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VOLUME DEPENDENCE OF THE GRÜNEISEN RATIO FOR EQUATION-OF-STATE STUDIES. PHENOMENOLOGICAL EXPRESSIONS

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Abstract: *This work presents an analysis of the existing self-contained expressions for the volume dependence of the Grüneisen ratio* γ *in view of their further application to EOS (equation of state) studies. Phenomenological expressions for* γ *are assessed and applied to materials with the major types of chemical bonds. Interpolation formulas were considered in a previous work of the author (Gospodinov, 2011). Predictions from regression analysis are compared to existing experimental data sets. All expressions predict with very good accuracy the values of* γ *at ambient conditions and its volume variation in the low and intermediate 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. Experiments, performed at higher pressures are necessary to clarify the ability of the assessed models to predict the infinite compression limit of* γ *. The equation, proposed by Jeanloz (1989) is the best fit to experimental data. A modification to this 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.*

ВЛИЯНИЕ НА ОБЕМНАТА ЗАВИСИМОСТ НА ПАРАМЕТЪРА НА ГРЮНАЙЗЕН ВЪРХУ УРАВНЕНИЕТО НА СЪСТОЯНИЕТО. ФЕНОМЕНОЛОГИЧНИ ИЗРАЗИ

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Резюме: *В настоящата работа са анализирани известните феноменологични изрази за зависимостта на параметъра на Грюнайзен γ от обема. Това е направено с оглед на тяхното използване за получаване на пълното уравнение на състоянието (УС) на твърди тела по реакцията им при взривноимпулсно въздействие. Тези изрази са приложени към материали с основните видове химична връзка. Резултатите, получени чрез регресионен анализ са сравнени със съществуващите експериментални резултати. Всички изрази описват с много добра точност стойностите на γ при атмосферни условия и изменението му в експериментално изследвания диапазон от налягания. Нито едно от разгледаните уравнения не предсказва правилно стойността на γ при P→∞. Веeоятна причина за това е, че всички експерименти са проведени при сравнително ниски налягания. Уравнението предложено от Jeanloz (1989) описва най-добре експерименталните резултати. В настоящата работа е предложена модификация на това уравнение, по-подходяща за приложение във физиката на ударните вълни. Тя може да се използва заедно със ударната адиабата за получаване на пълното УС на твърди тела по реакцията им при взривноимпулсно въздействие.*

Introduction

To determine the functional dependence of the Grüneisen ratio on volume is a key problem in shock physics. 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 differentiation.

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 the volume dependence of γ together with the shock Hugoniot. That is why it is important to obtain the form of γ independently of the shock Hugoniot or of an isotherm.

The Grüneisen ratio has both a statistical mechanics (microscopic) and thermodynamic (macroscopic) definition.

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

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

where α 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 γ may be considered the measure of the change of pressure resulting from the increase of internal energy at constant volume. The experimental determination of γ, based on its thermodynamic definition implies the concurrent measurement of the involved thermodynamic properties at high pressures or the experimental determination of the partial derivative in Eq.(2).

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

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

where ν_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

(4) $$\gamma = -\left(\frac{\partial \ln \nu}{\partial \ln V}\right)_T .$$

The experimental determination of the Grüneisen 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 γ have been reported in literature. They predict a varying dependence of γ 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 [2], and by Anderson [3]. Their accuracies are also compared in recent works by X. Peng *et al.* [5] and by Cui and Yu [6]. These papers are in the field of geophysics. It is characteristic of them that there is an intrinsic relationship between the expressions for γ, examined there, and the cold or the normal isotherm. Many of these expressions relate γ at atmospheric pressure ($P = 0$) to the first derivative of the bulk modulus with respect to pressure or volume ($B_{T'}$).

To the author's knowledge, a comparison of the self-contained phenomenological expressions for the Grüneisen 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 γ and analyze and compare them to existing experimental data. It differs from previous approaches [4-6, 8] 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, ε-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.

1. Phenomenological expressions for the Grüneisen ratio

There are several stand-alone expressions for the Grüneisen ratio which predict a varying dependence of γ on volume.

Jeanloz [7], starting from the second Grüneisen ratio,

$$q = \left(\frac{\partial \ln \gamma}{\partial \ln V} \right)_T , \tag{5}$$

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

$$q = q_0 \left(\frac{V}{V_0} \right)^{q'} . \tag{6}$$

The logarithmic derivative of q,

$$q' = \frac{\mathrm{d} \ln q}{\mathrm{d} \ln V}, \tag{7}$$

known as the third Grüneisen ratio, is supposed to be a material-dependent constant.

Then, for the particular volume dependence of γ, Jeanloz obtained

$$\gamma = \gamma_0 exp \left\{ \left(\frac{q_0}{q'} \right) \left[\left(\frac{V}{V_0} \right)^{q'} - 1 \right] \right\}, \tag{8}$$

where γ_0, q_0, and V_0 are the values of γ, q, and V at ambient conditions.

Srivastava and Sinha [8] modify Eq.(8) to introduce in it the infinite compression limit of γ. They assume γ_∞ =(12). For $P \to \infty$, i.e. $V \to 0$, Eq.(8) yields

$$\gamma_\infty = \gamma_0 exp \left(-\frac{q_0}{q'} \right). \tag{9}$$

Now, following the model of an oscillating lattice of ions in a uniform neutralizing background of electrons, Eq.(9) gives

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

or $q_0 / q' = \ln(2\gamma_0)$. Then, Eq.(8) takes the form

$$\gamma = \gamma_0 exp \left\{ \ln(2\gamma_0) \left[\left(\frac{V}{V_0} \right)^{q'} - 1 \right] \right\}. \tag{10}$$

This equation satisfies the infinite compression limit for γ, i.e. at $P \to \infty$ or $V \to 0$, $\gamma = \gamma_\infty$ = (12).

Other researchers [9-12] have favored for solids γ_∞ =(23) which follows from the degenerate electron gas model. Therefore, Eq.(9) with γ_∞ = (23) should be considered as well. With (23) as the infinite compression limit in Eq.(8), we have

$$\gamma = \gamma_0 exp \left\{ \ln \left(\frac{3}{2} \gamma_0 \right) \left[\left(\frac{V}{V_0} \right)^{q'} - 1 \right] \right\}. \tag{11}$$

Here I propose a general form of Eq.(8) which incorporates both Eqs.(10) and (11)

$$\gamma = \gamma_0 exp \left\{ \ln \left(\frac{\gamma_0}{\gamma_\infty} \right) \left[\left(\frac{V}{V_0} \right)^{q'} - 1 \right] \right\}. \tag{12}$$

In this equation γ_0, γ_∞, 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 γ [13] based on its thermodynamic definition. He makes two assumptions: first, that the Grüneisen 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:

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

After some rearrangements we obtain:

(14) $$\gamma = \gamma_0(1-\varepsilon)(1+\gamma_0\varepsilon)^{-1},$$

where $\varepsilon = 1 - V / V_0$ is the dimensionless volume.

Equations (13) and (14) give incorrect value for γ_∞, 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 γ_∞, obtained by regression analysis, are given careful consideration there as well.

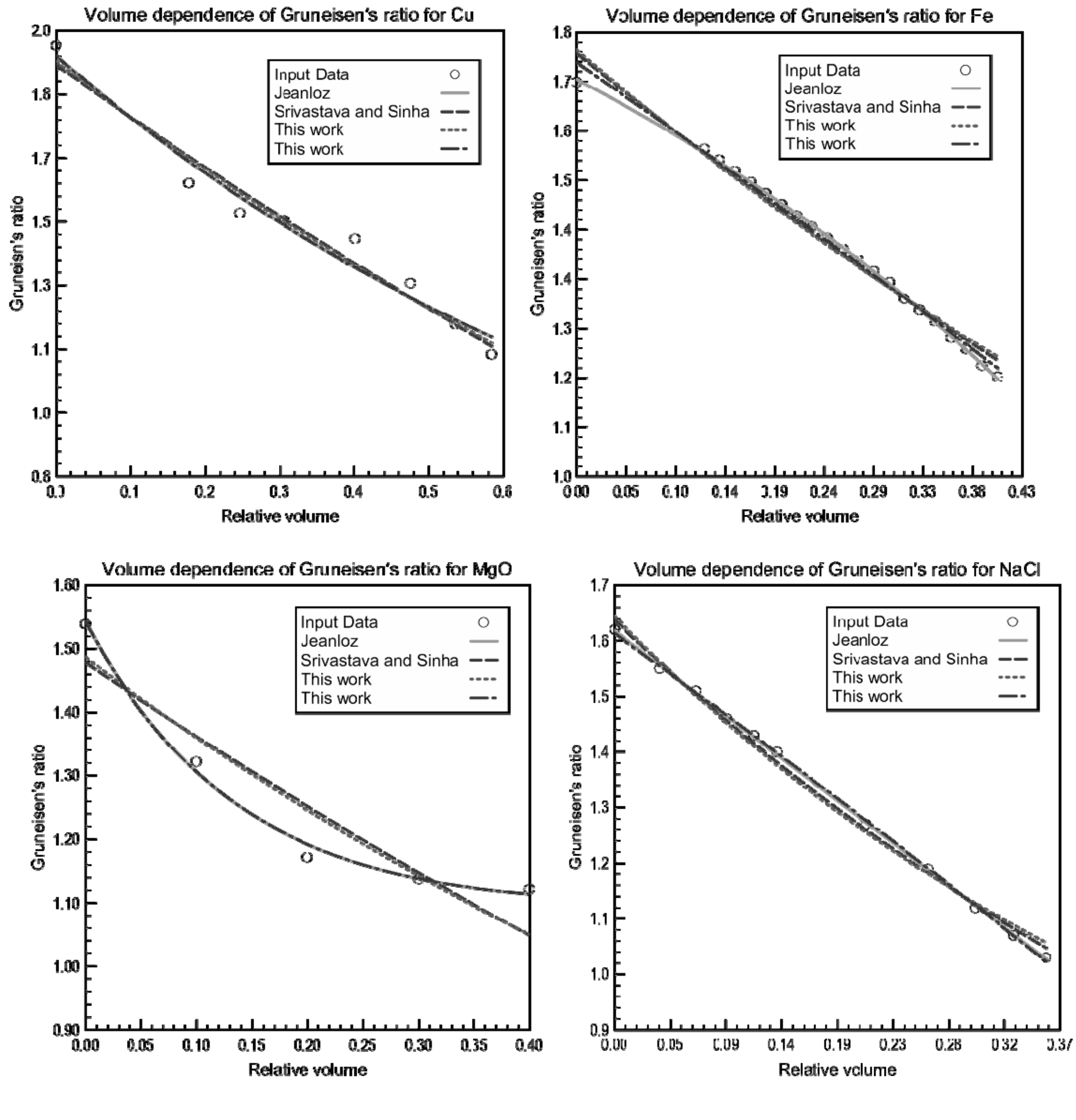

Figure 1. Volume dependence of the Grüneisen ratio for Cu, Fe, MgO and $NaCl$

2. Fitting the expressions for $\gamma(V)$ to experimental data

The experimental points for the regression analysis of the models (Eqs.(8, 10, 11, 12) are taken from [14-19]. In these papers diverse variables are used for the volume dependence of γ --- ρ/ρ_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.

Table 1. Experimental and calculated values of γ_0

γ_0	Cu	ε -Fe	K	NaCl	MgO
Experimental value	2.0	1.71	1.27	1.62	1.539
Jeanloz [7]	1.933	1.715	1.267	1.618	1.542
Srivastava and Sinha [8]	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 2. Coefficient of multiple determination R^2 and error in γ [%] for *Cu*, ε *-Fe*, and *K*

Equations	Cu		ε-Fe		K	
	R^2	Error in γ [%]	R^2	Error in γ [%]	R^2	Error in γ [%]
Jeanloz [8]	0.966	5.634	0.999	0.342	0.998	1.067
Srivastava and Sinha [9]	0.962	5.437	0.984	1.828	0.998	0.972
This work	0.964	5.263	0979	2.126	0.988	2.259
This work	0.966	5.634	0.994	1.162	0.998	1.067

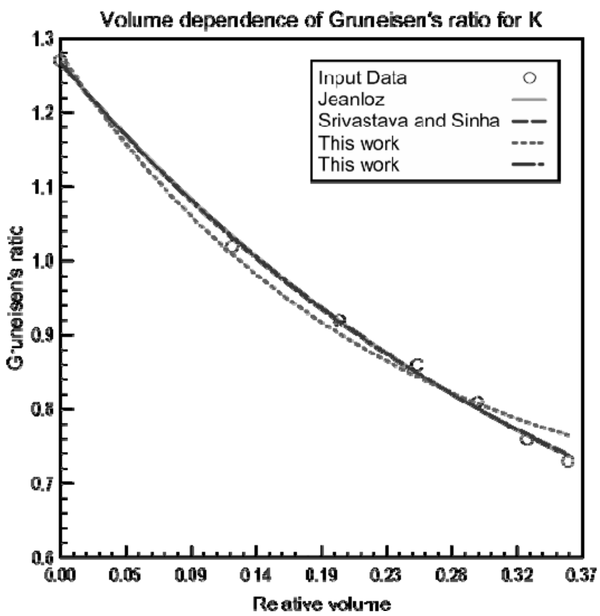

Figure 2. Volume dependence of the Grüneisen ratio for K

Table 3. Coefficient of multiple determination R^2 and error in γ [%] for *NaCl* and *MgO*

Equations	NaCl		MgO	
	R^2	Error in γ [%]	R^2	Error in γ [%]
Jeanloz [7]	0.999	0.423	0.994	1.922
Srivastava and Sinha [8]	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

The value of γ at ambient conditions γ_0, γ_∞ -- the value of γ at $P \to \infty$, the second and the third Grüneisen ratios q and q' are the parameters to be determined from the best fit of the experimental datasets.

The calculated results are presented in Tabls.(1) - (3) and in Figs.(1) - (2) along with the experimental data points for comparison.

From Tabls.(1) - (3) and Figs.(1) - (2) we can see that Eqs.((8) and (10) - (12) are in good agreement with the experimental datasets. In all cases Eqs. (8) and (12) have the highest and practically coinciding coefficients of multiple determination R^2 and the smallest error in γ. The errors in γ 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.

3. The infinite compression limit of γ

One of the considered models --- Eq. (12) contains γ_∞ (the value of γ 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 [20, Ch.~17]. A number of theoretical works predict γ = 1/2 for this limiting state of a solid. Kopyshev [21] calculated $\gamma(V)$ in the Thomas-Fermi approximation and found γ = 1/2 as $P \to \infty$. Various theoretical studies by other authors [22-24] as well as simple dimensional arguments by Hubbard [25, p.~34] also lead to γ = 1/2 as $P \to \infty$. Other researchers [12, and references cited therein] consider (2/3) a more appropriate value of γ_∞ 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* [14] assume 2/3 to be the infinite compression limit of γ for all materials except alkali metals, for which γ_∞=1/2.

Unfortunately, none of the expressions for $\gamma(V)$, considered in the present work follow either of these constraints at infinite pressure. Values for γ_∞, obtained by regression analysis from Eq.(12) are far from (1/2) or (2/3). The values of γ_∞, calculated from Eq.(9) 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, ε-Fe, K, MgO, and $NaCl$.

All expressions predict with very good accuracy values for γ at ambient conditions and its volume variation in the low and intermediate pressure region, but fail to give correct values for its infinite compression limit. The model proposed by Jeanloz [7] and its modification in the present work are the best fits to the experimental data sets. In view of its possible application to deriving a complete EOS for solids from their response to shock-wave loading Eq.(12) is more convenient to use than Eq.(8) because it contains γ_∞ instead of q_0, which is not frequently used in shock physics.

None of the models, considered here, predict correct values for γ_∞. According to Young [20, Ch.17] matter approaches its infinite compression state when ρ / ρ_0 : 10, or, in terms of relative volume $\varepsilon :$ 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 ε-Fe [16] at $P = 359.5GPa$ (the highest pressure in the experiments considered here) $\rho / \rho_0 = 1.684$. That is why the predictions for γ_∞ from the regression analysis are not good.

It is obvious that experiments at higher pressures are necessary to determine more reliably the infinite compression limit of γ. 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 γ.

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 elucidate their ability to predict γ_∞.

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