

COMPARING RESEARCH ON THE VOLUME DEPENDENCE OF THE GRÜNEISEN RATIO WITH REGARD TO ITS USE IN SHOCK PHYSICS

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Abstract: To determine the functional dependence of the Grüneisen ratio on volume is a key problem in dynamic high-pressure physics. This dependence is of crucial importance for the construction of a complete equation of state (EOS) for solids from shock-wave data. The inaccuracies that semiempirical formulas for γ might contain affect the determination of the zero isotherm. The high-temperature corrections to the EOS at high pressures are affected even to a greater extent. In order to obtain the complete EOS from shock-wave data it is necessary to choose the form of γ independently of the shock adiabat. There are several standalone formulations of the Grüneisen ratio in use in shock physics which predict a varying dependence of γ as a function of volume (or pressure). In the present paper these formulations are assessed and applied to substances with diverse chemical bonds. The theoretical predictions are compared with experimental results. The equation, proposed by Al'tshuler et al fits best experimental results. It could be used in the construction of a complete EOS for solids from shock-wave data.

СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА УРАВНЕНИЯТА ЗА ОБЕМНАТА ЗАВИСИМОСТ НА ПАРАМЕТЪРА НА ГРЮНАЙЗЕН, ИЗПОЛЗВАНИ ВЪВ ФИЗИКАТА НА ВЗРИВНИТЕ ПРОЦЕСИ

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Резюме: Определянето на функционалната зависимост на параметъра на Грюнайзен γ от обема е един от основните проблеми на физиката на високите динамични налягания. Тази зависимост е от решаващо значение за получаване на пълното уравнение на състоянието на твърди тела по резултати от динамични експерименти. Неточностите, които се съдържат в полумпиричните изрази за γ оказват влияние при определяне на нулевата изотерма. Това влияние е още по-голямо при високотемпературните поправки към уравнението на състоянието. За да се получи пълното уравнение на състоянието по резултати от динамични експерименти е нужен израз за γ , който не зависи от ударната адиабата. Във физиката на високите динамични налягания съществуват няколко такива формулировки. В настоящата работа те са приложени към материали с различна химична връзка и получените резултати са сравнени с наличните експериментални данни. Извършеният регресионен анализ показва, че уравнението на Алтшулер най-добре описва експерименталните резултати. То би могло да се използва при получаването на пълното уравнение на състоянието на твърди тела по резултати от динамични експерименти.

1. Introduction

To determine the functional dependence of the Grüneisen ratio on volume is a key problem in shock physics. This dependence is of crucial importance for the construction of a complete equation of state (EOS) for solids from shock wave experiments. The Grüneisen ratio has both a microscopic and a macroscopic definition. The former relates it to the vibrational frequencies of the atoms in the crystal lattice of a material

$$(1) \quad \gamma_i = -\frac{V}{v_i} \left(\frac{\partial v_i}{\partial V} \right)_T = -\left(\frac{\partial \ln v_i}{\partial \ln V} \right)_T.$$

The volume dependence of all lattice vibrational frequencies is assumed one and the same [1], so

$$(2) \quad \gamma = -\left(\frac{\partial \ln \nu}{\partial \ln V} \right)_T.$$

The latter represents it in terms of several well-known thermodynamic properties - specific heat, thermal expansion, and bulk modulus

$$(3) \quad \gamma = V \left(\frac{\partial P}{\partial E} \right)_V = \frac{\alpha V B_T}{C_V} = \frac{\alpha V B_S}{C_P}.$$

The experimental determination of the Grüneisen ratio, based on its macroscopic definition implies the concurrent measurement of these thermodynamic properties at high pressures. Such experiments have been performed by Birch [2].

The experimental determination of the Grüneisen ratio from its microscopic definition is extremely difficult, since it requires a detailed knowledge of the phonon dispersion spectrum of a material [3].

Because of the scarce experimental results and the lack of first-principle analytic equation, numerous approximate expressions have been reported in literature. Most of them are analyzed in two extensive reviews - by Knopoff and Shapiro [4], and by Anderson [5]. Their accuracies are also compared in a recent work by X. Peng *et al.* [6] and by Srivastava and Sinha [7]. All of these papers are in the field of geophysics. The expressions for the Grüneisen ratio treated in them are derived from diverse isotherms $P_T = P_T(V)$ and are used to justify them.

The relationship which is experimentally determined in shock physics is the shock Hugoniot. It is the lokus of all states in the (P, V, E) space that can be reached by single shock waves with different amplitudes starting from one and the same initial state. Here P is the pressure, V --- the volume, and E --- the internal energy.

A single shock Hugoniot is not enough to derive an EOS. One more independently derived relation is necessary. In the case of solids such relation could be the volume dependence of the Grüneisen ratio $\gamma = \gamma(V)$. Possible inaccuracies that semiempirical formulas for γ might contain affect the determination of the zero isotherm. The high-temperature corrections to the EOS at high pressures are affected even to a greater extent.

In order to obtain a complete EOS from shock wave experiments it is important to choose the form of γ independently of the shock adiabat. There are several formulations of the Grüneisen ratio in use in shock physics which predict a varying dependence of γ as a function of volume.

It has been observed from shock wave analyses that for small compressions, γ is nearly inversely proportional to density (i.e. $\gamma_0 \rho_0 = \gamma \rho = const$). Theoretical arguments in support of this approximation are given by Anderson [9]. Many authors have combined this result with the fact that at large compressions, the limiting value of γ for all materials is $\frac{2}{3}$ to write down interpolation formulas for the volume variation of γ . Some of these are

$$(4) \quad \gamma = \gamma_0 \rho_0 / \rho + \gamma_\infty (1 - \rho_0 / \rho), \text{ [Bennet et al,1978]}$$

$$(5) \quad \gamma = \gamma_0 \rho_0 / \rho + \gamma_\infty (1 - \rho_0 / \rho)^2, \text{ [Thomson and Lauson,1972]}$$

$$(6) \quad \gamma = \gamma_0 - a(1 - \rho_0 / \rho), \text{ [Royce,1971]}$$

$$(7) \quad \gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty) / \sigma^m, \text{ [Altshuler et al,1987]}$$

where a is a material dependent constant, $\sigma = \rho / \rho_0$, and $m = \gamma_0 / (\gamma_0 - \gamma_\infty)$.

In the present work the validity of Eqs.(4) - (7) together with the standard approximation $\gamma_0 \rho_0 = \gamma \rho = const.$ have been tested against available experimental results for copper, iron, potassium, sodium chloride, and magnesium oxide. It differs from previous approaches [6-8] in that the definitions of γ assessed and applied to substances with diverse chemical bonds are those most frequently used in shock physics. Predictions from regression analysis are compared to experimental results. The relation that best fits experimental data may be used in the construction of a complete EOS for solids from shock wave experiments.

2. Calculation results

The experimental points for the regression analysis of the four models (Eqs. (4) - (7)) and the standard approximation are taken from Refs. [2, 13-17]. Since in these papers the dependencies of γ on the relative volume $\varepsilon = 1 - V/V_0$ are experimentally determined this variable is introduced in the present work. The standard approximation and Eqs. (4) - (7) take the form

$$(8) \quad \gamma = \gamma_0(1 - \varepsilon),$$

$$(9) \quad \gamma = \gamma_0(1 - \varepsilon) + \gamma_\infty \varepsilon,$$

$$(10) \quad \gamma = \gamma_0(1 - \varepsilon) + \gamma_\infty \varepsilon^2,$$

$$(11) \quad \gamma = \gamma_0 - a\varepsilon,$$

$$(12) \quad \gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)(1 - \varepsilon)^m, m = \gamma_0 / (\gamma_0 - \gamma_\infty).$$

The value of the Grüneisen ratio at ambient conditions γ_0 and γ_∞ (the value of γ at $P \rightarrow \infty$) are treated as the parameters to be determined from the best fit of the experimental points. The fitted quantities for Eq.(11) are γ_0 and the material dependent constant a .

The calculated results are presented in Tables (1) - (3) and Figs. (1), (2) and (3) along with the experimental data [2,13-17] for comparison. Figs. (1) - (3) show the curves for the volume dependence of the Grüneisen ratio for the three metals, sodium chloride and magnesium oxide.

Table 1: Coefficient of multiple determination R^2 and error in γ_0 [%] for Cu, Fe, and K.

Metals →	Cu		Fe		K	
Equations ↓	R^2	Error in γ_0 [%]	R^2	Error in γ_0 [%]	R^2	Error in γ_0 [%]
Al'tshuler et al	0.964	1.611	0.999	0.766	0.997	0.336
LANL	0.957	3.505	0.991	2.482	0.982	2.842
Sandia Labs	0.963	0.828	0.969	5.226	0.969	4.453
LLNL	0.957	3.505	0.991	2.482	0.982	2.842
Std. appx.	0.670	6.667	0.852	9.562	0.945	7.299

From Tables (1) - (3) and Figs. (1) - (3), we can see that Eqs. (9) - (12) are all in good agreement with the experimental data. In all cases Eq. (12) has the highest coefficient of multiple determination R^2 and the smallest error in γ_0 . The errors in γ_0 for Eqs.(9) - (11) 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. The common approximation (Eq.(8)) is the worst in all cases except sodium chloride. The volume variation of the Grüneisen ratio for *NaCl* is adequately described by all models, although a slight departure of the ' $(\gamma/V) = const.$ ' approximation from the other curves can be observed as ε increases.

Table 2: Coefficient of multiple determination R^2 and error in γ_0 [%] for NaCl and MgO .

Compounds →	NaCl		MgO	
Equations ↓	R^2	Error in γ_0 [%]	R^2	Error in γ_0 [%]
Altshuler <i>et al</i>	0.999	0.12	0.995	0.21
LANL	0.999	0.14	0.84	4.99
Sandia Labs	0.999	0.26	0.927	4.07
LLNL	0.999	0.14	0.84	4.99
Std. appx.	0.999	0.5	0.598	1.13

It can be readily seen from Figs.(1), (2) and (3) that in all cases Eq.(9) and Eq.(11) completely overlap. This is explained by the fact that both equations are represented by a linear model. If we write Eq.(9) in the form

$$(13) \quad \gamma = \gamma_0 - (\gamma_0 - \gamma_\infty) \varepsilon$$

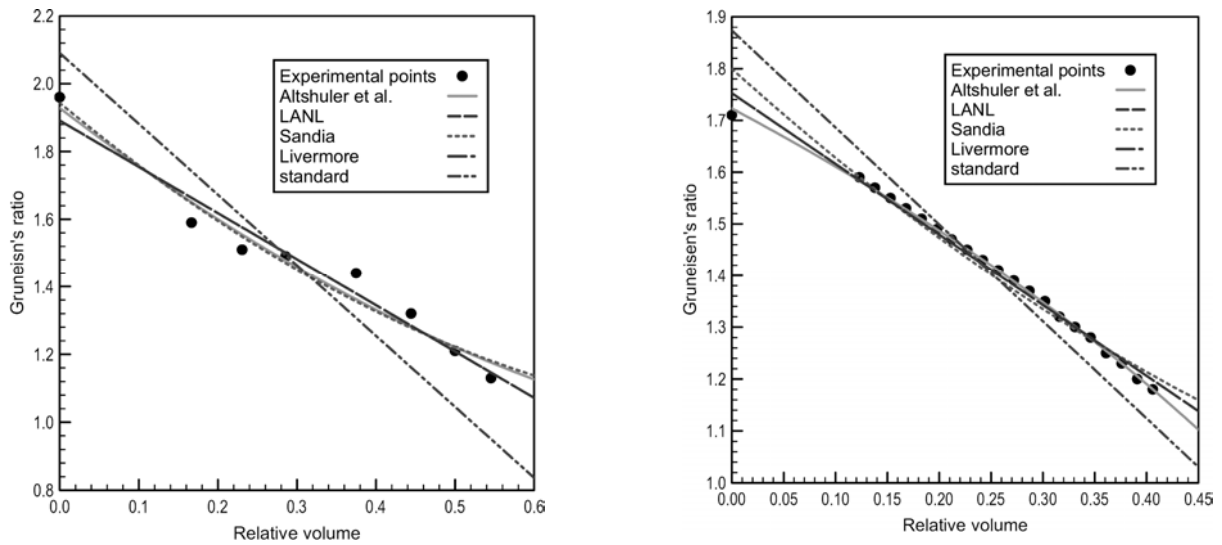


Fig. 1. Volume dependence of the Grüneisen ratio for Cu and Fe

Table 3: Values of γ_∞ for all substances, considered in this paper.

γ_∞	Cu	Fe	K	NaCl	MgO
LANL	0.525	0.387	-0.219	-3.119	0.444
Sandia	1.001	0.838	-0.504	-0.085	1.321
Altshuler <i>et al</i>	0.936	-8.423	0.552	-1.511	1.105

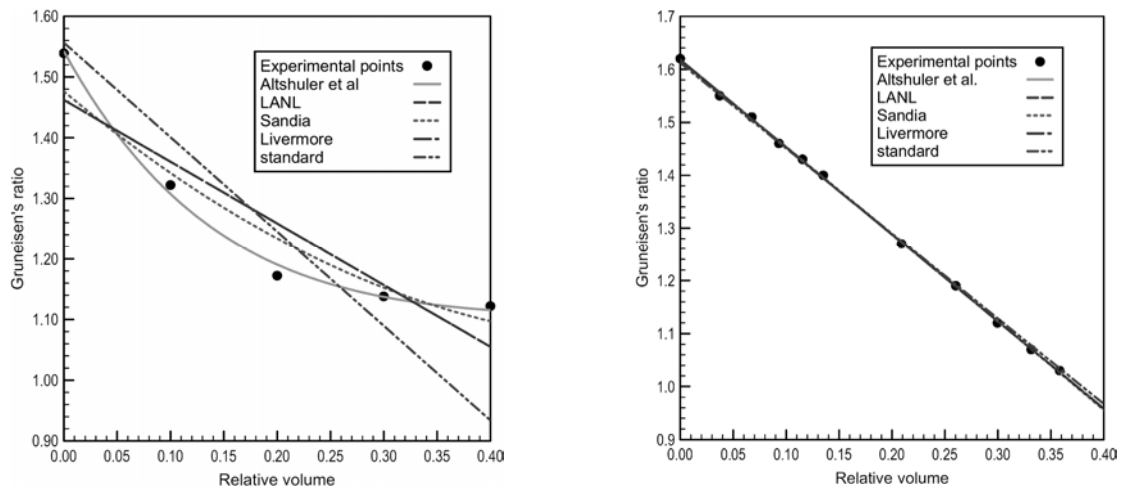


Fig. 2. Volume dependence of the Grüneisen ratio for MgO and NaCl

we can see that Eq.(9) and Eq.(11) will coincide if we assume $a = \gamma_0 - \gamma_\infty$. This assumption is confirmed by the regression analysis.

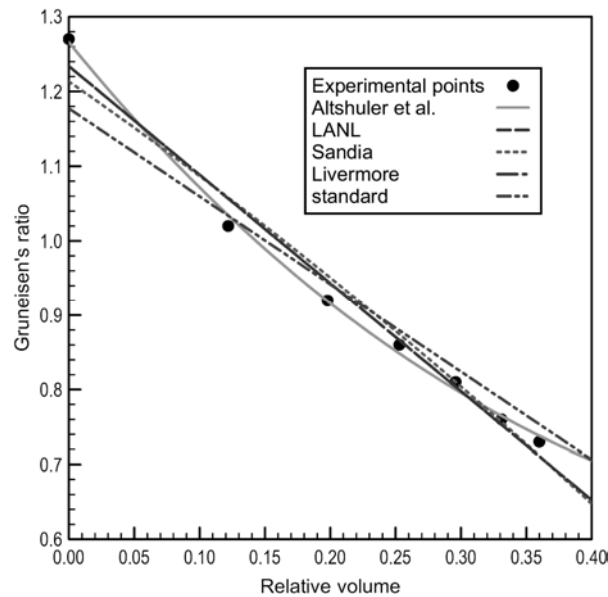


Fig. 3. Volume dependence of the Grüneisen ratio for K

Three of the considered models - Eqs.(9), (10), and (12) contain γ_∞ (the value of γ at $P \rightarrow \infty$). As pressures tend towards infinity, the values of the Grüneisen ratio tend to $\frac{2}{3}$ according to the model of Fermi's free electron gas, and tend to $\frac{1}{2}$ on the basis of the theory of an oscillating lattice of ions in a uniform neutralizing background of electrons. Al'tshuler *et al.* [13] assume $\frac{2}{3}$ to be the high pressure limit of γ for all materials except alkali elements, for which $\gamma_\infty = \frac{1}{2}$. It can be noted that the results for γ_∞ predicted from Eqs.(9), (10), and (12) are far from $\frac{2}{3}$ or $\frac{1}{2}$ (Table (3)).

3. Conclusions

The most frequently used in shock physics equations for the volume dependence of the Grüneisen ratio have been tested in the present work against available experimental data for Cu, Fe, MgO and $NaCl$. The model, proposed by Al'tshuler *et al.* [13] is found to be superior to all other equations. All equations with the exception of the common approximation, i.e. Eq.(8), predict with good accuracy values of γ at ambient conditions. The ' $\gamma/V = const.$ ' model fails at higher compressions. The models, proposed by Bennet *et al.* [10] and by Royce [12] seem to be equivalent. None of the models gives correct predictions for the high pressure limit of γ .

The equation of Al'tshuler *et al.* [13] could be used in the construction of a complete EOS for solids from shock wave experiments at moderate pressures. If an expression for γ , valid in a wider range of pressures is needed, more research in the field is necessary. This could be a possible line for the continuation of the present work.

References:

1. Grüneisen, E., in: *Handbuch der Physik*, ed. H.Greiger and K.Scheel. Springer, Berlin, 1926, vol.10, p.1.
2. Birch, F., "Equation of State and Thermodynamic Parameters of NaCl to 300 kbar in the High-Temperature Domain", *J.Geophys.Res.*, 91, 4949-4954 (1986).
3. Vaccaro, L., J.P. Poirer, and G.D. Price, "Grüneisen parameters and isothermal equations of state" *Am. Mineral.*, 85(2), 390-395 (2000).
4. Knoppoff, 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. A n d e r s o n, O. L., "The Grüneisen ratio for the last 30 years", *Geophys. J. Int.*, 143, 279-294 (2000).
6. P e n g, X., L. X i n g, and Zh. F a n g, "Comparing research on the pressure or volume dependence of Grüneisen parameter", *Physica B*, 394, 111-114 (2007).
7. S r i v a s t a v a, S.K. and P. S i n h a, "Analysis of volume dependence of Grüneisen ratio", *Physica B*, 404, 4316-4320 (2009).
8. G u a n g - l e i C u l and R u i - l a n Y u, "Volume and pressure dependence of the Grüneisen parameter γ for solids at high temperature", *Physica B*, 390, 220-224 (2007).
9. A n d e r s o n, O. L., "Evidence Supporting the Approximation $\gamma\rho = const$ for the Grüneisen parameter of the Earth's Lower Mantle", *J.Geophys.Res.*, 84, 3537-3542 (1979).
10. B e n n e t, B.I., J.D. J o h n s o n, G.I. K e r l e y, and G.T. R o o t, *Los Alamos Scientific Laboratory report LA--7130* (1978).
11. T h o m s o n, S.L. and H.S. L a u s o n, *Sandia Corporation report SC-RR-710714* (1972).
12. R o y c e, E. *Lawrence Livermore Laboratory report UCRL 51121* (1971).
13. A l t s h u l e r, L.V., S.E. B r u s n i k i n, and E.A. K u z m e n k o v, "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)
14. A n d e r s o n, O. L., L. D u b r o v i n s k y, S. K. S a x e n a, and T. L e B i h a n, "Experimental vibrational Grüneisen ratio values for ϵ -iron up to 330 GPa at 300 K", *Geophys. Res. Lett.*, 28(2), 399-402 (2001).
15. A n d e r s o n, O. L., L. D u b r o v i n s k y, S. K. S a x e n a, and T. L e B i h a n, Correction to "Experimental vibrational Grüneisen ratio values for ϵ -iron up to 330 GPa at 300 K", *Geophys. Res. Lett.*, 28(12), 2359 (2001).
16. B o e h l e r, R., "Melting temperature, adiabats, and Grüneisen parameter of lithium, sodium and potassium versus pressure", *Phys. Rev. B* 27, 6754 (1983).
17. A n d e r s o n, O. L., H. O d a, A. C h o p e l a s, and D. G. I s a a k, "A thermodynamic theory of the Grüneisen ratio at extreme conditions: MgO as an example", *Phys.Chem.Min*, 19(6), 369-380 (1993).