Volume dependence of the Grüneisen ratio for shock-wave equation-of-state studies

Valentin Gospodinov
Space Research and Technology Institute – BAS
BG-1000, Sofia, P.O. Box 799, BULGARIA
e-mail: v.gospodinov@gmail.com

Abstract

This work presents an analysis of the existing self-contained expressions for the volume dependence of the Grüneisen ratio $\gamma$ in view of their further application to EOS (equation of state) studies. These expressions are assessed and applied to materials with the major types of chemical bonds. Predictions from regression analysis are compared to existing experimental data sets. All expressions predict with very good accuracy the values of $\gamma$ at ambient conditions, its volume variation in the low pressure region, but fail to give correct values for its infinite compression limit. A possible reason for this is that all experiments are performed at comparatively low pressures. The interpolation formula by Al'tshuler et al. (1987) and the equation, proposed by Jeanloz (1989) are the best fit to experimental data. A modification to Jeanloz’s equation, more convenient for use in shock physics, is proposed in the present work. It could be used jointly with the shock Hugoniot to derive a complete EOS for solids from their response to shock-wave loading.

Key words: Grüneisen ratio, shock-wave loading, complete equation of state.

Introduction

The Grüneisen ratio $\gamma$ is an important quantity in condensed matter physics, shock physics and geophysics as it often occurs in the research of thermodynamic behavior of matter at high pressures and temperatures.

It may be used to estimate the value of the Debye characteristic temperature ($\theta_D$) from the Debye-Grüneisen definition of $\gamma$ [1] p. 133]

$$d \ln \theta_D / d \ln V = -\gamma \quad \text{or} \quad d \ln \theta_D / dV = -\gamma / V.$$  

It is also important to predict the melting curve [2] p. 280]. Thermal EOS (equations of state) require knowledge of the Grüneisen ratio as well. In geophysics the value of $\gamma$ is used to put constraints on geophysically important parameters such as the pressure and temperature dependence of the mantle and core, the adiabatic temperature gradient, and in the geophysical interpretation of Hugoniot data [3].

The Grüneisen ratio has both a statistical mechanics (microscopic) and thermodynamic (macroscopic) definition. The former relates it to the vibrational frequencies of the atoms...
in the crystal lattice of a material, and the latter represents it in terms of well-known
thermodynamic properties. The experimental determination of $\gamma$ from its thermodynamic
definition implies measurements of thermodynamic properties at high pressures. The exper-
imental determination of the Gr"uneisen ratio from its microscopic definition is very difficult,
since it requires a detailed knowledge of the phonon dispersion spectrum of a material.

Because of the scarce experimental results and the lack of first principle analytic equation,
numerous phenomenological expressions for the volume dependence of $\gamma$ have been reported
in literature. They predict a varying dependence of $\gamma$ as a function of volume and some of
them even give different values for it at ambient pressure. Most of them are analyzed in two
extensive reviews — by Knopoff and Shapiro [4], and by Anderson [5]. Their accuracies are
also compared in recent works by X. Peng et al. [6] and by Cui and Yu [7]. These papers are
in the field of geophysics. It is characteristic of them that there is an intrinsic relationship
between the expressions for $\gamma$, examined there, and the cold or the normal isotherm. Many
of these expressions relate $\gamma$ at atmospheric pressure ($P = 0$) to the first derivative of the
bulk modulus with respect to pressure or volume ($B'_T$).

To determine the functional dependence of the Gr"uneisen ratio on volume is a key prob-
lem in shock physics as well. Results from shock-wave experiments provide direct information
on the compressional and thermal behavior of metals, ceramics, rocks, and minerals at high
pressures and high temperatures. Unfortunately, data points are often sparsely deployed and
irregularly distributed. That is why it is a challenge, using this information, to have a go
on deriving the complete EOS for solids from their response to shock-wave loading. Have
it, one can easily obtain all their thermodynamic properties by simple differentiatiation.

In this way, it is possible not only to obtain a reliable interpolation tool, but to predict all
compressional and thermal properties of solids in the whole high-pressure high-temperature
region, attainable by shock-wave loading, standing on a sound physical basis.

One of the ways to derive a complete EOS for solids from their response to shock-wave
loading is to use the specific form of this dependence together with the shock Hugoniot.
That is why it is important to obtain the form of $\gamma$ independently of the shock Hugoniot
or of an isotherm.

To the author’s knowledge, a comparison of the self-contained expressions for the
Gr"uneisen ratio, used in shock physics, has not been performed so far. Therefore, the
objective of the present work is to collect the most commonly used expressions for $\gamma$
and analyze and compare them to existing experimental data. It differs from previous ap-
proaches [3,6,7,15] in that:

- there is no intrinsic relationship between the expressions for $\gamma(V)$ analyzed
  here and the shock Hugoniot $P_H(V)$, the cold isotherm $P_c(V)$, or an arbitrary
  isotherm $P_T(V)$,
- the expressions are applied to materials with various chemical bonds — metallic ($Cu$, $\varepsilon-Fe$, $K$), ionic ($NaCl$), and covalent ($MgO$).

The scope of the research with respect to the examined materials and the maximum applied
pressure is limited by the availability of experimental data.

The paper is structured as follows. The question about the relation between $\gamma(V)$ and
$P_c(V)$ is clarified in Sect. (1). In Sect. (2) the most commonly used self-contained ex-
pressions for $\gamma(V)$, mentioned above, are considered. In Sect. (3) regression analysis of
the experimental datasets is performed with these expressions. The values of $\gamma$ at ambient
conditions — \( \gamma_0 \), and at infinite pressure — \( \gamma_{\infty} \) are treated as free parameters and are determined by the method of least squares. The analysis and the discussion of the results started in Sect.(3) is finalized in Sect.(4). Also, conclusions are drawn there, and a possible direction for continuing the research is outlined.

1 The Grüneisen ratio and the cold isotherm

The thermodynamic definition of the Grüneisen ratio represents it in terms of specific heat, thermal expansion coefficient, and bulk modulus

\[
\gamma = V \left( \frac{\partial P}{\partial E} \right)_V = \frac{\alpha V B_T}{C_V} = \frac{\alpha V B_S}{C_P},
\]

where \( \alpha \) is the thermal expansion coefficient, \( C_V \) – the specific heat at constant volume, \( C_P \) – the specific heat at constant pressure, \( B_T \) – the isothermal bulk modulus, and \( B_S \) – the adiabatic bulk modulus. In terms of its thermodynamic definition \( \gamma \) may be considered the measure of the change of pressure resulting from the increase of internal energy at constant volume. The experimental determination of \( \gamma \), based on its thermodynamic definition implies the concurrent measurement of the involved thermodynamic properties at high pressures.

The statistical mechanics definition relates it to the vibrational frequencies of the atoms in the crystal lattice of a material

\[
\gamma_i = -\frac{V}{\nu_i} \left( \frac{\partial \nu_i}{\partial V} \right)_T = -\left( \frac{\partial \ln \nu_i}{\partial \ln V} \right)_T \quad (i = 1, 2, \ldots, 3N),
\]

where \( \nu_i \) are the \( 3N \) vibrational frequencies of the crystal lattice. The volume dependence of all lattice vibrational frequencies is assumed one and the same [1, p. 130], so

\[
\gamma = -\left( \frac{\partial \ln \nu}{\partial \ln V} \right)_T. \quad (3)
\]

In principle, if we knew the interatomic potential, we could calculate the frequency spectrum of the crystal and its change with volume and in this way specify the form of \( \gamma(V) \). However, this problem is mathematically so complex that has not been solved so far. That is why we have to resort to various model concepts to obtain the volume dependence of \( \gamma \).

**Slater – Landau formula.** Slater [18] and Landau [19] derived the following expression for the Grüneisen ratio on the basis of a model of an elastic medium, and assuming that the Poisson ratio does not vary with volume:

\[
\gamma = -\frac{V}{P_c} \frac{d^2 P_c / dV^2}{2 \left( d^2 P_c / dV \right)} - \frac{2}{3},
\]

where \( P_c = P_c(V) \) is the cold compression curve.

Later Slater [20] and Gilvarry [21], using the values of the first and second derivatives at zero pressure (derived from Bridgman’s data on compressibility) calculated \( \gamma \) from Eq. (4) and compared it to thermodynamic values of the Grüneisen ratio. A good agreement was obtained for the majority of metals.

**The Dugdale – MacDonald relation.** Dugdale and MacDonald in a short note [22] proposed to modify Eq. (4) and wrote the following expression for the Grüneisen parameter:
\[
\gamma = -\frac{V}{2} \frac{d^2 \left(P_c V^{2/3}\right)}{dV^2} \frac{1}{d (P_c V^{2/3})/dV} - \frac{1}{3}.
\]  

(5)

However, there were some erroneous assumptions in their reasoning. Subsequently, Rice et al. [23] have proposed a somewhat different derivation for Eq. (5). They obtained it for a cubic lattice, assuming that all force constants depend on volume in the same way. The values of \(\gamma\), obtained from Eq. (5) at zero pressure, are in good agreement with the thermodynamic values of \(\gamma_0\).

The Grüneisen ratio in the free volume approximation. Zubarev and Vashchenko [24] studied the vibration of atoms in the spherically symmetric field of their neighbors (the free volume theory). They have obtained the following expression for the Grüneisen parameter:

\[
\gamma = -\frac{V}{2} \frac{d^2 \left(P_c V^{4/3}\right)}{dV^2}.
\]  

(6)

Generalized formula for \(\gamma\). All three equations (4), (5) and (6) can be combined into one

\[
\gamma = -\frac{V}{2} \frac{d^2 \left(P_c V^{2m/3}\right)}{dV^2} + \frac{m - 2}{3},
\]  

(7)

which at \(m = 0\) turns into Eq. (4), for \(m = 1\) into Eq. (5), and for \(m = 2\) into Eq. (6).

At atmospheric pressure (taken as \(P = 0\)) all expressions for the Grüneisen ratio depend solely on \(B'_T\) \((dB_T/dP)\) at \(P = 0\).

\[
\gamma_S = \frac{1}{2} B'_T - \frac{1}{6}, \quad \gamma_{DM} = \frac{1}{2} B'_T - \frac{1}{2}, \quad \gamma_{VZ} = \frac{1}{2} B'_T - \frac{5}{6}.
\]

They give different values for the Grüneisen ratio which are connected to each other by the following relation:

\[
\gamma_{m=0} = \gamma_{m=1} + \frac{1}{3} = \gamma_{m=2} + \frac{2}{3}.
\]

It can be readily seen from Eqs. (4) - (7) that within the framework of these approaches the Grüneisen ratio is a direct function of the chosen cold isotherm, which defines \(P_c\) as a function of \(V\).

Expressions for \(\gamma(V)\), independent of the cold isotherm, the normal isotherm, and the shock Hugoniot are considered in the next section.

2 The Grüneisen ratio in shock physics

There are a plethora of stand-alone expressions for the Grüneisen ratio which predict a varying dependence of \(\gamma\) on volume. Perhaps the most commonly used one is the empirical law

\[
\gamma \rho^q = \text{const},
\]  

(8)

proposed by Anderson [8], where \(q\) is a quantity near unity. In his paper [8] Anderson considers the possible application of Eq. (8) for temperature calculations pertaining to the lower mantle. He points out that a value of \(q\) anywhere in the range \(0.8 < q < 2.2\) is acceptable on the basis of seismic data. Using regression analysis, Anderson shows that the
'\( \gamma \rho^q = \text{const} \)' approximation is not sensitive to the choice of \( q \) if it is in the above interval. In his opinion this is due to the restricted range of compression, corresponding to the lower mantle. He chooses the simplest function (with \( q = 1 \))

\[
\gamma \rho = \text{const},
\]

and further assumes that

\[
\gamma \rho = \gamma_0 \rho_0.
\]

This expression seems to be the most commonly used in shock physics. As to its validity it is usually stated that Eq.(10) is valid for not very high pressures. Actually, Anderson \cite{8} lays stress on the narrow range of compression, corresponding to the lower mantle, not on the absolute value of the specific pressure.

Many authors \cite{9,10,11} have combined Eq.(10) with the fact that at large compressions the limiting value of \( \gamma \) for all materials is that of the degenerate electron gas \cite{12}, namely \( \frac{2}{3} \), to write down interpolation formulae for the volume variation of \( \gamma \). Some of these are

\[
\gamma = \gamma_0 \rho_0 / \rho + \frac{2}{3}(1 - \rho_0 / \rho),
\]

\[
\gamma = \gamma_0 \rho_0 / \rho + \frac{2}{3}(1 - \rho_0 / \rho)^2,
\]

\[
\gamma = \gamma_0 - a(1 - \rho_0 / \rho).
\]

Al’tshuler et al. \cite{13} have proposed the following expression:

\[
\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty) / \sigma^m,
\]

where \( \gamma_\infty = \frac{2}{3} \) for all elements except alkali elements, for which \( \gamma_\infty = \frac{1}{2} \). In Eqs.\( 11 ) - (14) \( a \) is a material dependent constant, \( \sigma = \rho / \rho_0 \), \( m = \gamma_0 / (\gamma_0 - \gamma_\infty) \), and \( \gamma_0 \) and \( \gamma_\infty \) are the values of \( \gamma \) at ambient conditions and at infinite pressure, respectively. According to the authors of \cite{13} the logarithmic derivative of Eq.(14) is close to the experimental derivative and the asymptotic values \( \gamma_\infty \) correspond to the quantum-statistical Grüneisen coefficients of the crystal lattice under extreme degrees of compression \cite{30}.

Jeanloz \cite{14}, starting from the second Grüneisen ratio,

\[
q = \left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_T,
\]

assumed it to depend on volume only. The particular volume dependence he used is given by

\[
q = q_0 \left( \frac{V}{V_0} \right)^{q'}.
\]

The logarithmic derivative of \( q \),

\[
q' = \frac{d \ln q}{d \ln V},
\]

known as the third Grüneisen ratio, is supposed to be a material-dependent constant.
Then, for the particular volume dependence of $\gamma$, Jeanloz obtained

$$\gamma = \gamma_0 \exp \left\{ \left( \frac{q_0}{q'} \right) \left[ \left( \frac{V}{V_0} \right)^{q'} - 1 \right] \right\}, \quad (18)$$

where $\gamma_0$, $q_0$, and $V_0$ are the values of $\gamma$, $q$, and $V$ at ambient conditions.

Srivastava and Sinha [15] modify Eq. (18) to introduce in it the infinite compression limit of $\gamma$. They assume $\gamma_\infty = (\frac{1}{2})$. For $P \to \infty$, i.e. $V \to 0$, Eq. (18) yields

$$\gamma_\infty = \gamma_0 \exp \left( -\frac{q_0}{q'} \right). \quad (19)$$

Now, following the model of an oscillating lattice of ions in a uniform neutralizing background of electrons, Eq. (19) gives

$$\gamma_0 \exp \left( -\frac{q_0}{q'} \right) = \frac{1}{2},$$

or $q_0/q' = \ln(2\gamma_0)$. Then, Eq. (18) takes the form

$$\gamma = \gamma_0 \exp \left\{ \ln(2\gamma_0) \left[ \left( \frac{V}{V_0} \right)^{q'} - 1 \right] \right\}. \quad (20)$$

This equation satisfies the infinite compression limit for $\gamma$, i.e. at $P \to \infty$ or $V \to 0$, $\gamma = \gamma_\infty = (\frac{1}{2})$.

Other researchers [9-12] have favored for solids $\gamma_\infty = (\frac{2}{3})$ which follows from the degenerate electron gas model. Therefore, Eq. (19) with $\gamma_\infty = (\frac{2}{3})$ should be considered as well. With $(\frac{2}{3})$ as the infinite compression limit in Eq. (18), we have

$$\gamma = \gamma_0 \exp \left\{ \ln \left( \frac{3}{2\gamma_0} \right) \left[ \left( \frac{V}{V_0} \right)^{q'} - 1 \right] \right\}. \quad (21)$$

Here I propose a general form of Eq. (18) which incorporates both Eqs. (20) and (21)

$$\gamma = \gamma_0 \exp \left\{ \ln \left( \frac{\gamma_0}{\gamma_\infty} \right) \left[ \left( \frac{V}{V_0} \right)^{q'} - 1 \right] \right\}. \quad (22)$$

In this equation $\gamma_0$, $\gamma_\infty$, and $q'$ are treated as free parameters and will be determined by regression analysis of the experimental data sets.

Rice has also derived an expression for $\gamma$ [16] based on its thermodynamic definition. He makes two assumptions: first, that the Grüneneisen ratio $\gamma = V(\partial P / \partial E)_V$ is a function of volume only; and second, that the adiabatic bulk modulus $B_S = -V(\partial P / \partial V)_S$ is also a function of volume only. His expression has the form:

$$(V_0/V)\gamma = (\varepsilon + 1/\gamma_0)^{-1}. \quad (23)$$

After some rearrangements we obtain:

$$\gamma = \gamma_0 (1 - \varepsilon)(1 + \gamma_0 \varepsilon)^{-1}. \quad (24)$$
where \( \varepsilon = 1 - \frac{V}{V_0} \) is the dimensionless volume.

Equations (23) and (24) give incorrect value for \( \gamma_\infty \), i.e. '0' and fail to describe adequately any of the datasets used here. That is why they are excluded from further consideration. The results from the calculations and a comparison of the other expressions are presented in the next section. The values of \( \gamma_\infty \), obtained by regression analysis, are given careful consideration there as well.

3 Fitting the expressions for \( \gamma(V) \) to experimental data

The experimental points for the regression analysis of the models (Eqs.(10) - (14), (18), (20) - (22)) are taken from [13, 17, 25–28]. In these papers diverse variables are used for the volume dependence of \( \gamma - \rho/\rho_0, \eta = V/V_0, \varepsilon = 1 - V/V_0 \). In the present work the relative volume \( \varepsilon = 1 - V/V_0 \) is introduced in all models. The original and the transformed expressions are given in Tabl. (1). The constant \( \left( \frac{2}{3} \right) \) in Eqs.(11) and (12) is replaced by \( \gamma_\infty \).

The values of the Grüneisen ratio at ambient conditions \( \gamma_0 \), \( \gamma_\infty \) — the value of \( \gamma \) at \( P \to \infty \), the second and the third Grüneisen ratios \( q \) and \( q' \), and the material constant \( a \) are the parameters to be determined from the best fit of the experimental datasets.

The calculated results are presented in Tabls.(2) - (4) and in Figs(1) - (2) along with the experimental data points for comparison.

From Tabls.(2) - (4) and Figs(1) - (2) we can see that Eqs.(10) - (14), (18), and (20) - (22) are in good agreement with the experimental datasets. In all cases Eqs.(14), (18), and (22) have the highest and practically coinciding coefficients of multiple determination \( R^2 \) and the smallest error in \( \gamma \). The errors in \( \gamma \) for the other expressions are within the range of the experimental errors and the coefficients of multiple determination \( R^2 \) are high enough for the models to be considered adequate.

Equation (10) stands aside in this classification. It has noticeably lower \( R^2 \) and is the worst in all cases except NaCl. The volume variation of \( \gamma \) for NaCl is adequately described by all models, although a slight departure of the '\((\gamma/V) = \text{const}\)' approximation can be observed as \( \varepsilon \) increases (Fig.(2)).

It can be readily seen from Figs(1) and (2) that in all cases Eq.(11) and Eq.(13) completely overlap. This might be explained by the fact that both expressions are represented by a linear model.

The infinite compression limit of \( \gamma \). Four of the considered models — Eqs.(11), (12), (14), and (18) contain \( \gamma_\infty \) (the value of \( \gamma \) at \( P \to \infty \)). It is assumed that at infinite pressure \( (P \to \infty) \) solids become a crystalline one-component plasma, i.e. an oscillating lattice of ions in a uniform neutralizing background of electrons [29, Ch. 17]. A number of theoretical works predict \( \gamma = \frac{1}{2} \) for this limiting state of a solid. Kopyshov [30] calculated \( \gamma(V) \) in the Thomas-Fermi approximation and found \( \gamma = \frac{1}{2} \) as \( P \to \infty \). Various theoretical studies by other authors [31–33] as well as simple dimensional arguments by Hubbard [34, p. 34] also lead to \( \gamma = \frac{1}{2} \) as \( P \to \infty \). Other researchers [12 and references cited therein] consider \( \left( \frac{2}{3} \right) \) a more appropriate value of \( \gamma_\infty \) for solids due to the fact that the linear temperature dependence of the electronic specific heat of the degenerate free electron gas dominates over the phonon contribution when the Debye temperature is increased sufficiently. Al'tshuler et al [13] assume \( \frac{2}{3} \) to be the infinite compression limit of \( \gamma \) for all materials except alkali metals, for which \( \gamma_\infty = \frac{1}{2} \).

Unfortunately, none of the expressions for \( \gamma(V) \), considered in the present work follow either of these constraints at infinite pressure. This can be readily seen from Tabl.(5),
| Reference                | Expressions for $\gamma$ | Eq. |
|-------------------------|--------------------------|-----|
| **Original equations**  |                          |     |
| Anderson [8]            | $\gamma \rho = \gamma_0 \rho_0 = \text{const}$ |     |
| Bennett et al [9]       | $\gamma = \gamma_0 \rho_0 / \rho + (2/3)(1 - \rho_0 / \rho)$ |     |
| Thomson and Lauson [10] | $\gamma = \gamma_0 \rho_0 / \rho + (2/3)(1 - \rho_0 / \rho)^2$ |     |
| Royce [11]              | $\gamma = \gamma_0 - a(1 - \rho_0 / \rho)$ |     |
| Al’tshuler et al [13]   | $\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty) / \sigma^m$, $\sigma = \rho / \rho_0$, $m = \gamma_\infty + (\gamma_0 - \gamma_\infty)(1 - \epsilon)^m$, $m = \gamma_\infty / (\gamma_0 - \gamma_\infty)$ |     |
| Jeanloz [14]            | $\gamma = \gamma_0 \exp \left\{ \left( \frac{\sigma_0}{\sigma_0} \right)^{q'} - 1 \right\}$ |     |
| Srivastava and Sinha [15]| $\gamma = \gamma_0 \exp \left\{ \ln(2\gamma_0) \left[ \left( \frac{\nu}{\nu_0} \right)^{q'} - 1 \right] \right\}$ |     |
| This work               | $\gamma = \gamma_0 \exp \left\{ \ln \left( \frac{3}{2} \gamma_0 \right) \left[ \left( \frac{\nu}{\nu_0} \right)^{q'} - 1 \right] \right\}$ |     |
| This work               | $\gamma = \gamma_0 \exp \left\{ \ln \left( \frac{\gamma_0}{\gamma_\infty} \right) \left[ \left( \frac{\nu}{\nu_0} \right)^{q'} - 1 \right] \right\}$ |     |
| Rice [16]               | $\nu = \frac{\nu_0}{\nu_0} \left[ 1 + \gamma_0 \left( 1 - \frac{\nu}{\nu_0} \right) \right]^{-1}$ |     |

Table 1: Original and transformed expressions for the Grüneisen ratio
Figure 1: Volume dependence of the Grüneisen ratio for Cu, ε-Fe and K
Figure 2: Volume dependence of the Grüneisen ratio for \textit{MgO} and \textit{NaCl}
Table 2: Experimental and calculated values of $\gamma_0$

| $\gamma_0$ | Cu | $\varepsilon$-Fe | K | NaCl | MgO |
|------------|----|------------------|---|------|------|
| Experimental value | 2.0 | 1.71 | 1.27 | 1.62 | 1.539 |
| Anderson [8] | 2.091 | 1.874 | 1.177 | 1.612 | 1.556 |
| Bennett et al [9] | 1.891 | 1.752 | 1.234 | 1.618 | 1.462 |
| Thomson and Lauson [10] | 1.944 | 1.799 | 1.213 | 1.618 | 1.476 |
| Royce [11] | 1.891 | 1.752 | 1.234 | 1.616 | 1.462 |
| Al’tsusher et al [13] | 1.928 | 1.723 | 1.266 | 1.634 | 1.542 |
| Jeanloz [14] | 1.933 | 1.715 | 1.267 | 1.618 | 1.542 |
| Srivastava and Sinha [15] | 1.908 | 1.761 | 1.268 | 1.637 | 1.478 |
| This work | 1.918 | 1.767 | 1.278 | 1.644 | 1.487 |
| This work | 1.933 | 1.745 | 1.267 | 1.620 | 1.542 |

Table 3: Coefficient of multiple determination $R^2$ and error in $\gamma$ [%] for Cu, $\varepsilon$-Fe, and K

| Equations | Cu | $\varepsilon$-Fe | K |
|-----------|----|------------------|---|
|           | $R^2$ | Error in $\gamma_0$ [%] | $R^2$ | Error in $\gamma_0$ [%] | $R^2$ | Error in $\gamma_0$ [%] |
| Al’tshuler et al [13] | 0.964 | 1.611 | 0.999 | 0.766 | 0.997 | 0.336 |
| Bennett et al [9] | 0.957 | 3.505 | 0.991 | 2.482 | 0.982 | 2.842 |
| Thomson and Lauson [10] | 0.963 | 0.828 | 0.969 | 5.226 | 0.969 | 4.453 |
| Royce [11] | 0.957 | 3.505 | 0.991 | 2.482 | 0.982 | 2.842 |
| Anderson [8] | 0.670 | 6.667 | 0.852 | 9.562 | 0.945 | 7.299 |
| Jeanloz [14] | 0.966 | 5.634 | 0.999 | 0.342 | 0.998 | 1.067 |
| Srivastava and Sinha [15] | 0.962 | 5.437 | 0.984 | 1.828 | 0.998 | 0.972 |
| This work | 0.964 | 5.263 | 0.979 | 2.126 | 0.988 | 2.259 |
| This work | 0.966 | 5.634 | 0.994 | 1.162 | 0.998 | 1.067 |
Table 4: Coefficient of multiple determination $R^2$ and error in $\gamma$ [%] for NaCl and MgO

| Equations          | NaCl | MgO |
|--------------------|-----|-----|
|                    | $R^2$ | Error in $\gamma$ [%] | $R^2$ | Error in $\gamma$ [%] |
| Al’tshuler et al [13] | 0.999 | 0.12 | 0.995 | 0.21 |
| Bennett et al [9] | 0.999 | 0.14 | 0.84 | 4.99 |
| Thomson and Lau-son [10] | 0.999 | 0.26 | 0.927 | 4.07 |
| Royce [11] | 0.999 | 0.14 | 0.84 | 4.99 |
| Anderson [8] | 0.999 | 0.5 | 0.598 | 1.13 |
| Jeanloz [14] | 0.999 | 0.423 | 0.994 | 1.922 |
| Srivastava and Sinha [15] | 0.996 | 1.378 | 0.861 | 7.562 |
| This work | 0.992 | 1.916 | 0.879 | 7.059 |
| This work | 0.999 | 0.438 | 0.994 | 1.922 |

Table 5: Calculated values of $\gamma_\infty$

| $\gamma_\infty$ | Cu | $\varepsilon$-Fe | K | NaCl | MgO |
|------------------|----|------------------|---|------|-----|
| Bennett et al [9] | 0.525 | 0.387 | -0.219 | -3.119 | 0.444 |
| Thomson and Lau-son [10] | 1.001 | 0.838 | -0.504 | -0.085 | 1.321 |
| Al’tshuler et al [13] | 0.936 | -8.423 | 0.552 | -1.511 | 1.105 |
| This work | 0.858 | $2.0 \times 10^{-4}$ | 0.474 | $3.1 \times 10^{-7}$ | 1.1 |
where there are given the values of $\gamma_\infty$, obtained by regression analysis. There are several exceptions. Equation (11), proposed by Bennet et al. [9] predicts for Cu and MgO values of $\gamma_\infty$ near $\frac{1}{2}$. Equation (14), proposed by Al’tshuler et al. [13] and Eq.(22) (this work) predict for K values of $\gamma_\infty$ close to $\frac{1}{2}$.

Srivastava and Sinha in their paper [15] have noticed that an infinite compression limit may be obtained from Eq.(18), i.e. Eq.(19). The values of $\gamma_\infty$, calculated from Eq.(19) are also far from theoretical predictions.

4 Conclusions

The most frequently used self-contained expressions for the volume dependence of the Grüneisen ratio have been considered in the present work and compared to available experimental data for Cu, Ė-Fe, K, MgO, and NaCl.

All expressions predict with very good accuracy values for $\gamma$ at ambient conditions. The $\gamma_0 = \text{const}$ approximation fails at higher compressions. The expressions proposed by Bennet et al. [9] and by Royce [11] are equivalent. The model proposed by Jeanloz [14], its modification in the present work, and the expression of Al’tshuler et al. [13] are the best fits to the experimental data sets. In the author’s opinion preference should be given to Jeanloz’s model (and its modification, proposed here) because it is based on physical assumptions, whilst the expression of Al’tshuler et al is just an interpolation formula. In view of its possible application to deriving a complete EOS for solids from their response to shock-wave loading Eq.(22) is more convenient to use than Eq.(15) because it contains $\gamma_\infty$ instead of $q_0$, which is not frequently used in shock physics.

With a few exceptions, none of the models, considered here, predict correct values for $\gamma_\infty$. According to Young [29, Ch. 17] matter approaches its infinite compression state when $\rho/\rho_0 \sim 10$, or, in terms of relative volume $\varepsilon \sim 0.9$. If we accept this criterion, we could say that the experimental data sets, used in this work are nearer to the origin of the pressure axis than to $P \to \infty$. In the case of Ė-Fe [25] at $P = 359.5$ GPa (the highest pressure in the experiments considered here) $\rho/\rho_0 = 1.684$. That is why the predictions for $\gamma_\infty$ from the regression analysis are not good. In the author’s opinion the values for Cu and MgO, obtained from the expression of Bennet et al. (Eq.(11)) are sooner random results than correctly predicted values. The case of K is somewhat different. It has a very small bulk modulus $- 3.09$ GPa [27], i.e. very large compressibility. It is reasonable to accept that the applied pressure drives it nearer to the maximum compression state than the same pressure, applied to the other materials considered here. Also, the values near ($\frac{1}{2}$) are predicted by two of the equations, having the highest coefficient of multiple determination.

It is obvious that experiments at higher pressures are necessary to determine more reliably the infinite compression limit of $\gamma$. Computer simulations easily surmount the limitations of laboratory experiments. They could be used to clarify the ability of the considered models to predict the infinite compression limit of $\gamma$.

These inferences trace out a possible line for continuation of the present research. A regression analysis of results from computer simulations, using the models, considered here, might give more reliable values of $\gamma_\infty$.

This work was partially presented at the Seventh scientific conference with international participation "SPACE, ECOLOGY, SAFETY", 29 November – 1 December 2011, Sofia, Bulgaria.


References

[1] Girifalco, L.A. *Statistical mechanics of solids*, Oxford University Press: New York, 2000.
[2] Anderson, O. L. *Equations of state of solids for geophysics and ceramic science*, Oxford University Press: New York, 1995.
[3] Vocadlo L., J.P. Poirer, and G.D. Price, "Grüneisen parameters and isothermal equations of state" *Am. Mineral.*, 85(2), 390–395 (2000).
[4] Knopoff L. and J. N. Shapiro, "Comments on the Interrelationships between Grüneisen’s Parameter and Shock and Isothermal Equations of State", *J.Geophys.Res.*, 74, 1439-1450 (1969).
[5] Anderson O. L., "The Grüneisen ratio for the last 30 years", *Geophys. J. Int.*, 143, 279-294 (2000).
[6] Peng X., L. Xing, and Zh. Fang, "Comparing research on the pressure or volume dependence of Grüneisen parameter", *Physica B*, 394, 111-114 (2007).
[7] Holzapfel, W. B., Hartwig, M., and Sievers, W. "Equations of state for Cu, Ag, and Au for wide ranges in temperature and pressure up to 500 GPa and above", *J. Phys. Chem. Ref. Data*, 30 (2), 515-530, (2001).
[8] Altshuler L.V., S.E. Brusnikin, and E.A. Kuzmenkov, "Isotherms and Grüneisen Functions for 25 Metals", *Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki*, 1987, No. 1, pp. 134-146. (English trans., *Journal of Applied Mechanics and Technical Physics*, Vol. 28, No. 1, 1987, pp. 129-141)
[9] Jeanloz, R., "Shock wave equation of state and finite strain theory", *J.Geophys.Res.*, 94(B5), 5873-5886 (1989).
[10] Royce E. *Lawrence Livermore Laboratory report UCRL 51121* (1971).
[11] Srivastava S.K. and P. Sinha, "Analysis of volume dependence of Grüneisen ratio", *Physica B*, 404, 4316-4320 (2009).
[12] Rice, M.H., “Pressure-volume relations for the alkali metals from shock-wave measurements”, *J. Phys. Chem. Solids*, 26, 483-492, (1965).
[13] Slater J.C., "Note on Grüneisen's Constant for the Incompressible Metals", *Phys.Rev. 57*, 744-746 (1940).
[22] Dugdale J. S. and D. K. C. Macdonald, “The Thermal Expansion of Solids”, Phys. Rev. 89(4), 832-834 (1953).

[23] Rice M. H., R. G. McQueen, and J. M. Walsh, “Compression of Solids by Strong Shock Waves”, Sol. St. Phys. 6, 1-63 (1958).

[24] Vaschenko V.Y. and V.N. Zubarev, "Concerning the Grüneisen constant", Sov. Phys. Sol. St. 5, 653-655 (1963).

[25] Anderson, O. L., L. Dubrovinsky, S. K. Saxena, and T. LeBihan, "Experimental vibrational Grüneisen ratio values for ε-iron up to 330 GPa at 300 K", Geophys. Res. Lett., 28(2), 399-402 (2001).

[26] Anderson, O. L., L. Dubrovinsky, S. K. Saxena, and T. LeBihan, Correction to "Experimental vibrational Grüneisen ratio values for ε-iron up to 330 GPa at 300 K", Geophys. Res. Lett., 28(12), 2359 (2001).

[27] Boehler R., "Melting temperature, adiabats, and Grüneisen parameter of lithium, sodium and potassium versus pressure", Phys. Rev. B 27, 6754 (1983).

[28] Anderson O. L., H. Oda, A. Chopelas, and D. G. Isaak, "A thermodynamic theory of the Grüneisen ratio at extreme conditions: MgO as an example", Phys. Chem. Min, 19(6), 369-380 (1993).

[29] Young, D. A. Phase diagrams of the elements. University of California Press: Berkeley, 1991.

[30] Kopyshev, V. P. "Konstanta Gryunajzena v priblizhenii Tomasa – Fermi", Dokl. AN SSSR, 161(5), 1067-1068, (1965). [in Russian]

[31] Holt, A. C., and Ross, M. "Calculations of the Grüneisen parameter for some models of the solid", Phys. Rev. B, 1(6), 2700, (1970).

[32] Ross, M. "Matter under extreme conditions of temperature and pressure", Rep. Progr. Phys., 48 (1), 1, (1985).

[33] Nagara, H., and Nakamura, T. "Theory of lattice-dynamical properties of compressed solids", Phys. Rev. B, 31 (4), 1844, (1985).

[34] Hubbard, W. B. Planetary interiors. Van Nostrand Reinhold Co: New York, 1984, 343 p.