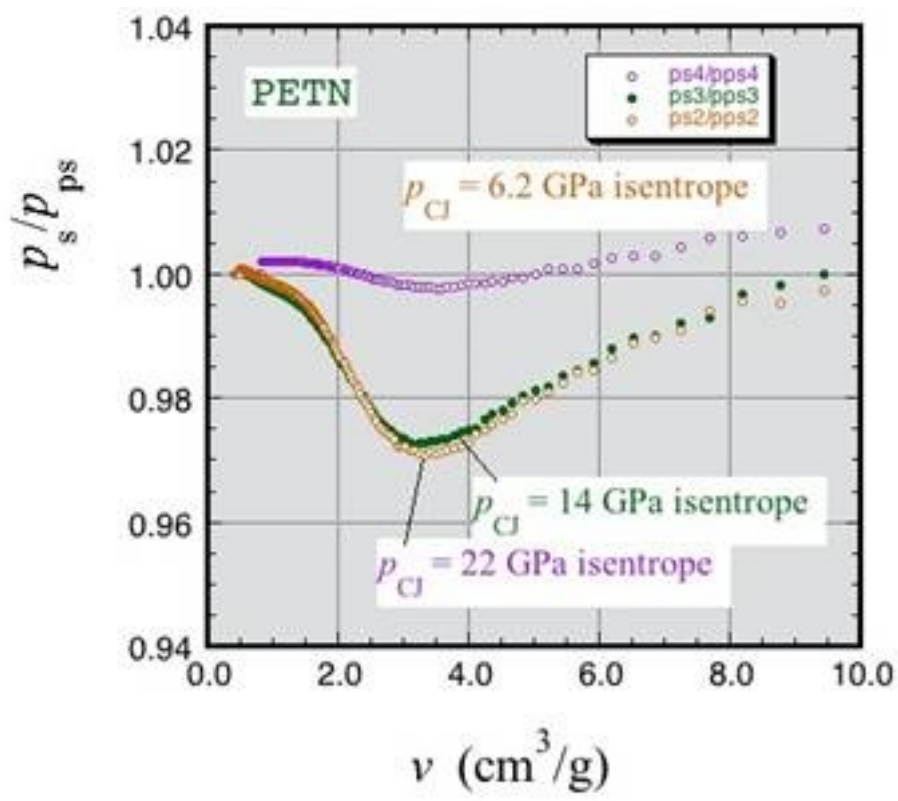


Fig. 4.11 Difference in the calculated isentropes and evaluated isentropes from cylinder expansion data. Pressure ratio of these two expressions is plotted for three isentropes.

4.4. Temperature Dependence of Detonation Velocity

4.4.1. Thermodynamic formulation by Chapman-Jouguet assumption

Temperature dependence of detonation velocity for various explosives has been measured, although the temperature range used in the experiments is limited to almost 100 degrees due to the relatively low decomposition temperature of these materials. Even so, detonation velocity is one of the most accurately measurable quantities of the detonation parameters, and one may obtain temperature coefficient with tolerable precision. Unlike the initial density dependence of the detonation velocity, change in the detonation velocity with the change in initial temperature is a modest one. One may not be very sure that the Chapman-Jouguet assumption can be safely applied to this slight difference in the detonation properties. This aspect will be discussed again later in this section.

By heating up the explosive, the specific internal energy increases, and at atmospheric condition, the specific volume also increases due to thermal expansion. In experimental conditions, changing temperature means the state change under fixed pressure condition. This is due to the fact that it is almost impossible to maintain specific volume while raising temperature of the substance. Isobaric condition is fulfilled even in the case of different initial density experiments. In the case of difference in the initial density, however, density change is realized not by quasi-static thermodynamic process but by changing the porosity of the explosive. In strict thermodynamic sense, powdered media is not in thermodynamic equilibrium due to the inhomogeneous spatial distribution of materials. Shocked states of these porous materials, however, can be regarded as continuous high pressure high temperature states jumped from low density state of the material.

Unlike the initial density dependence of the detonation velocity, the change in the initial thermodynamic state of explosive by changing the temperature is regarded as homogeneous and equilibrium variation of state. Therefore, the temperature dependence can be discussed in thermodynamic terms as in Eq. (4.5).

The experimentally obtained data for the variation of detonation velocity can be read as

$$\left(\frac{\partial D(v_0, \varepsilon_0)}{\partial T_0} \right)_{p_0} \quad (4.34)$$

Eq.(4.34) can be rewritten as

$$\begin{aligned} \left(\frac{\partial D(v_0, \varepsilon_0)}{\partial T_0} \right)_{p_0} &= \left(\frac{\partial D(v_0, \varepsilon_0)}{\partial \varepsilon_0} \right)_{p_0} \left(\frac{\partial \varepsilon_0}{\partial T_0} \right)_{p_0} \\ &= \left(\frac{\partial D(v_0, \varepsilon_0)}{\partial \varepsilon_0} \right)_{p_0} [C_{p_0}(T_0) - p_0 v_0 \beta_0] \end{aligned} \quad (4.35)$$

which connects the coefficient to the internal energy dependence of the detonation velocity. Where β_0 denotes the thermal expansion coefficient.

$$\beta_0 = \frac{1}{v_0} \left(\frac{\partial v_0}{\partial T_0} \right)_{p_0} \quad (4.36)$$

According to the experimental results, the coefficient of Eq.(4.34) is known to have the negative value. Detonation velocity slows down with increasing temperature.

We will begin the analysis with Eq.(4.5). At the condition of $dp_0=0$, Eq.(4.5) can be rewritten to

$$\begin{aligned}
\frac{dD}{D} &= -A \frac{dv_0}{v_0} + B \frac{d\varepsilon_0}{D^2} = \left[-\frac{A}{v_0} \left(\frac{\partial v_0}{\partial \varepsilon_0} \right)_{p_0} + \frac{B}{D^2} \right] d\varepsilon_0 \\
&= \left[-\frac{A}{v_0} \left(\frac{\partial v_0}{\partial T_0} \right)_{p_0} \left(\frac{\partial T_0}{\partial \varepsilon_0} \right)_{p_0} + \frac{B}{D^2} \right] d\varepsilon_0 \\
&= \left[-\frac{A\beta_0}{C_{p_0} - p_0 v_0 \beta_0} + \frac{B}{D^2} \right] d\varepsilon_0
\end{aligned} \tag{4.37}$$

The relation at constant pressure

$$\begin{aligned}
d\varepsilon_0 &= \left(\frac{\partial \varepsilon_0}{\partial T_0} \right)_{p_0} dT_0 + \left(\frac{\partial \varepsilon_0}{\partial p_0} \right)_{T_0} dp_0 \\
&= \left(\frac{\partial \varepsilon_0}{\partial T_0} \right)_{p_0} dT_0 = [C_{p_0} - p_0 v_0 \beta_0] dT_0
\end{aligned} \tag{4.38}$$

is used to rewrite Eq.(4.37) and is given by

$$\begin{aligned}
\frac{dD}{D} &= \left[-\frac{A\beta_0}{C_{p_0} - p_0 v_0 \beta_0} + \frac{B}{D^2} \right] d\varepsilon_0 \\
&= \left[-\frac{A\beta_0}{C_{p_0} - p_0 v_0 \beta_0} + \frac{B}{D^2} \right] [C_{p_0} - p_0 v_0 \beta_0] dT_0 \\
&= \left[-A\beta_0 + \frac{B}{D^2} \{C_{p_0} - p_0 v_0 \beta_0\} \right] dT_0
\end{aligned} \tag{4.39}$$

Temperature derivative of the detonation velocity is then given by

$$\left(\frac{\partial D}{\partial T_0} \right)_{p_0} = -AD\beta_0 + \frac{B}{D} \{C_{p_0} - p_0 v_0 \beta_0\} \tag{4.40}$$

By using Eq.(4.6) and (4.7), we obtain

$$\begin{aligned}
\left(\frac{\partial D}{\partial T_0} \right)_{p_0} &= -\frac{\Gamma - 1 - \alpha}{\alpha + 2} D\beta_0 + \frac{\alpha(\Gamma + 1)^2}{D(\alpha + 2)} \{C_{p_0} - p_0 v_0 \beta_0\} \\
&= \frac{D}{\alpha + 2} \left[-(\Gamma - 1 - \alpha)\beta_0 + \frac{\alpha(\Gamma + 1)^2}{D^2} \{C_{p_0} - p_0 v_0 \beta_0\} \right]
\end{aligned} \tag{4.41}$$

From this equation, one may predict the temperature coefficient of high explosive material with the knowledge of several parameters such as α , Γ , β_0 , and C_{p0} . Among these, α and Γ are the values at C-J state that are not easy to estimate.

Equation (4.41) shows that temperature coefficient consists of two competing terms, the first negative term including volume expansion coefficient and the second positive term including specific heat at constant pressure. The first term in the parenthesis in Eq.(4.41) comes from the decrease in initial density by the thermal expansion due to heating the explosive, while the second term comes from the internal or thermal energy increase by heating. Since the experimental data for the temperature derivative of detonation velocity for many explosives are found to be negative, the change in detonation velocity by heating is mainly due to the decrease in initial density by thermal expansion.

4.4.2. Envelope Approximation

Even in this case, it is possible to apply the envelope approximation. Let us start with the equation for the Rayleigh line.

$$\begin{aligned} p &= p_0 + \rho_0 Du_p = p_0 + \rho_0 D^2 \left(1 - \frac{v}{v_0} \right) \\ &= p_0 + \frac{D^2(v_0, \varepsilon_0)}{v_0^2} (v_0 - v) = p_0 + Z^2(v_0, \varepsilon_0) (v_0 - v) \end{aligned} \quad (4.42)$$

As before, the C-J states should be on the Rayleigh line for any initial states defined by (v_0, ε_0) .

With increasing initial temperature T_0 , detonation velocity and detonation pressure changes. With a slight change of them due to the change in the initial state, the C-J states on different Rayleigh lines are close to the crossing points of two Rayleigh lines on p - v plane.

If one shifts the initial state parameter infinitesimally, the C-J state must be very close to the cross point of two successive Rayleigh lines. One may derive the necessary condition of envelope approximation under the assumption of constant pressure,

$$\frac{D^2(v_0, \varepsilon_0)}{v_0^3} (2v - v_0) \left(\frac{\partial v_0}{\partial T_0} \right)_{p_0} + \frac{v_0 - v}{v_0^2} \left(\frac{\partial D^2}{\partial T_0} \right)_{p_0} = 0 \quad (4.43)$$

From this equation, we have for the temperature derivative of the detonation velocity is represented as

$$\begin{aligned} \left(\frac{\partial D}{\partial T_0} \right)_{p_0} &= - \frac{D(v_0, \varepsilon_0)}{2v_0} \frac{2v - v_0}{v_0 - v} \left(\frac{\partial v_0}{\partial T_0} \right)_{p_0} \\ &= - \frac{D\beta_0}{2} \frac{2v - v_0}{v_0 - v} \\ &= - \frac{D\beta_0}{2} (\Gamma - 1) \end{aligned} \quad (4.44)$$

The last expression is derived by using the relations,

$$\frac{v_0}{v_0 - v} = \frac{\rho_0 D^2(v_0, \varepsilon_0)}{p_{CJ} - p_0} = 1 + \Gamma \quad (4.45)$$

In this case, the envelope approximation gives the contribution only due to the decrease in initial density by the thermal expansion due to heating the explosive, which must be the main cause in the change in detonation velocity by heating.

Eq.(4.44) can then be rewritten to the following formula by using the Grüneisen parameter for the material at the initial uncompressed state

$$\left(\frac{\partial D}{\partial T_0} \right)_{p_0} = -\frac{D}{2}(\Gamma - 1) \frac{C_{p_0}}{a_b^2} \gamma_0 \quad (4.46)$$

where we have used the modified thermodynamic relation of the Grüneisen parameter of Eq.(1.5)

$$\gamma = \frac{v\kappa_s \beta}{C_p} = \frac{a_b^2 \beta}{C_p} \quad (4.47)$$

where isentropic bulk modulus is replaced by the so-called bulk sound velocity appeared in Eq.(2.61).

The advantage of the envelope approximation over full thermodynamic theory of Wood and Fickett is simply to predict the temperature derivative of detonation velocity by measurable parameters including detonation velocity, pressure, and thermal expansion coefficient. For the full C-J theory, one also needs the value of the parameter α at the C-J state.

4.4.3. Difference between envelope theory and C-J rigorous theory and the possibility of estimating the Grüneisen parameter at C-J state

Although both the data for thermal expansion coefficient and the temperature dependence of the detonation velocity for various explosives are limited, we will first show fundamental data for selected explosives are summarized in Table 4.1.

Table 4.1 Measured thermodynamic properties published for several explosives.

explosive	density (kg/m ³)	D (m/s)	C _p (J/kg/K)	β (1/K)	source
comp. B	1717	7990	980	5.46X10 ⁻³	LASL databook
PBX9404	1840	8800	937	4.7X10 ⁻³	LASL databook
XTX 8003	1500	7260	1055	1.65X10 ⁻⁶	LASL databook
nitromethane	1135	6350	1733	1.164X10 ⁻³	LLNL handbook

By using these values, it is now possible to predict the temperature derivative of detonation velocity for these explosives. Table 4.2 shows the experimental data for the temperature coefficient and the theoretical prediction by the envelope approximation of Eq.(4.44) for selected high explosives. One may see the qualitative agreement except for XTX 8003.

Table 4.2 Measured and estimated temperature dependence of detonation velocity for several explosives.

explosive	D (m/s)	p _{CJ} (GPa)	(∂D/∂T ₀)p ₀ ((m/s) ² /K) measured	(∂D/∂T ₀)p ₀ ((m/s) ² /K) estimated	source
comp. B	7990	29.2	-0.5	-0.383	LASL + LLNL databook
PBX9404	8800	36.8	-1.165	-0.387	LASL + LLNL databook
XTX 8003	7260	17	-2.34	-0.0159	LASL + LLNL databook
nitromethane	6350	14.1	-3.7	-4.60	LASL + LLNL databook

In this section, difference between the C-J rigorous theory, Eq.(4.41) and envelope approximation, Eq.(4.44) is discussed in order to understand the discrepancy between theory and experiment for several explosives. Possible factors affecting the discrepancy would be (i) C-J assumption is not valid especially for non-ideal explosives, (ii) the envelope approximation neglects some important parameters, etc.

For the non-ideal explosives, the temperature coefficient is seen to have quite different values from those of ideal explosives. Sign of the coefficient for those two kinds of explosives is sometimes different. This might seem very important characteristics of the materials and must be sought out to investigate the properties of non-ideal explosives.

We will now consider the second possibility, i.e., the error involved in the envelope approximation against the C-J theory. To see this, we will calculate the difference between the coefficients by Eq.(4.41) and Eq.(4.44). Subtraction of rhs of Eq.(4.44) and (4.41) leads to the following form

$$\begin{aligned}
 & \frac{D}{\alpha + 2} \left[-(\Gamma - 1 - \alpha)\beta_0 + \frac{\alpha(\Gamma + 1)^2}{D^2} \{C_{p_0} - p_0 v_0 \beta_0\} \right] \\
 & + \frac{D\beta_0}{2}(\Gamma - 1) \\
 & = \frac{\alpha(\Gamma + 1)}{\alpha + 2} \left[\frac{D\beta_0}{2} + \frac{\Gamma + 1}{D} \{C_{p_0} - p_0 v_0 \beta_0\} \right]
 \end{aligned} \tag{4.48}$$

Alternative expression of the same quantity is derived by using Eq.(4.46) and Eq.(4.41) with the definition of the Grüneisen parameter at the initial state as

$$\Delta \left(\frac{\partial D}{\partial T_0} \right)_{p_0} = \frac{\alpha(\Gamma + 1)}{\alpha + 2} C_{p_0} \left[\frac{D}{2} \frac{\gamma_0}{a_b^2} + \frac{\Gamma + 1}{D} \left\{ 1 - \frac{p_0 v_0 \gamma_0}{a_b^2} \right\} \right] \tag{4.49}$$

Envelope theory assumes that the quantity of Eq.(4.48) or (4.49) can be neglected. These expressions suggest that one may consider the envelope approximation can be the approximation such that the value of is assumed to be zero. Other possibilities are excluded by the estimation of other terms in Eq.(4.48) or (4.49).

By the use of the relationship between α and γ , Eq.(4.11), the assumption of $\alpha=0$ is equal to the assumption of $\gamma=0$. The assumption of neglecting the Grüneisen parameter is the same as the envelope approximation used in the initial density dependence of the detonation velocity in the previous section.

It is found that unlike the envelope approximation based on the initial density dependence of detonation velocity, envelope approximation based on the temperature dependence gives good results only for a few explosives, while it gives large discrepancy between theory and experiments for other explosives.

From Eq.(4.49), the value of difference is seen to be a positive value. This means that the envelope approximation must be an overestimation of the temperature coefficient. In Table 4.2, data satisfying this condition is only the one for the nitromethane. Unlike the initial density dependence of the detonation velocity, temperature dependence of the detonation velocity is too sensitive to predict by the Chapman-

Jouguet theory. Various possibilities attributed to this result can be pointed out. One of the fundamental questions for the Chapman-Jouguet hypothesis is the plausible possibility of 3-d structure of the detonation wave. Although the pressure jump is enough abrupt to hold the shock jump conditions, state variables of the compressed state will change with time. Therefore, state variables of the compressed state is an averaged one with time or is an ensemble averaged one in the sense of statistical mechanics. One may need to take into account of these spatial and temporal variations of the detonation wave in order to discuss the slight change in the detonation properties like temperature dependence.

4.5. EOS for Unreacted High Explosives

4.5.1. Two Debye temperature solid as a model for high explosive substances

Large number of high explosives consists of relatively large and organic molecules. This gives rise to the very high frequency modes of vibration associated with the freedom of a molecule, whereas they also have very low frequency modes associated with intermolecular vibrations.

Compression of these substances will take place first by the large compression of the molecular distance, since the elastic constant of the small strain must be attributed to that of intermolecular properties. After enough compression between molecules, intermolecular forces and intra-molecular forces will be of the same level, compressibility of the material will be determined by both forces. Thermal behavior may also follow the similar temporal history as the impact mechanical behavior.

It is assumed here that the equation of state of these materials before onset of the reaction or decomposition is the Grüneisen type equation of state. Thermal component of the internal energy and pressure must be described by the Grüneisen parameter.

In order to take into account of the contributions of the intermolecular low eigen frequency modes (phonons) and of the intra-molecular high frequency modes (vibrons), we will assume here that these modes both have a different Debye temperature independently. If both Debye temperatures have no temperature dependence, we have the Grüneisen type equation of state as

$$\begin{aligned}\varepsilon &= \varepsilon_c(v) + \varepsilon_1(v, T) + \varepsilon_2(v, T) \\ &= \varepsilon_c(v) + C_1(S_1)\Theta_1(v) + C_2(S_2)\Theta_2(v) \quad (4.50) \\ p &= p_c(v) + p_1(v, T) + p_2(v, T) \\ &= p_c(v) + \frac{\gamma_1(v)}{v} \varepsilon_1(v, T) + \frac{\gamma_2(v)}{v} \varepsilon_2(v, T) \\ &= p_c(v) + \frac{\gamma_1(v)}{v} C_1(S_1)\Theta_1(v) + \frac{\gamma_2(v)}{v} C_2(S_2)\Theta_2(v) \quad (4.51)\end{aligned}$$

where we have introduced two Grüneisen parameters associated with each Debye temperature. By these equations, we are assuming that thermal properties can be described by independent density of states attributing to phonon and vibron modes. It is also seen in Eq.(4.51) that two Grüneisen parameters are a function only of volume. One may also see that entropy functions should be a function of entropy determined by the number of microstates of both vibrational modes. These two independent Grüneisen parameters in the equation of state apparently have similar or the same properties as seen in the thermal energy consisting of lattice vibration and electronic contribution.

It is possible to follow similar procedure to treat these two modes. First differentiate internal energy along an isochoric, we have

$$\begin{aligned}d\varepsilon &= d\varepsilon_1(v, T) + d\varepsilon_2(v, T) \\ &= C_{v1}(v, T)dT + C_{v2}(v, T)dT \\ &= [C_{v1}(v, T) + C_{v2}(v, T)]dT \\ &= C_v(v, T)dT \quad (4.52)\end{aligned}$$

$$\begin{aligned}
dp &= dp_1(v, T) + dp_2(v, T) \\
&= \frac{\gamma_1(v)}{v} d\varepsilon_1(v, T) + \frac{\gamma_2(v)}{v} d\varepsilon_2(v, T) \\
&= \frac{\gamma_1(v)}{v} C_{v1}(v, T) dT + \frac{\gamma_2(v)}{v} C_{v2}(v, T) dT \\
&= \left[\frac{\gamma_1(v)}{v} C_{v1}(v, T) + \frac{\gamma_2(v)}{v} C_{v2}(v, T) \right] dT \quad (4.53)
\end{aligned}$$

The averaged Grüneisen parameter for these two Debye solids is given by

$$\gamma = v \left(\frac{\partial p}{\partial \varepsilon} \right)_v = \frac{\gamma_1(v) C_{v1}(S_1) + \gamma_2(v) C_{v2}(S_2)}{C_{v1}(S_1) + C_{v2}(S_2)} \quad (4.54)$$

This equation states that the averaged Grüneisen parameter with two independent Grüneisen parameters for two Debye solids must not be a function only of volume but a function of volume and temperature. One needs to consider the temperature dependence of the Debye parameter.

Debye temperature for phonons is expected to be lower than that for high frequency vibrons. Deposition of an appreciable amount of energy on high explosive substance will produce compression of lattice spacing as well as the excitation of phonons, and eventually gives rise to temperature increase. Non-dimensional parameter x defined in Eq.(2.47) for both modes is different from each other for a common value of temperature. These situations are the cause of temperature dependence of the Grüneisen parameter.

4.5.2. Temperature dependent Grüneisen parameter

In order to see this effect at least qualitatively, simple simulations for two-Debye solids is performed. For simplicity, we have assumed the following;

- (i) For both Grüneisen parameters, it is assumed that $\rho\gamma = \text{constant}$.
- (ii) Two Debye temperatures are assumed to be $\Theta_1 = 300$ K, and $\Theta_2 = 600$ K, 1500 K, and 3000 K, respectively.
- (iii) Two Grüneisen parameters at standard condition is assumed to be $\gamma_1 = 1.0$ and $\gamma_2 = 0.1$, respectively.

The small Grüneisen parameter for higher frequency modes will be due to its higher Debye temperature and low compressibility, but simply, it is easy to see how these two parameters change with compression and also with temperature.

Very high Debye temperature for higher frequency domain is apparently hypothetical. For the case of quite different Debye temperatures, one may easily see how they change with compression and temperature.

Figure 4.12 shows the assumed density of state function for three cases. It is also assumed here that number of both modes is equal. They contribute equally to thermal energy and pressure, if all modes are excited.

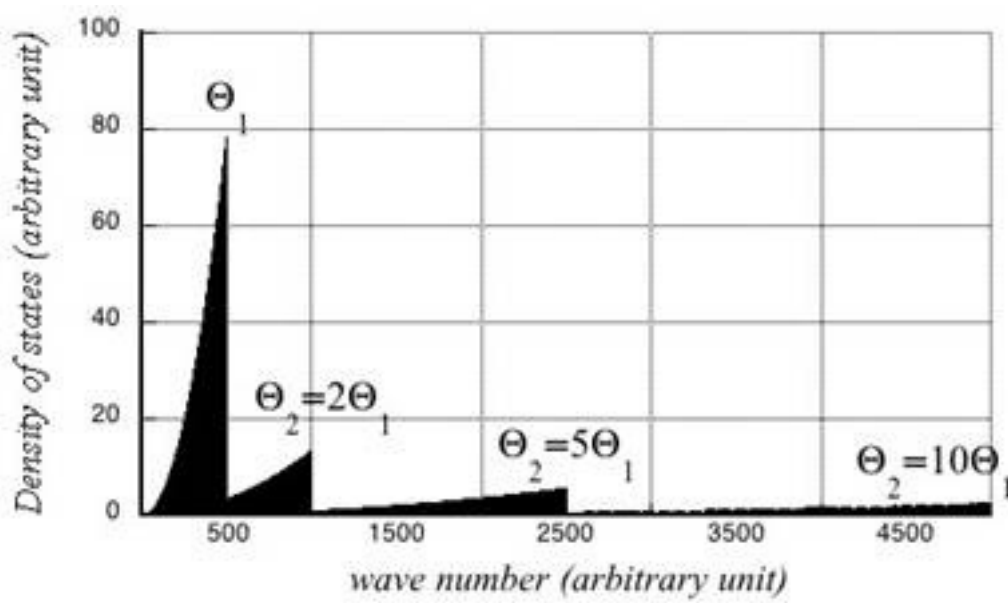


Fig. 4.12 Assumed density of states for higher and lower frequency modes. Lower frequency modes are attributed to lattice vibration, whereas higher ones to vibrons modes.

Figure 4.13 shows the simulated temperature dependence of averaged Grüneisen parameter, starting from the 300 K to 1000 K. In this calculation, we assume the process is isochoric, which is also hypothetical, since isochoric process during heating cannot be realized. One may see that averaged Grüneisen parameter decrease with temperature. Note that in the region of temperature higher than $\Theta_2=600$ K, i.e., $\Theta_2/\Theta_1=2$, Grüneisen parameter approaches almost constant value. In this case, change in the Grüneisen parameter itself is very small. For the other two cases, changes in gamma are appreciable.

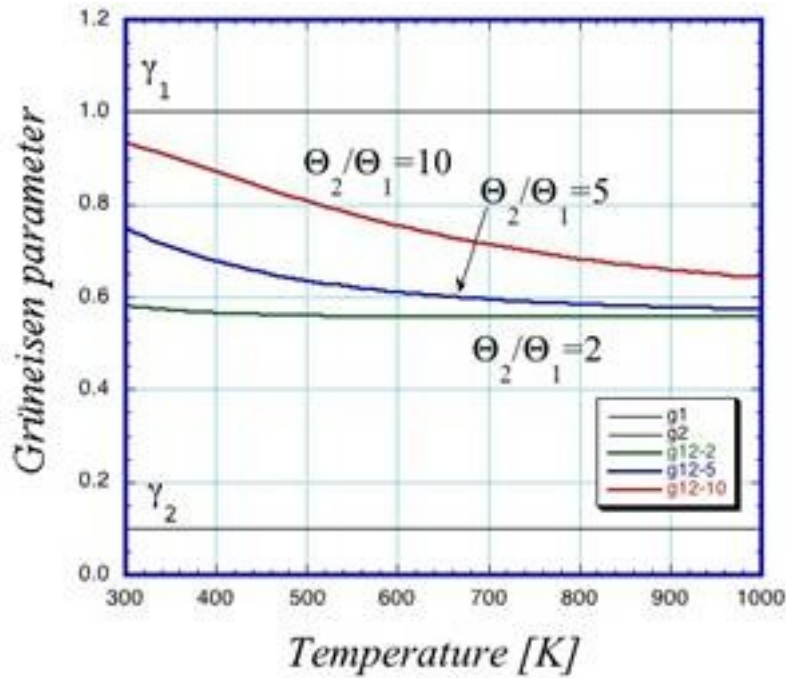


Fig. 4.13 Typical temperature dependence results for two Debye temperatures whose ratios are assumed to be 2, 5 and 10. Isochoric process is assumed.

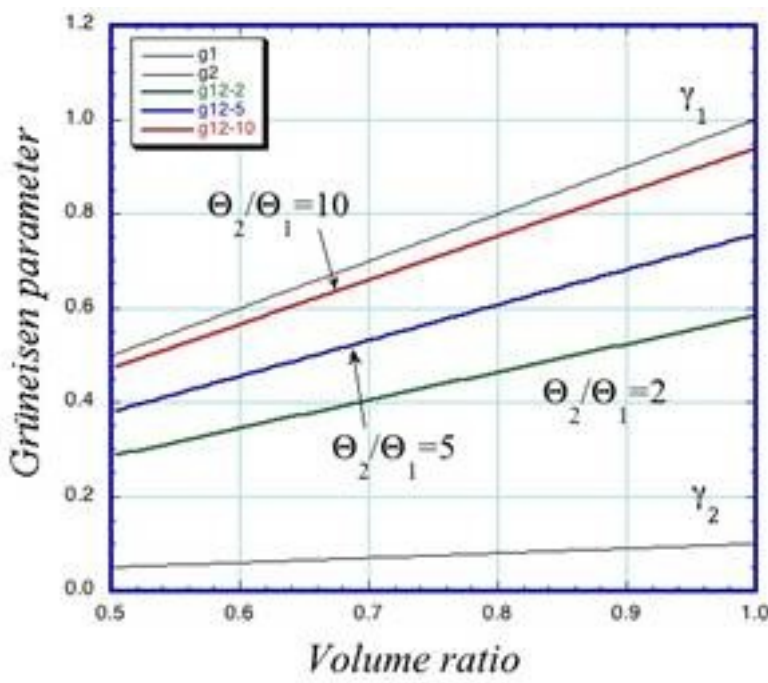


Fig. 4.14 Volume dependence of averaged and two Grüneisen parameters under isothermal compression for solids with two Debye temperatures whose ratios are assumed to be 2, 5 and 10.

Figure 4.14 shows the simulated volume dependence of averaged Grüneisen parameter. In this calculation, isothermal process of compression is assumed. From Fig. 4.14, it is seen that behavior of Grüneisen parameter with compression is governed basically by higher Grüneisen parameter or lower Debye temperature modes.

Both compression and temperature behavior in mind, one may imagine shock compression behavior of the two-Debye solids. Along a shock Hugoniot compression curve, or an isentrope, the Grüneisen parameter decreases. The reason of the decrease in the Grüneisen parameter is two fold. It decreases with compression. The other reason is irreversible heating by shock compression.

From these considerations, thermal contribution of these materials to the equation of state of (p, v, ϵ) surface can be summarized as follows:

- (i) Grüneisen parameter changes both compression and temperature depending on the ratio of two Debye temperatures,
- (ii) Grüneisen parameter decreases both compression and heating, so that it may decrease faster by shock compression, which means that
- (iii) Thermal contribution in pressure will become relatively smaller with compression.

4.5.3. Shock Hugoniot and isentropes

Let us consider the change in the Grüneisen parameter and thermal contribution with isothermal compression, isentropic compression and shock compression for two-Debye solids. Since the change in the Grüneisen parameter for these compression curves should be determined as

$$\text{Isotherm} : \gamma(v, T_0)$$

$$\text{Isentrope} : \gamma(v, T_S(v))$$

$$\text{Hugoniot} : \gamma(v, T_H(v))$$

where $T_S(v)$ and $T_H(v)$ denote the value of temperature along an isentrope and shock Hugoniot. If one starts from the room temperature condition, $T_H(v)$ is always higher than $T_S(v)$ due to irreversible heating by shock compression. For the same value of specific volume, the Grüneisen parameter on shock Hugoniot is

therefore smaller than that on an isentrope.

As we assumed in this section, the Grüneisen parameter is a function of temperature as well as volume, the Grüneisen type equation of state may not be expressed in the form of Eq.(2.9),

$$p = f(v) + \frac{\gamma}{v} \varepsilon \quad . \quad (4.55)$$

In this case, we have no simple analytical expression for the Grüneisen equation of state by using the averaged Grüneisen parameter. As seen in the hypothetical simulation of the temperature dependence of the Grüneisen parameter, one may approximate the behavior of the Grüneisen parameter independent of temperature. Under this approximation, reference compression curve such as an isentrope or shock Hugoniot is convenient to express the equation of state. Details of the behavior of the Grüneisen parameter, however, should be known to study the onset of initiation of these materials.

Various theoretical studies have been made to describe the form of the equation of state in unreacted conditions. (Olinger et al 1975, Miller and Alexander 1989, Byrd and Rice 2007, Davis 2000, Kuhl 2010, Mattson et al 2010) They are inevitable to implement them to the numerical simulation code to predict the shock to detonation transition and/or other initiation studies. Almost all of these approaches were made by the assumption of the Grüneisen law. Measurement of shock Hugoniot curve for various high explosives has been published so far, although it contains uncertainty concerning the possibility of partial reaction at the shock front. (Gibbs and Popolato 1980, Marsh 1980) Shock velocity particle velocity relationship seems non-linear unlike other inert solid materials. A plausible explanation of the slight curvature of shock Hugoniot may be attributed to two different sources of compressibility by very weak lattice compression and by the compression of molecules.

As explained in the previous chapters, the Grüneisen equation of state is suitable for the description of flow problems, since the EOS is written in terms of pressure, volume and internal energy, which are the only members of thermodynamic state variables in flow equations. In this chapter, some of the examples of the application of the Grüneisen EOS to flow problems are discussed.

5.1. The Grüneisen type EOS and other EOSes applied to flow problems

5.1.1 Tait type equation of state

Before discussing the application of the Grüneisen EOS to flow problems, we will compare material functions calculated in Chapter 3 with those previously published so far in various areas. Previously used EOS models by various authors include (i) Tait type EOS, (ii) Model cold function adopted by Russian authors, (iii) JWL EOS, and (iv) Birch-Murnaghan EOS. Various forms of these material functions are sometimes quite suitable for numerical calculations of flow equations. We intend to compare basically isentropes, since isentrope appears in various release waves. One exception is the discussion of the comparison with Birch-Murnaghan EOS which mostly represents high-pressure isotherm.

Among those, Tait equation is used for water or other liquids in relatively low pressure region. (Zel'dovich and Raizer 1966, Ridah 1988, Dymond and Malhotra 1988) As a cold potential functions, Russian authors adopt exponential repulsive term plus a term inversely proportional to the specific volume. (Zharkov and Kalinin 1971) In this function, the exponential term corresponds to quantum repulsion, while the second term describes Coulomb interaction in metal elements. They have successfully used this function even for non-metals. JWL EOS is commonly used to represent extremely dense gas produced by detonation of condensed high explosives as well as unreacted high explosives. (Jones 1949, Kuhl 2010) Birch-Murnaghan EOS is an EOS derived by finite strain theory, and this type of EOS is used to represent high-pressure isotherms of solids. (Zharkov and Kalinin 1971)

One may note that if one try to discuss high speed flow problems, or more specifically dynamic flow problems containing shock waves, thermodynamic states achieved in these flows are mostly limited to shock Hugoniot and release isentrope and states in between. For the purpose of considering states in these flow problems, section of the entire state surface to cover these areas of states is a narrow one. One does not need to consider isothermal process, since isothermal compression or expansion requires long time in the sense of high speed flow. Equation of state necessary to describe fast flow problems will be the one for isentropes and adjacent state region including shock Hugoniot. First we will discuss several EOSes from this standpoint.

Although all of the EOSes cited above may not be deduced by microscopic theoretical models, they are sometimes convenient for the description of condensed media at high pressures.

Tait type equation of state is given by

$$p(\rho, S) = D(S) \left[\left(\rho / \rho_0 \right)^n - 1 \right], \quad (5.1)$$

where $D(S)$ and n are material parameters to fit the available pressure data. Tait equation was first introduced as an isotherm, but is used as an isentrope to use it in dynamic problems. (Dymond and Malhotra 1988) As an example, water shock data is proved to be quite compatible with the Tait equation. (Nagayama et al 2002, Nakahara et al 2008) Starting from Eq.(5.1), one may derive local sound velocity as

$$a^2 = \left(\frac{\partial p}{\partial \rho} \right)_S = nD(S) \frac{\rho^{n-1}}{\rho_0^n} \quad (5.2)$$

Following calculation for Tait equation is always along an isentrope, all the derivatives will be represented by a total differential notation as

$$a^2 = \frac{dp}{d\rho} = nD(S) \frac{\rho^{n-1}}{\rho_0^n} \quad (5.3)$$

By differentiation of Eq.(5.3) with density, we have

$$\frac{da^2}{d\rho} = \frac{d^2 p}{d\rho^2} = n(n-1)D(S)\frac{\rho^{n-2}}{\rho_0^n}, \quad (5.4)$$

which can be read as

$$\begin{aligned} da^2 &= 2ada = n(n-1)D(S)\frac{\rho^{n-2}}{\rho_0^n}d\rho \\ &= \frac{n-1}{\rho}dp = \frac{n-1}{\rho}\rho adu = (n-1)adu \end{aligned} \quad (5.5)$$

To derive the last two expressions, the momentum conservation equation for isentropic waves is used. From this equation, we have

$$da = \frac{n-1}{2}du \quad (5.6)$$

Integration of this expression gives

$$a = a_0 + \frac{n-1}{2}u \quad (5.7)$$

where a_0 denotes an integration constant. This equation shows that the sound velocity inside the compression or rarefaction wave is a linear function of the particle velocity of the wave.

The sound velocity just behind the shock-compressed state, a_H , can be expressed by the shock wave parameters in the form of Eq.(3.24). (Nagayama 2002a)

$$\begin{aligned} a_H^2 &= \frac{dp_H}{d\rho} - \frac{\gamma}{v} \frac{u_p^2}{u_s} \frac{du_s}{du_p} \frac{du_p}{d\rho} \\ &= \frac{(u_s - u_p)^2}{u_s - u_p \frac{du_s}{du_p}} \left[u_s + u_p \frac{du_s}{du_p} - \gamma \frac{u_p^2}{u_s - u_p} \frac{du_s}{du_p} \right] \end{aligned} \quad (5.8)$$

The last term in the parenthesis corresponds to the contribution by the entropy production due to shock compression. This equation can be used to predict sound velocity, if the Grüneisen parameter as well as shock wave parameters is known. Due to detailed discussion of the entropic contribution to the internal energy, pressure and sound velocity of shock waves in fluids such as water, the magnitude of it for the sound velocity is less than 1% up to less than $M=2$, where M is the shock Mach number. (Nagayama 1994, Nakahara et al 2008)

One may safely omit the entropic term in Eq.(5.8) to predict sound velocity just behind the shock wave front, unless shock wave is very strong. In this case, we have an approximate formula

$$\begin{aligned}
 a_H^2 &= \frac{(u_s - u_p)^2}{u_s - u_p \frac{du_s}{du_p}} \left[u_s + u_p \frac{du_s}{du_p} \right] \\
 &= \frac{(u_s - u_p)^2}{A} [u_s + Bu_p] \quad (5.9)
 \end{aligned}$$

where we have used the empirical linear relationship for shock Hugoniot between shock velocity and particle velocity.

By using this equation together with the empirical Hugoniot, one may plot the sound velocity as a function of particle velocity for the comparison with Eq.(5.7). Figure 5.1 shows sound velocity and shock velocity plotted against particle velocity based on the shock Hugoniot data for water. (Nagayama et al 2002)

$$\begin{aligned}
 u_s &= A + Bu_p \\
 A &= 1.50 \text{ (km / s)} \\
 B &= 1.99 \quad (5.10)
 \end{aligned}$$

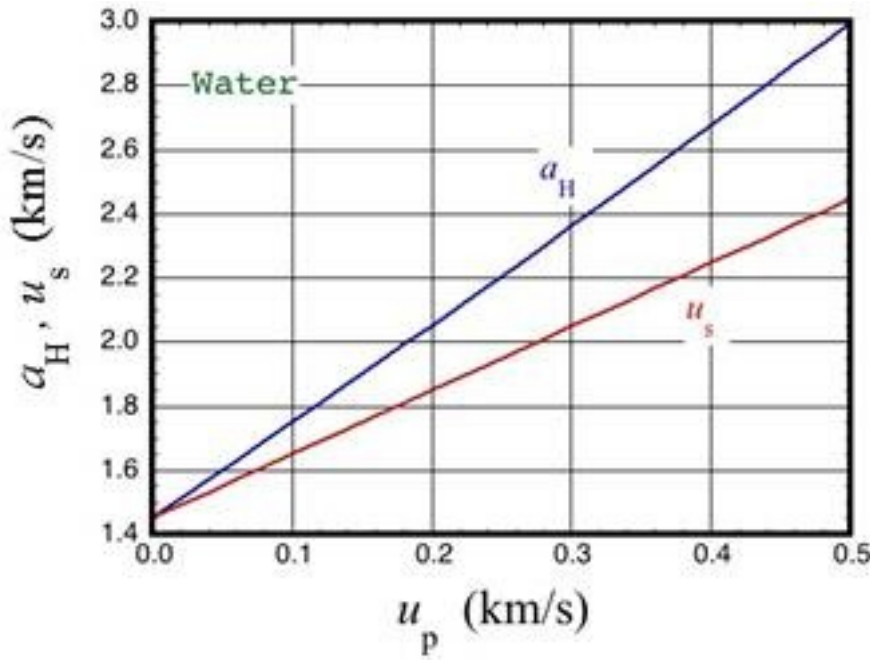


Fig. 5.1 Shock velocity and sound velocity just behind shock front as a function of particle velocity for water.

As is seen in the figure, sound velocity as well as shock velocity is almost a linear function of particle velocity in harmony with Eq.(5.7). It is then possible to determine the parameter n in Eq.(5.7) based on this plot. Taylor series expansion of Eq.(5.9) up to 1st order of particle velocity is written as

$$a = A + (2B - 1)u_p \quad (5.11)$$

Comparing this relationship with Eq.(5.7), we have

$$a_0 = A \quad (5.12)$$

$$n = 1 + 2(2B - 1) \quad (5.13)$$

Equation (5.12) shows the sound velocity of the fluid at uncompressed state. For water, parameter n is then estimated based on the shock Hugoniot relationship of Eq.(5.10) (Nagayama et al 2002) as

$$n = 1 + 2(2 \times 1.99 - 1) = 6.96 \quad (5.14)$$

which is very close to the previously published value for the equation of state of water by various authors. (Cole 1948, Ridah 1988) Taking into account of slight curvature in the sound velocity-particle velocity relationship in Fig. 5.1, parameter n is corrected to be

$$n = 1 + 2 \times 3.06 = 7.12 \quad (5.15)$$

By using this parameter, resultant expression for the isentrope for water centering standard condition is written as

$$\begin{aligned} p &= D(S_0) \left[\left(\frac{\rho}{\rho_0} \right)^n - 1 \right] \\ D(S_0) &= 0.2959 \text{ GPa} \\ n &= 7.12 \end{aligned} \quad (5.16)$$

For a constant Grüneisen parameter, the characteristic temperature is a function of some power of volume or density as is understood from Eq.(2.24).

$$\Theta(v) = \Theta(v_0) \left(\frac{v}{v_0} \right)^{-\gamma_0} \quad (5.17)$$

In this case, pressure is given by

$$\begin{aligned} p &= p_r(v) + \frac{\gamma_0}{v} C(S) \Theta(v) \\ &= p_r(v) + \frac{\gamma_0}{v_0} C(S) \Theta(v_0) \left(\frac{v}{v_0} \right)^{-\gamma_0 - 1} \end{aligned} \quad (5.18)$$

where $p_r(v)$ denotes the reference isentropic pressure. Tait type equation of state will be obtained, if the reference isentrope is a linear function of $v^{-\gamma_0 - 1}$. This may not be the case at least for water, since the Grüneisen parameter for water was found to be very small. (Boehler and Kennedy 1977) For fluids whose Grüneisen parameter is very small, isentropes on p - v plane must be very close with each other, although they may differ on ε - v plane.

By the analysis of the contribution of irreversible heating by shock compression to internal energy, pressure, and sound velocity for water, and it is confirmed that it cannot be neglected in the estimation of internal energy or temperature. (Nakahara et al 2008) These considerations lead to the application of numerical schemes of hydrodynamics using conservation equations excluding energy equations in cases where pressure propagation is of primary importance.

5.1.2. Other models for cold isotherms or isentropes

Russian researchers adopt the form of the cold internal energy and cold pressure for ionic crystals in the form

$$\begin{aligned}\varepsilon_c(x) &= \frac{3A}{b\rho_0} \exp \left[b \left(1 - x^{1/3} \right) \right] - \frac{3K}{\rho_0} x^{-1/3} \\ p_c(x) &= Ax^{-2/3} \exp \left[b \left(1 - x^{1/3} \right) \right] - Kx^{-4/3} \\ x &= v / v_0\end{aligned}\tag{5.19}$$

where the first term in energy and pressure function corresponds to quantum repulsion, while the second term corresponds to electrostatic energy. (Zharkov and Kalinin 1971) This is intended to apply to ionic crystals, but similar form is also applied to basically all materials. In this equation, A , b and K are parameters which should be chosen to match shock data or other compression data. Basic idea for JWL equation of state for detonation product gases by the detonation of condensed phase high explosives is also the same as those of the above equation, although JWL EOS is not a cold function. They have the density of around 3 g/cm^3 just at the completion of the reaction, and are high temperature dense media where repulsion is dominant over other forces between reaction products. In case of JWL EOS, they have to fit to the cylinder expansion test, which is approximately assumed to be an isentropic expansion for very dense gas to low pressures. In order to fit the data, further parameter is found to be necessary, and second exponential term is added. (Kuhl 2010)

Exponential function for thermal contribution of the Grüneisen EOS is obtained as a characteristic temperature function, provided that $\rho\gamma=\text{const}$. This can be checked by Eq.(2.24). We have, however, no physical basis of these similarities between cold function, isentrope and characteristic temperature function. We will show one typical topics later, where the relationship between the cold pressure and characteristic temperature function plays a special role in a flow problem.

5.2. Description of Shock Wave Propagation in Condensed Media in Symmetric Geometry

5.2.1 Shock Jump Equations in Symmetrical Flow

We encounter decaying shock waves and/or converging shock waves in various situations. For example, in the dynamic material processing, the shock propagation is not one-dimensional, but complex flow field is realized. In practice, the dynamic treatment process of materials by using cylindrically symmetrical assemblies using high explosive inevitably includes the phenomena of cylindrically converging shock wave propagation. (Syono et al 1982, Prümmer 1989) Even in the case of using a plane wave generator, numerical simulation has revealed that converging wave may propagate in the powdered thin specimen layer, placed perpendicular to the incident plane shock direction.

In medical applications, tiny pulse shock waves are created by a small amount of high explosive, pulse laser or intense acoustic pulse, etc. In these cases, one may also encounter spherically diverging or converging waves. (Kodama et al 1998) Converging shock waves in condensed media has sometimes been used to generate ultrahigh pressures. (Fedotov et al 2007) Another example of the use of cylindrically converging shock waves is for the generation of ultrahigh magnetic field by magnetic flux cumulation by shock waves. (Nagayama 1981, Nagayama et al 1982, Nagayama and Mashimo 1987) One may also note that inertial confinement fusion also will use spherically converging shock waves induced by intense pulse laser.

In order to study converging or diverging shock propagation, let us consider shock wave propagation in symmetrical systems. Consider a converging shock wave propagating at velocity $u_s(t)$ through a medium of initial density ρ_0 . We assumed here that no elastic strength effect is considered and the medium in which shock wave is propagating is regarded as a fluid. In the following, we will pay our attention only on the physical quantities just behind the shock front, which are uniquely determined by the shock strength at each instant.

Observing the shock wave from the coordinate system moving at $u_s(t)$, three conservation equations of fluid dynamics can be written for the variables ρ , u , p , and the local speed of sound a . Instead of the usual energy equation, the entropy equation is used, which expresses that the entropy along a fluid particle is kept constant.

$$\frac{\delta \rho_f}{\delta t} - [u_s(t) - u_f] \left(\frac{\partial \rho}{\partial r} \right)_f + \rho_f \left(\frac{\partial u}{\partial r} \right)_f + \frac{\alpha \rho_f u_f}{R(t)} = 0 \quad (5.20)$$

$$\begin{aligned} \rho_f \frac{\delta u_f}{\delta t} + u_f \frac{\delta \rho_f}{\delta t} - u_f [u_s(t) - u_f] \left(\frac{\partial \rho}{\partial r} \right)_f \\ + \rho_f [u_s(t) - u_f] \left(\frac{\partial u}{\partial r} \right)_f + \left(\frac{\partial p}{\partial r} \right)_f + \frac{\alpha \rho_f u_f^2}{R(t)} = 0 \end{aligned} \quad (5.21)$$

$$\begin{aligned} \frac{\delta p_f}{\delta t} - [u_s(t) - u_f] \left(\frac{\partial p}{\partial r} \right)_f \\ = a_f^2 \left\{ \frac{\delta \rho_f}{\delta t} - [u_s(t) - u_f] \left(\frac{\partial \rho}{\partial r} \right)_f \right\} \end{aligned} \quad (5.22)$$

$$\frac{\delta}{\delta t} \equiv \left(\frac{\partial}{\partial t} \right)_f + u_s(t) \left(\frac{\partial}{\partial r} \right)_f \quad (5.23)$$

where suffix f is used to stress that the quantities in the equations are the one just behind the shock front. Special symbol of the time derivative in Eq. (5.23) is the differentiation in a frame moving with time-dependent shock velocity, $u_s(t)$. By combining these equations, one obtains

$$\frac{\delta \rho_f}{\delta t} = - \frac{\frac{\alpha \rho_f u_f (u_s - u_f)}{R} + \left\{ a_f^2 - (u_s - u_f)^2 \right\} \left(\frac{\partial \rho}{\partial r} \right)_f}{\rho_f \frac{du_f}{d\rho_f} + u_s - u_f + \frac{1}{u_s - u_f} \left[\frac{dp_f}{d\rho_f} - a_f^2 \right]} \quad (5.24)$$

(Nagayama and Murakami 1976) In this equation, α is a constant which depends on the geometry being 0, 1, 2 for plane, cylindrical and spherical symmetry. In Eq.(5.24), $du_f/d\rho_f$, $dp_f/d\rho_f$ denote the derivative along the Hugoniot curves. One may also note that shock velocity and the particle velocity should have a negative sign for converging shock waves.

Equation (5.24) states that the time variation of density ρ_f is determined by the following three variables, i.e., ρ_f , the shock strength at that instant, $R(t)$, the position of shock front, and $(\partial \rho / \partial r)_f$, the density gradient just behind the shock front. The first term in the numerator of Eq.(5.24) gives the contribution from the area convergence or divergence. While the second term corresponds to the effect of the spatial profile of shock wave on the propagation at the instant. For the given value of ρ_f , the denominator can be estimated by means of the equation of state for the fluid. Entropy production by shock compression appears in the last term of the denominator in Eq.(5.24).

The values of gradients of other quantities, $(\partial u / \partial r)_f$, $(\partial p / \partial r)_f$, etc. are restricted by the definite relationship, which provides a constraint on the form of the shock wave.

$$\begin{aligned} \left(\frac{\partial u}{\partial r} \right)_f = & - \frac{\frac{\alpha u_f}{R} \left\{ \rho_f \frac{du_f}{d\rho_f} + \frac{1}{u_s - u_f} \left[\frac{dp_f}{d\rho_f} - a_f^2 \right] \right\}}{\rho_f \frac{du_f}{d\rho_f} + u_s - u_f + \frac{1}{u_s - u_f} \left[\frac{dp_f}{d\rho_f} - a_f^2 \right]} \\ & - \frac{\left\{ \frac{a_f^2}{\rho_f} + (u_s - u_f) \frac{du_f}{d\rho_f} + \frac{1}{\rho_f} \left[\frac{dp_f}{d\rho_f} - a_f^2 \right] \right\} \left(\frac{\partial \rho}{\partial r} \right)_f}{\rho_f \frac{du_f}{d\rho_f} + u_s - u_f + \frac{1}{u_s - u_f} \left[\frac{dp_f}{d\rho_f} - a_f^2 \right]} \end{aligned} \quad (5.25)$$

$$\left(\frac{\partial p}{\partial r} \right)_f = a_f^2 \left(\frac{\partial \rho}{\partial r} \right)_f + \frac{1}{u_s - u_f} \left[\frac{dp_f}{d\rho_f} - a_f^2 \right] \frac{\delta \rho_f}{\delta t} \quad (5.26)$$

Form of a shock wave has constrained by these mutual relationships. Apparently, these gradients are influenced also by the initial profile of a shock wave and are not determined solely by Eqs.(5.24)-(5.26). One

of the applications of these analytical formulae is recently sought to develop the experimental method of obtaining shock Hugoniot data by the measurement of a decaying shock wave.

5.2.2 Approximate Shock Equations in Symmetrical Flow

If the density gradient $(\partial\rho/\partial r)_f$ is given, Eq.(5.24) can be integrated over t directly to know the density growth with time. In the weak shock approximation, the density gradient term in Eq.(5.24) is a higher order quantity than the first term in the numerator so that density gradient term can be neglected compared with the first term. In this case, we have

$$\frac{\delta\rho_f}{\delta t} = - \frac{\alpha\rho_f u_f (u_s - u_f)}{R(t) \left\{ \rho_f \frac{du_f}{d\rho_f} + u_s - u_f + \frac{1}{u_s - u_f} \left[\frac{dp_f}{d\rho_f} - a_f^2 \right] \right\}} \quad (5.27)$$

(Nagayama and Murakami 1976)

Before giving numerical examples by using this approximation, let us summarize the formulae, Eqs. (5.24)-(5.27) into different formats, by using various formula derived in Chapter 3 concerning shock Hugoniot. They are shown in Eqs.(5.28)-(5.32). Again the following formulae contain spatial gradient so that the formulae is not approximate but exact except for Eq.(5.32).

$$\frac{\delta \ln \rho_f}{\delta t} = - \frac{u_f \left\{ \frac{\alpha}{R(t)} \left(u_s - u_f \frac{du_s}{du_f} \right) + \left(u_s - u_f \right) \frac{du_s}{du_f} \left(2 - \frac{\gamma_f u_f}{u_s - u_f} \right) \left(\frac{\partial \ln \rho}{\partial r} \right)_f \right\}}{2u_s - u_f \frac{du_s}{du_f} + \frac{\gamma_f u_f^2}{u_s - u_f} \frac{du_s}{du_f}} \quad (5.28)$$

$$\frac{\delta u_f}{\delta t} = - \frac{u_s u_f (u_s - u_f) \left\{ \frac{\alpha}{R(t)} + \frac{(u_s - u_f) \frac{du_s}{du_f}}{u_s - u_f \frac{du_s}{du_f}} \left(2 - \frac{\gamma_f u_f}{u_s - u_f} \right) \left(\frac{\partial \ln \rho}{\partial r} \right)_f \right\}}{2u_s - u_f \frac{du_s}{du_f} + \frac{\gamma_f u_f^2}{u_s - u_f} \frac{du_s}{du_f}} \quad (5.29)$$

$$\left(\frac{\partial \ln \rho}{\partial r} \right)_f = - \frac{\frac{\alpha}{R(t)} \left[u_s + \frac{\gamma_f u_f^2}{u_s - u_f} \frac{du_s}{du_f} \right]}{(u_s - u_f) \left(2u_s + u_f \frac{du_s}{du_f} \right)} - \frac{\left[2u_s - u_f \frac{du_s}{du_f} + \frac{\gamma_f u_f^2}{u_s - u_f} \frac{du_s}{du_f} \right] \left(\frac{\partial u}{\partial r} \right)_f}{(u_s - u_f) \left(2u_s + u_f \frac{du_s}{du_f} \right)} \quad (5.30)$$

$$\left(\frac{\partial p}{\partial r}\right)_f = \frac{\gamma_f u_f^2 \frac{du_s}{du_f} \frac{\delta \rho_f}{\delta t} + (u_s - u_f)^2 \left\{ u_s + u_f \frac{du_s}{du_f} - \frac{\gamma_f u_f^2}{u_s - u_f} \frac{du_s}{du_f} \right\} \left(\frac{\partial \rho}{\partial r}\right)_f}{u_s - u_f \frac{du_s}{du_f}} \quad (5.31)$$

$$\frac{\delta u_f}{\delta t} = - \frac{\alpha u_s u_f (u_s - u_f)}{R(t) \left\{ 2u_s - u_f \frac{du_s}{du_f} + \frac{\gamma_f u_f^2}{u_s - u_f} \frac{du_s}{du_f} \right\}} \quad (5.32)$$

In order to implement shock wave data obtained by shock velocity particle velocity relationship, these formulae were derived by using u_s , and u_f except for the gradient term as in Eqs.(5.29)-(5.31). Thermodynamic Grüneisen parameter is also introduced here. (Nagayama 1992, Nagayama 1994)

One may note that Eq.(5.32) with no gradient term can be integrated over t provided that compression behavior of the Grüneisen parameter is known. Eq.(5.32) is then slightly rewritten for the direct integration of the equation.

$$\frac{\delta u_f}{\delta \ln R(t)} = - \frac{\alpha u_f (u_s - u_f)}{2u_s - u_f \frac{du_s}{du_f} + \frac{\gamma_f u_f^2}{u_s - u_f} \frac{du_s}{du_f}}, \quad (5.33)$$

where we have used the following relationship.

$$\delta R(t) = u_s \delta t \quad (5.34)$$

In order to have an approximate but analytical expression for the shock history, the following several assumptions have been made.

- (i) Present material obeys the Grüneisen type EOS with the Grüneisen parameter being a function only of volume.
- (ii) The Grüneisen parameter has the volume dependence as $\rho\gamma = \rho_0\gamma_0 = \text{constant}$.
- (iii) Shock Hugoniot of the material is expressed as an empirical linear relationship between shock velocity and particle velocity, i.e., $|u_s| = A + B|u_p|$, where A and B are material constants defined in Chapter 3. Notation of absolute value is used to include converging waves, where shock and particle velocities are negative.

Under these assumptions, Eq.(5.33) can be rewritten to

$$\frac{\delta \ln u_f}{\delta \ln R(t)} = - \frac{\alpha (u_s - u_f)}{A + u_s + \frac{\gamma_0 B u_f^2}{u_s}} \quad (5.35)$$

This equation can be integrated together with the linear relation between shock and particle velocities. The resultant expression for the particle velocity as a function of shock front position is given by

$$\frac{\text{const}}{R^\alpha} = \left(\frac{u_f}{A}\right)^2 \left\{1 + (B-1)\frac{u_f}{A}\right\}^{(2-B)/(B-1)} \left[\frac{\left\{1 + (B-1)\frac{u_f}{A}\right\}^{B/(B-1)}}{1 + B\frac{u_f}{A}} \right]^{\gamma_0} \quad (5.36)$$

(Nagayama 1992, Nagayama 1994) Now we have a closed form solution of converging or diverging shock waves for symmetrical geometries including a constant of integration. The most serious assumption in the course of the derivation of this approximate formula is the one that the density gradient just after the shock front is negligible. Eq.(5.36) is not applicable for flows with arbitrary initial conditions, but suitable for flows under the almost constant-pressure support from outer boundary. In other words, this assumption will be a plausible one only when high explosive layer outside of the plane slab, or cylindrical rod or spherical sample has enough thickness to drive shock wave into the sample. Present solution showed good agreement with some example numerical calculation of cylindrically converging shock wave in solid. (Nagayama and Murakami 1974)

Very simple numerical calculation for cylindrical converging shock wave with varying the nonlinearity parameter B in Eq.(5.36), and the result is shown in Fig. 5.2. As shown in Eq.(5.36), relationship between shock position $R(t)$ and the reduced particle velocity u_p/A contains only two material parameters, B and γ_0 . Calculations have been made on hypothetical materials with different values of B and γ_0 but with the same A , although one need not use the value of it in the calculation. In real materials, B and γ_0 have close relationship. It is assumed here that Slater model for the Grüneisen parameter is valid. Then γ_0 is given by $\gamma_0 = 2B - 2/3$. Shock growth is calculated with the initial shock strength of $u_p/A = 0.2$ at the reduced radius of $R/R_0 = 1$. It is shown that converging shock growth with radius is larger for larger value of B . (Nagayama 1992, Nagayama 1994) Note here that the Hugoniot parameter B is one of representative material parameter of nonlinearity. It is the complex reflections of cold potential function, and eventually close connection to thermal contribution of pressure or of sound velocity through the Grüneisen parameter. Fig. 5.2 therefore is one of the typical example of the dependence of flow field on EOS for materials.

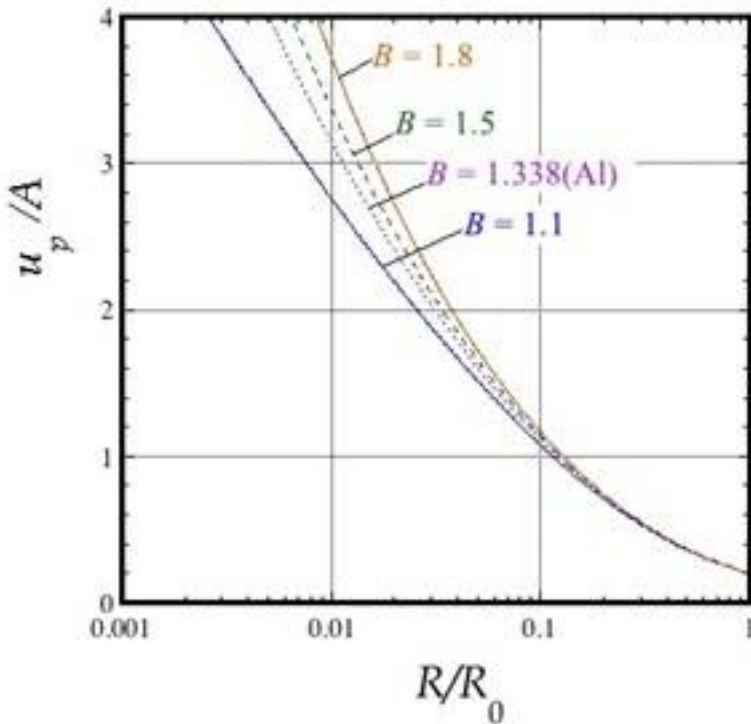


Fig. 5.2 Approximate solution of cylindrically converging shock growth in hypothetical materials with several different shock Hugoniot parameter B .

5.3. The High Pressure Riemann Problem for Condensed Media

5.3.1 Statement of the problem

Riemann problem is one of fundamental flow problems which is also called shock tube problem. In case of solid materials, the problem is stated simply by a pressure difference at some surface at time zero. Successive flow field must contain shock wave propagation into lower pressure area, while rarefaction wave travels just to reverse direction in high-pressure section. This problem was of course originally stated for gases. In gas dynamics, basically stable interface with pressure difference cannot be realized without using thin solid film or other means. It is impossible to realize material interface of different gaseous states in contact with each other with no alien substances. On the contrary, solid material interface is easy to realize, and the existence of material interface is one of the base concept for the experimental assembly for high-pressure shock study of solids.

Numerical simulation or hydrodynamic simulation is sometimes inevitable to study complex or reactive flow including shock propagation. (Mader 1998, Wilkins 1999) Historically, the Glimm's method or the so-called random choice method has been widely applied to various flows, since the method is considered to have several advantages over conventional finite difference schemes. (Sod 1978) This method, however, has been used almost exclusively in the gasdynamic problems, since it requires the exact solution of the Riemann problem for arbitrary discontinuities, and is well known at least in case of ideal gases. It is therefore desirable to obtain the exact and analytical solution of the Riemann problem for fluids with equation of state of arbitrary form. An attempt to extend the random choice method to non-ideal gases has been proposed by Colella and Glaz, although it is a too tedious task to apply their method to the equation of state, the form of which is quite different from that of ideal gases. (Colella and Glaz 1983) There has already been an attempt to extend the method to the case of solids made at least in the range of two-dimensional elastic flows, although it can't be applied to the flow phenomena of very high-pressure shock wave propagation. (Esser and Grönig 1985)

Random choice method, itself has been proved to be especially effective for 1-d problem, and their use for the numerical method survives as a Riemann solver implemented in the numerical scheme. Even so, there still is an interesting physical topics and the solution will be used to understand the flows realized by various initial and boundary conditions.

In this section, an exact solution can be obtained for generalized shock tube initial conditions, if the Grüneisen type equation of state for solids has some special form. We will have discussions on the functional form of the EOS, and furthermore, the solution can be extended into the form including elastic strength effects. (Nagayama 1989)

5.3.2 Idealized Grüneisen equation of state for condensed media

We will seek an appropriate form in the scheme of the Grüneisen type equation of state suitable for the exact solution of high pressure Riemann problem. For this purpose, we will assume the following:

- (i) The EOS has one standard isentrope that have a special form defined later. We do not assume empirical linear relation between shock and particle velocity.
- (ii) Grüneisen parameter obeys volume dependence in the form,
$$\rho\gamma = \rho_0\gamma_0 = \text{constant}.$$
- (iii) we will only consider 1-d shock tube initial condition.
- (iv) rigidity effect is implemented by a fixed value of Hugoniot elastic limit.
- (v) characteristic temperature is assumed to be a Debye temperature of the material.

From these assumptions, the idealized Grüneisen EOS is written as

$$\varepsilon = \varepsilon(v, S_0) + [C(S) - C(S_0)]\Theta(v) \quad (5.37)$$

$$p = p(v, S_0) + \rho_0 \gamma_0 [C(S) - C(S_0)] \Theta(v) \quad (5.38)$$

$$\begin{aligned} \Theta(v) &= \Theta(v_0) \exp \left[- \int_{v_0}^v \frac{\gamma_0}{v_0} dv \right] = \Theta(v_0) \exp \left[- \frac{\gamma_0}{v_0} (v - v_0) \right] \\ &= \Theta(v_0) \exp [\gamma_0 \eta] \end{aligned} \quad (5.39)$$

where we have introduced an isentrope whose entropy is the value at the uncompressed initial state of the material. One may note also that this isentrope can be written as

$$\begin{aligned} \varepsilon_{S_0}(\eta) &= \varepsilon_c(\eta) + C(S_0) \Theta(\eta), \\ p_{S_0}(\eta) &= p_c(\eta) + \rho_0 \gamma_0 C(S_0) \Theta(\eta), \\ \Theta(\eta) &= \exp [\gamma_0 \eta] \end{aligned} \quad (5.40)$$

where all the material functions are written as a function of the volume compression, η . Comparing Eqs. (5.37)-(5.39) with Eqs.(5.40), arbitrary isentropes other than that of standard entropy, S_0 differs the product of the characteristic temperature function $\Theta(\eta)$ with the difference in the value of the variable C . In the last equation of Eq.(5.40), we define Θ as a non-dimensional variable for later convenience, so that variable C has a dimension of specific internal energy.

One needs to calculate the so-called Riemann integral along an isentrope. From the discussion below, the integral can be made to produce an elementary function, if the isentrope has a special form of the characteristic temperature function $\Theta(\eta)$. Condition of this is such that square of acoustic impedance at an arbitrary state can be a quadratic function of $\Theta(\eta)$. Based on the definition of long wavelength sound velocity together with thermodynamics, square of the acoustic impedance is given by

$$(\rho a)^2 = \rho^2 \left(\frac{\partial p}{\partial \rho} \right)_s = - \left(\frac{\partial p}{\partial v} \right)_s \quad (5.41)$$

then we will present the condition to obtain an analytical function for Riemann integral can be written by

$$(\rho a)^2 = - \left(\frac{\partial p}{\partial v} \right)_s = \rho_0^2 \varphi(\Theta(\eta)) \quad (5.42)$$

where function $\varphi(\eta)$ is defined as

$$\varphi(\Theta(\eta)) = A_0(C(S_0)) + A_1(C(S_0)) \Theta(\eta) + A_2(C(S_0)) \Theta^2(\eta) \quad (5.43)$$

In this equation, parameters, A_0 - A_2 must be determined so as to match this function with the one calculated from the cold isotherm or 0K isentrope based on the shock Hugoniot data.

By integrating Eq.(5.42) in terms of specific volume, one may obtain isentropic pressure as a function of the characteristic temperature function $\Theta(\eta)$.

$$\begin{aligned}
p_{S_0}(\eta) &= p_{S_0}(\Theta) = -\int_{v_0}^v (\rho a)^2 dv = + \frac{1}{\rho_0 \gamma_0} \int_1^\Theta \frac{(\rho a)^2}{\Theta} d\Theta \\
&= \frac{\rho_0}{\gamma_0} \left[A_0 \ln \Theta + A_1 (\Theta - 1) + \frac{A_2}{2} (\Theta^2 - 1) \right]
\end{aligned} \tag{5.44}$$

where the initial pressure is assumed negligible. Arbitrary isentrope can easily be given simply by adding $\rho_0 \gamma_0 (C(S) - C(S_0)) \Theta(\eta)$ to Eq.(5.44).

In order to study whether this approximation of isentropes is compatible with the shock wave data, acoustic impedance of several metals have been calculated by using the cold material function under the assumption of $\rho\gamma = \rho_0\gamma_0 = \text{constant}$. Figure 5.3 shows the calculated values of the square of acoustic impedance for several metals as a function of reduced characteristic temperature. It is found that functional form of the acoustic impedance cannot be fitted to a quadratic function of $\Theta(\eta)$ for an extremely wide range of pressure exceeding several hundred GPa. In this in mind, Fig. 5.3 shows the range of the characteristic function to twice that of initial value. This roughly corresponds to the volume compression of $v/v_0 = 0.65$.

Table 5.1 shows fitted parameters used in Fig. 5.3 for selected materials. Apparently, fitting looks very well, but not perfect. Correlation R is also given in the table.

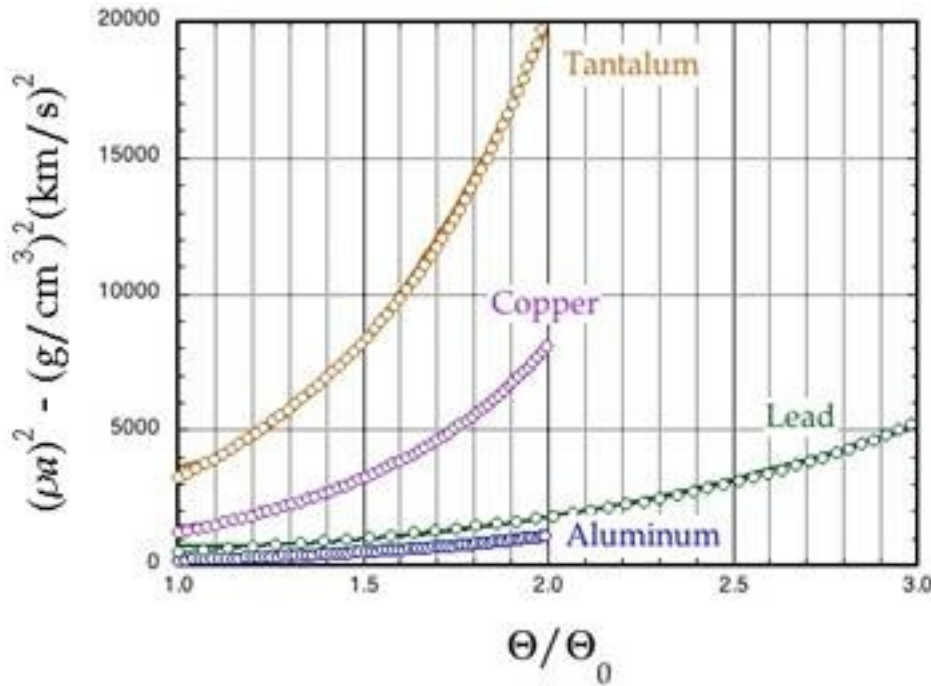


Fig. 5.3 Square of the acoustic impedance as a function of characteristic temperature for several metals. Open circles denote calculated isentropic curve, and solid lines show 2nd order polynomial fit to the data.

Table 5.1 Fitting parameters of square of acoustic impedance function along the standard isentrope for several materials.

material	A0	A1	A2	R
aluminum	606.34	-986.65	618.11	0.99957
copper	6570.9	-10935	5797.8	0.99904
lead	1907.5	-2337.5	1137.9	0.99823
tantalum	16129	-26681	14266	0.99906

Material function $f(v)$ as in Eq.(2.9) can be obtained by integrating Eq.(5.44) as

$$\begin{aligned}
 f(v) &= p_{s_0}(v) - \frac{\gamma}{v} \varepsilon_{s_0}(v) \\
 &= p_{s_0}(\Theta) + \rho_0 \gamma_0 \int_{v_0}^v p_{s_0}(\Theta) dv - \rho_0 \gamma_0 \varepsilon_0 \\
 &= p_{s_0}(\Theta) - \int_1^\Theta p_{s_0}(\Theta) \frac{d\Theta}{\Theta} - \rho_0 \gamma_0 \varepsilon_0 \\
 &= -\rho_0 \gamma_0 \varepsilon_0 + \frac{\rho_0}{\gamma_0} \left[A_0 \ln \Theta \left(1 - \frac{1}{2} \ln \Theta \right) \right. \\
 &\quad \left. + A_1 \ln \Theta + \frac{A_2}{4} (\Theta^2 - 1) + \frac{A_2}{2} \ln \Theta \right] \quad (5.45)
 \end{aligned}$$

The form of the Grüneisen equation of state in this approximation is given by Eq.(2.9) combined with Eq.(5.45). Now, it is an easy and straightforward task to write not only the form of arbitrary isentropes but also the Hugoniot curve explicitly by using this equation of state.

5.3.3 Linear elasticity law and the yielding condition

For shock waves in crystalline solids with moderate strength, shock wave splits into the plastic wave and the preceding elastic wave due to the elastic plastic transition. For simplicity, it is assumed here that yielding strength is constant up to very high pressures. Furthermore, it is assumed that the empirical linear correspondence between stress and strain holds within the elastic region. For homogeneous materials, it can be expressed as

$$\dot{\sigma}_1 = \lambda \frac{\dot{v}}{v} + 2\mu \dot{e}_1, \quad \dot{\sigma}_2 = \lambda \frac{\dot{v}}{v} + 2\mu \dot{e}_2, \quad \dot{\sigma}_3 = \lambda \frac{\dot{v}}{v} + 2\mu \dot{e}_3 \quad (5.46)$$

(Wilkins 1999)

where λ and μ are the Lamé constants, and $\sigma_1 \sim \sigma_3$ and $e_1 \sim e_3$ are the stresses and strains in the directions of principal axes, and v denotes the volume, respectively. The dot on variables means a time derivative along a particle path, and second terms in Eq.(5.46) denote the strain rate terms in the corresponding direction.

Each stress, $\sigma_1 \sim \sigma_3$ at highly compressed states is assumed to be consisted of stress component associated with the corresponding hydrostatic pressure, p , and of remaining component associated with elastic deviating forces due to shear, s ,

$$\dot{\sigma}_1 = -p + s_1, \quad \dot{\sigma}_2 = -p + s_2, \quad \dot{\sigma}_3 = -p + s_3, \quad (5.47)$$

so that the hydrostatic pressure, $-p$, is given by the mean of three stresses, i.e. $p = -(\sigma_1 + \sigma_2 + \sigma_3)/3$, and $s_1 + s_2 + s_3 = 0$. Similarly, it is possible to define the mean normal strain, θ and also the deviatric strain components, $\theta_1 \sim \theta_3$ as

$$\theta = \frac{1}{3} (e_1 + e_2 + e_3) \quad (5.48)$$

$$\theta_1 = e_1 - \theta, \quad \theta_2 = e_2 - \theta, \quad \theta_3 = e_3 - \theta. \quad (5.49)$$

Mass conservation can be expressed as

$$\dot{\theta}_1 + \dot{\theta}_2 + \dot{\theta}_3 = 0, \dot{\theta} = \frac{1}{3} \frac{\dot{v}}{v}. \quad (5.50)$$

In terms of these notations, Hooke's law for solids under very high pressures can be written as

$$\dot{s}_1 = 2\mu \left[\dot{e}_1 - \frac{1}{3} \frac{\dot{v}}{v} \right], \dot{s}_2 = 2\mu \left[\dot{e}_2 - \frac{1}{3} \frac{\dot{v}}{v} \right], \dot{s}_3 = 2\mu \left[\dot{e}_3 - \frac{1}{3} \frac{\dot{v}}{v} \right] \quad (5.51)$$

and the other part of the stress, i.e., hydrostatic pressure, p is expressed by the Grüneisen equation of state described previously.

It is assumed here that the yielding condition can be written as

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \leq 2Y_0^2 \quad (5.52)$$

or

$$s_1^2 + s_2^2 + s_3^2 \leq \frac{2}{3} Y_0^2 \quad (5.53)$$

where Y_0 has the meaning of the value of shear strength of simple tension. Eq.(5.52) or (5.53), the von Mises yielding condition, represents that yielding occurs when elastic energy of distortion per unit volume reaches some limiting value.

5.3.4 High-pressure Riemann problem for elastic-plastic solids

Let us construct a high-pressure shock tube initial conditions for elastic-plastic solids satisfying the Grüneisen type equation of state given in the previous sections.

Low-pressure section $p_1=0$ (GPa), $u_1=0$ (km/s), T_1 =room temperature,

High-pressure section $p_4=25$, or 100(GPa), $u_4=0$ (km/s), $T_4=T_1$,

In the present problems, both the low-pressure and high-pressure sections are assumed to be in the hydrostatic state, although it is easy and straightforward to include the deviatoric stress components for both states.

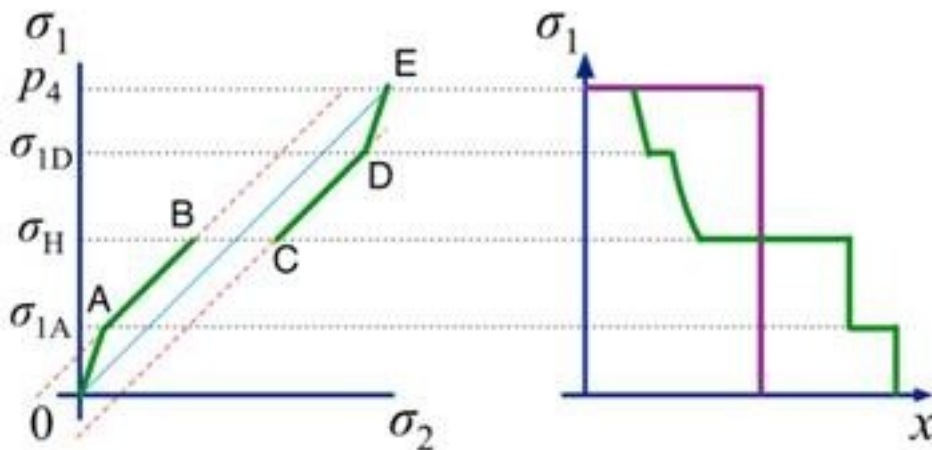


Fig. 5.4 Schematic illustration of the stress path and associated stress profile for the high-pressure elastic-plastic

Initial conditions and expected stress wave profile are schematically shown in Fig. 5.4. Stress paths along shock loading and along unloading wave on stress plane are also shown in Fig. 5.4. If the pressure in the high-pressure section has a value less than some limiting value, two-wave structure has been expected for both compression ($\sigma_1=0$ to σ_{1A} and σ_{1A} to σ_H) and release paths (p_4 to σ_{1D} and σ_{1D} to σ_H). Two straight lines from point A to point B, and from point C to point D correspond to the Hugoniot compression curve, and the release isentrope, respectively. It is noticeable from this stress diagram that σ_1 , the stress component parallel to the propagation direction should be continuous at the contact surface from the continuity condition of the surface, whereas the other components, σ_2, σ_3 and also p should not. In the stress diagram in the lhs figure of Fig. 5.4, two dashed lines, lying on both sides of a solid line passing through the origin, corresponds to the envelope of the von Mises yield circle in uniaxial strain condition, i.e., $\sigma_1 - \sigma_2 = \pm Y_0$. Each stress path drawn in thick lines corresponds to four kinds of waves, elastic precursor, plastic shock wave, elastic release wave and plastic unloading wave schematically depicted in rhs figure in Fig. 5.4.

Parameters of elastic compression wave and successive plastic high-pressure shock wave can be calculated by combining the elasticity law, Eqs.(5.51), (5.52), the finite yielding strength, Y_0 , and the equation of state, Eqs.(5.37)-(5.40), and Eq.(5.45) with the conservation equations of continuum mechanics for plane flow. Hence, we proceed to derive the formulae representing release isentropic waves for elastic and plastic portion. This is the critical process of providing the Riemann integral by using acoustic impedance with special functional form given by Eqs.(5.42), (5.43). For this, we again start with the hydrodynamic discussion i.e., without taking into account of the rigidity.

The particle velocity change within the isentropic expansion processes can be derived from the relation $du = -\sqrt{\{dpdv\}}$ together with Eqs.(5.42), (5.43). In case of a simple rarefaction wave centering the state, ($p=p_4$, $u=u_4$), the change in particle velocity along the release isentrope is given by the following Riemann integral

$$\begin{aligned} u - u_4 &= -\int_{p_4}^p \sqrt{\{-dpdv\}} = -\int_{v_4}^v \sqrt{\left\{-\frac{dp}{dv}\right\}} dv \\ &= -\int_{v_4}^v (\rho a) dv = -\int_{\Theta_4}^{\Theta} (\rho a) \frac{dv}{d\Theta} d\Theta \\ &= \frac{1}{\rho_0 \gamma_0} \int_{\Theta_4}^{\Theta} (\rho a) \frac{1}{\Theta} d\Theta = \frac{1}{\gamma_0} \int_{\Theta_4}^{\Theta} \frac{\sqrt{\varphi^*(\Theta)}}{\Theta} d\Theta \end{aligned} \quad , \quad (5.54)$$

where

$$\varphi^*(\Theta) = A_0 + A_1^* \Theta + A_2 \Theta^2 \quad (5.55)$$

$$A_1^* = A_1 + \frac{\gamma_0}{\rho_0} [C(S_4) - C(S_0)] \quad (5.56)$$

Coefficient A_1^* contains a difference in entropy of the high-pressure state, S_4 and that of the low-pressure state $S_1=S_0$.

Integration of Eq.(5.54) gives

$$u - u_4 = -u_\infty + \frac{1}{\gamma_0} \left[\sqrt{\varphi(\Theta)} + \frac{A_1^*}{2\sqrt{A_2}} \log \left| 2A_2\Theta + A_1^* + 2\sqrt{A_2\varphi(\Theta)} \right| \right. \\ \left. + \sqrt{A_0} \log \left| \frac{\Theta}{A_1^*\Theta + 2A_0 + 2\sqrt{A_0\varphi(\Theta)}} \right| \right] \quad (5.57)$$

where $-u_\infty$ is the escape velocity defined as

$$u_\infty = \frac{1}{\gamma_0} \left[\sqrt{\varphi(\Theta_4)} + \frac{A_1^*}{2\sqrt{A_2}} \log \left| 2A_2\Theta_4 + A_1^* + 2\sqrt{A_2\varphi(\Theta_4)} \right| \right. \\ \left. + \sqrt{A_0} \log \left| \frac{\Theta_4}{A_1^*\Theta_4 + 2A_0 + 2\sqrt{A_0\varphi(\Theta_4)}} \right| \right] \quad (5.58)$$

The above integral should be valid for the case of $A_0 > 0$, which is proved to be satisfied for at least several metals at least within the compression range presented previously. Note again that the parameter C in the coefficient A_1^* in Eq.(5.56) represents new thermal variable as a function of entropy introduced in Chapter 2, so that the formulae for velocity obtained here are valid for arbitrary isentropes. Based on these equations, it is straightforward to derive an exact solution for the Riemann problem for solids with no yield strength.

5.3.5 Effects of rigidity and relationship for the elastic waves

For the plane elastic plastic flow, hydrostatic pressure should be replaced by the stress, σ_1 . Especially for the states on release isentropes along von Mises yield circle (along the line from point D to C in Fig. 5.4, for example), σ_1 can be given by $\sigma_1 = Y_0 + p$, so that the square of the acoustic impedance, $\{-dp/dv\}$ includes no contribution of the finite but constant yield strength, Y_0 . From this discussion, formulae for the particle velocity, Eqs.(5.54)-(5.57) remain valid and have the same form as in the case of no yield strength. It should be kept in mind that these discussions have a meaning only when the yield strength, Y_0 is constant up to very high pressures, and that if Y_0 is pressure dependent, Eqs.(5.54)-(5.57) must be rewritten including the Y_0 term.

The corresponding relationship of velocity change in the elastic compression and release wave can be obtained by combining the elasticity law with the isentropic flow equations. Plane flow is characterized by the one-dimensional strain, and this condition is written as

$$e_1 \neq 0, e_2 = 0, e_3 = 0, \dot{\theta} = \frac{1}{3} \dot{e}_1, \dot{e}_1 = \frac{\dot{v}}{v} \quad (5.59)$$

$$\dot{\sigma}_1 = \frac{4}{3} \mu \frac{\dot{v}}{v}, \dot{\sigma}_2 = -\frac{2}{3} \mu \frac{\dot{v}}{v}, \dot{\sigma}_3 = -\frac{2}{3} \mu \frac{\dot{v}}{v}, \quad (5.60)$$

The change in particle velocity associated with the change in stress is given by

$$du = -\frac{d\sigma_1}{\rho a_1} = (\rho a_1) dv = \frac{1}{\rho_0 \gamma_0} (\rho a_1) \frac{1}{\Theta} d\Theta \quad (5.61)$$

where a_1 , the speed of the longitudinal sound wave, is defined as

$$\begin{aligned}
a_1^2 &= \left(-\frac{\partial \sigma_1}{\partial \rho} \right)_s = \left(\frac{\partial p}{\partial \rho} \right)_s + \left(-\frac{\partial s_1}{\partial \rho} \right)_s \\
&= \left(\frac{\rho_0}{\rho} \right)^2 \varphi^*(\Theta) + \frac{4\mu}{3\rho}
\end{aligned} \tag{5.62}$$

where the last expression is obtained from Eq.(5.60). The first term in Eq.(5.62) can be calculated from Eqs.(5.41), (5.42) and (5.55) and consequently the longitudinal sound velocity can be a function of density, and can be defined as a local sound velocity at arbitrary thermodynamic state in terms of density and $C(S)$.

The integration of Eq.(5.61) along isentrope seems difficult by observing Eqs.(5.61) and (5.62). Except for brittle solids, however, high-pressure shock waves of several tens of GPa or more, has a dominant plastic wave than a preceding elastic one. For example, for aluminum, the yield strength, Y_0 is estimated to be $Y_0=0.298$ (GPa). (Wilkins 1999) This value is rather small, and the associated density change due to the change in stress of this magnitude is estimated to be around 0.4 %. By this reason, it is possible to estimate the integration of Eq.(5.61) approximately, but in very high precision.

We expand (ρa_1) into simple power series in Θ up to less than third order around its initial value, Θ_i , which gives

$$u = u_i + B_1 (\Theta - \Theta_i) + B_2 (\Theta - \Theta_i)^2 + B_3 (\Theta - \Theta_i)^3 \tag{5.63}$$

$$\begin{aligned}
B_1 &= \frac{(\rho a_1)_i}{\Theta_i}, \\
B_2 &= \frac{1}{2B_1} \left[\rho_0^2 (A_1 + 2A_2 \Theta_i) + \frac{4\mu}{3} \frac{\rho_i^2}{\rho_0 \gamma_0 \Theta_i} \right] - \frac{1}{2} \frac{B_1}{\Theta_i}, \\
B_3 &= \frac{1}{3B_1} \left[\rho_0^2 A_2 + \frac{4\mu}{3} \frac{\rho_i^3}{(\rho_0 \gamma_0 \Theta_i)^2} \right] - \frac{1}{3} \frac{B_2}{\Theta_i}.
\end{aligned} \tag{5.64}$$

This simple approximation is proved to give very accurate values, if the relative change in density associated with the change in stress of several hundreds of MPa remains within a few percent.

5.3.6 Numerical examples

Combining the equations derived above, we calculate the solution of the Riemann problem for solid aluminum and tantalum with several initial conditions given in the previous section. Figure 5.5 shows the calculated profile of the stress component to the direction of wave propagation, σ_1 and of pressure for the elastic-plastic Riemann problem. Pressure of the high-pressure section is assumed to be 100 GPa.

In the figure, only the profiles at the reduced time, $t = 0.5$ are shown. Note that profiles at any time after diaphragm break of virtual shock tube are self-similar. Of all the calculations, the reduced time is defined by using the bulk speed of sound at the high-pressure section, c_4 . One may see the difference in the resultant wave propagation for two materials.

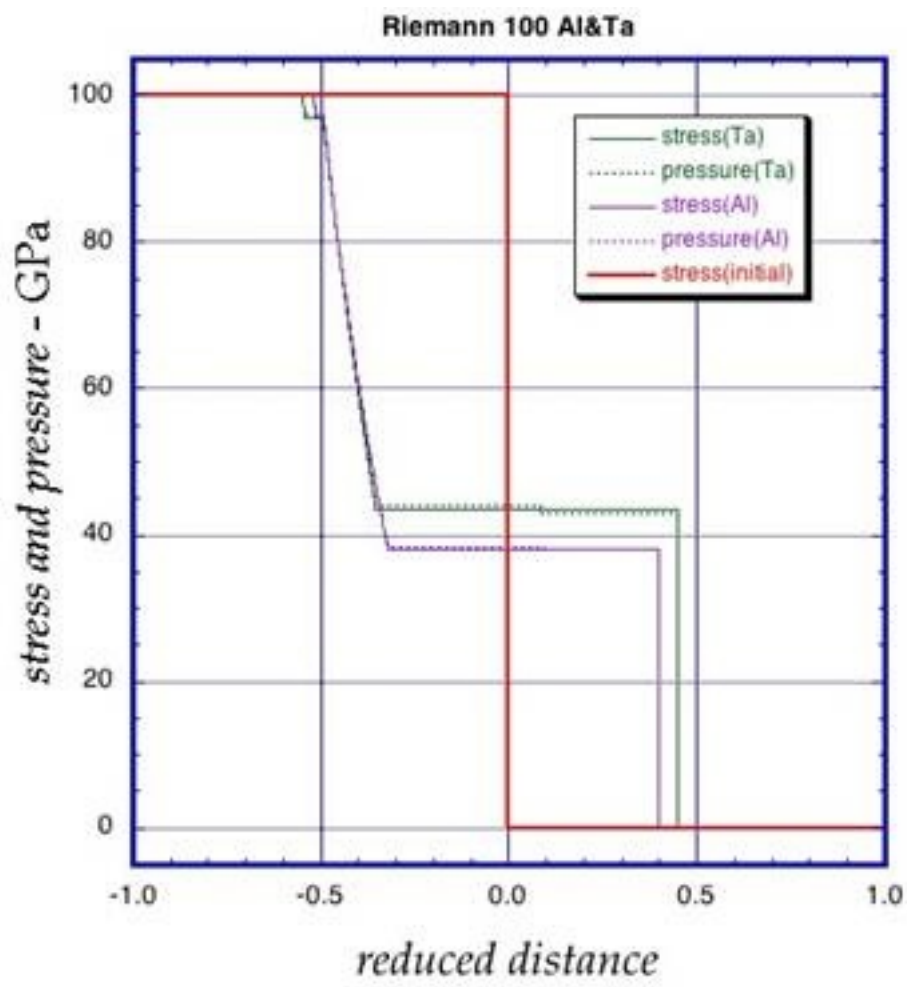


Fig. 5.5 Calculated exact solution of high-pressure elastic-plastic Riemann problems for Aluminum and Tantalum including rigidity effects. Value of pressure of high-pressure section in the initial conditions is 100 GPa.

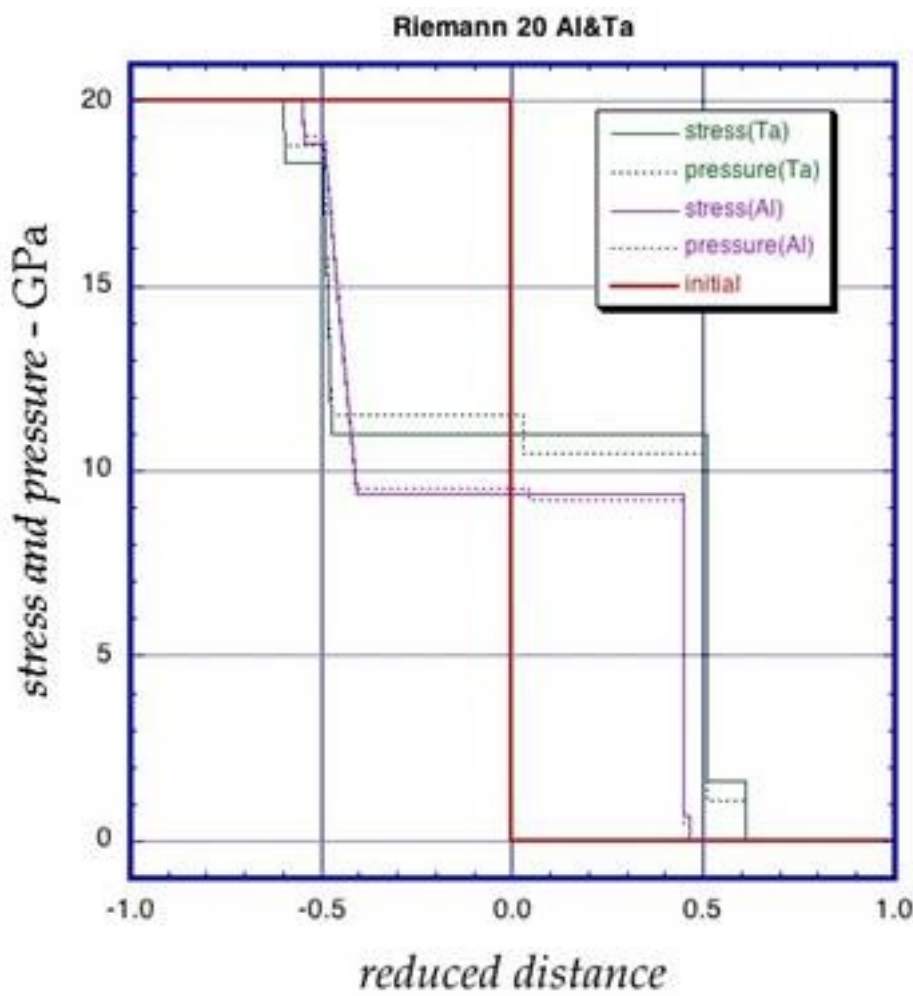


Fig. 5.6 Calculated exact solution of high-pressure elastic-plastic Riemann problems for Aluminum and Tantalum including rigidity effects. Value of pressure of high-pressure section in the initial conditions is 20 GPa.

For this initial condition, the compression shock is stable, i.e., wave-splitting doesn't occur. Two rarefaction waves, however, can be noticed, and they gradually smear out during propagation self-similarly. Since the value of the pressure in the high-pressure section is rather higher than the yield strength, the influences of yield strength are not so noticeable. It is seen in Fig. 5.5, the profile of p has a clear but very slight discontinuity at the contact surface within plastic state region.

In Fig. 5.6, two profiles of stress components, σ_1 and p are shown for the case of $p_4=25$ GPa, to see the effects of finite yield strength. And it can also be noted from the figure that the profile of p has a clear discontinuity at the contact surface within plastic state region, as pointed out previously. In this case, one may see elastic plastic two-wave structure for both metals.

The present solution may be considered to be at least a good example of the checking ground for the feasibility or applicability of finite difference methods used in the simulation of solid flow problems. Furthermore, it is also possible to obtain the solution of any shock tube initial conditions in a similar manner, which makes it possible to construct the numerical method based on the Godunov scheme or rather to apply it to the random choice method.

Only for brittle solids with very high elastic strength or solids having complex mechanical properties during shock loading process, like Baushinger effect, etc., more rigorous treatment is required.

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Appendices

Table A-1 Periodicity of atomic mass, atomic volume, density and Grüneisen parameter at atmospheric pressure

atomic number	element name	atomic mass	initial density	atomic volume per bar	A	B	T thermodynamic	T Star	T Duplicate-MacDonald	T Vachaneo-Zubarev	d Inverse Star	d Inverse Duplicate-MacDonald	d Inverse Vachaneo-Zubarev
1	H(1)	1.0070	0.0008000										
2	He	4.0026	0.20500		1.1000	1.6400		2.6133	2.2800	1.9467	-0.53580	-0.84492	-2.0160
3	Li	6.9410	0.54200	12.806	4.5890	1.1540	0.02000	1.9413	1.3090	0.97467	-0.57182	-0.87049	-1.6826
4	Be	9.0122	1.8200	4.9517	7.9980	1.1240	1.1100	1.5813	1.2480	0.91467	-0.57252	-0.86411	-1.8021
5	B	10.810	2.4700	4.3705									
6	C	12.011	3.5160	3.4161	4.7500	1.5000	0.24000	2.3333	2.0000	1.6667	-0.54902	-0.86747	-2.0680
7	N	14.007	1.0000	13.599	1.6000	1.4000		2.1333	1.8000	1.4667	-0.55749	-0.87852	-2.0497
8	O(1)	15.999	1.5680	10.204									
9	F(1)	18.998	1.5300	12.417									
10	Ne	20.179	1.5100	13.364									
11	Na	22.990	1.0130	22.095	2.5630	1.2430	1.2500	1.8173	1.4840	1.1507	-0.56817	-0.88117	-1.8737
12	Mg	24.305	1.7400	13.968	4.4620	1.2630	1.5400	1.6593	1.5260	1.1927	-0.56791	-0.88222	-1.8091
13	Al	26.982	2.7000	8.9602	5.3280	1.3380	2.0000	2.0093	1.6760	1.3477	-0.56217	-0.88220	-2.0046
14	Si	28.086	2.3300	12.054			0.74000						
15	P(1a)	30.974	2.7000	11.472									
16	S	32.060	2.1000	15.267	2.4200	1.3600		2.0533	1.7200	1.3867	-0.56057	-0.88129	-2.0239
17	Cl	35.453	2.0300	17.466									
18	Ar	39.948	1.7700	22.569	1.1900	1.6200		2.5733	2.2400	1.9067	-0.53786	-0.84850	-2.0285
19	K	39.098	0.91000	42.905	1.9500	1.1880	1.3400	1.7099	1.3700	1.0427	-0.57066	-0.87590	-1.7645
20	Ca	40.080	1.5300	26.196	3.5500	0.91200	1.09	1.1573	0.82400	0.49067	-0.58517	-0.78064	-0.87106
21	Sc	44.956	2.9900	15.035	0.0500	0.74600	0.82533	0.49200	0.15867	-0.53267	-0.56964	-0.25588	
22	Ti	47.880	4.8100	10.616	5.2200	0.76700	1.2300	0.86733	0.53400	0.20067	-0.53840	-0.60123	-0.32905
23	V	50.942	6.0900	8.3646	0.0770	1.0170	1.4000	1.7353	1.4020	1.0667	-0.57013	-0.87755	-1.7932
24	Cr	51.996	7.1900	7.2517	5.1730	1.4730	1.1900	2.2793	1.9480	1.6127	-0.55140	-0.87097	-2.0994
25	Mn	54.938	7.4700	7.3545			2.4000						
26	Fe	55.847	7.8700	7.0692	3.8000	1.5800	1.6900	2.4933	2.1600	1.8267	-0.54167	-0.85535	-2.0479
27	Co	58.933	8.9000	6.6217	4.7500	1.3300	1.9900	1.9933	1.6900	1.3267	-0.56273	-0.88245	-1.9966
28	Ni	58.690	8.9100	6.5870	4.6500	1.4500	1.9300	2.2333	1.9000	1.5667	-0.55338	-0.87367	-2.0967
29	Cu	63.546	8.9300	7.1160	3.9400	1.4890	2.0200	2.3113	1.9790	1.6447	-0.55060	-0.86884	-2.0996
30	Zn	65.380	7.1300	8.1697	3.0500	1.5600	2.2700	2.4533	2.1200	1.7867	-0.54364	-0.85859	-2.0554

atomic number	element name	atomic mass	total density	atomic volume cm ³ /mol	A	B	T thermodynamic	T Bohr	T Dugdale-MacDonald	T Vashchenko-Zubov	Δ T Bohr	Δ T Dugdale-MacDonald	Δ T Vashchenko-Zubov
31	Ga	69.720	5.9100	11.797									
32	Ge	72.580	5.3200	13.045	2.1900	1.5400	0.72000	2.4133	2.0800	1.7467	-0.54526	-0.86170	-2.2618
33	As	74.922	5.7700	12.985									
34	Se	78.960	4.8100	16.416	1.6600	1.3100		1.9533	1.6200	1.2867	-0.56410	-0.88284	-1.9741
35	Br	79.904	4.0500	19.729									
36	Kr	83.800	3.0900	27.120									
37	Rb	85.468	1.6290	52.496	1.1840	1.2320	1.0900	1.7973	1.4640	1.1307	-0.56889	-0.89049	-1.8554
38	Sr	87.620	2.5800	33.961	2.1000	0.94000		1.2133	0.88000	0.54967	-0.56779	-0.78165	-0.97766
39	Y	88.906	4.4800	19.845	3.3300	0.75300	0.83933	0.50900	0.17267	-0.53426	-0.58057	-0.28005	
40	Zr	91.220	6.5100	14.012	3.7570	1.0180	1.0900	1.3690	1.0360	0.70267	-0.57207	-0.82712	-1.2641
41	Nb	92.906	8.5800	10.828	4.4380	1.2070	1.6900	1.7473	1.4140	1.0807	-0.56967	-0.87622	-1.8058
42	Mo	95.940	10.220	9.3875	5.1240	1.2330	1.5900	1.7993	1.4660	1.1327	-0.56864	-0.88396	-1.8573
43	Tc	98.000	11.500	8.5217									
44	Ru	101.07	12.360	8.1772									
45	Rh	102.91	12.420	8.2855	4.8070	1.3790	1.8800	2.0853	1.7520	1.4187	-0.55896	-0.88028	-2.0351
46	Pd	106.42	12.000	8.6983	3.9480	1.5880	1.9700	2.5090	2.1760	1.8427	-0.54091	-0.85401	-2.0446
47	Ag	107.87	10.500	10.273	3.2400	1.5600	2.4000	2.5133	2.1800	1.8467	-0.54072	-0.83368	-2.0436
48	Cd	112.41	8.6500	12.995	2.4400	1.6700	2.2790	2.6730	2.3400	2.0067	-0.53301	-0.83937	-1.9678
49	In	114.82	7.2900	15.750	2.3700	1.6100	2.2400	2.5533	2.2200	1.8867	-0.53882	-0.85025	-2.0338
50	Sn	118.69	5.7600	20.606	2.6400	1.6800	2.2933	1.9800	1.6267	1.2507	-0.87010	-2.0697	
51	Sb	121.75	6.6900	18.199	2.0000	1.6000	0.88000	2.5333	2.2000	1.8867	-0.53677	-0.85198	-2.0388
52	Te	127.60	6.2500	20.416	1.4700	1.8500	3.0333	2.7000	2.3967	0.51567	-0.80324	-1.8518	
53	I	126.90	4.9500	25.637	1.3500	1.7000	2.7333	2.4000	2.0667	-0.52006	-0.83385	-1.9786	
54	Xe	131.29	3.7800	34.733									
55	Cs	132.91	1.9970	66.553	0.58000	1.3700	2.0733	1.7400	1.4067	-0.55862	-0.88366	-2.0314	
56	Ba	137.33	3.5900	36.253	1.1100	1.3660	2.0933	1.7320	1.3987	-0.56612	-0.88090	-2.0285	
57	La	138.91	6.1700	22.513	2.1800	1.0000	1.3333	1.0000	0.69667	-0.57143	-0.81818	-1.2000	
58	Ce	140.12	6.7700	20.897	1.2700	1.5880	2.5259	2.1920	1.8587	-0.54015	-0.85298	-2.0408	
59	Pr	140.91	6.7800	20.783									
60	Nd	144.24	7.0000	20.606	2.0600	1.0150	1.3633	1.0300	0.69967	-0.57187	-0.82599	-1.2535	
61	Pm	145.00											
62	Sm	150.36	7.5400	19.942	2.1900	0.88000	1.0933	0.76000	0.42967	-0.56134	-0.73315	-0.74880	
63	Eu	151.96	5.2600	28.945									

[illegible]