Grüneisen function and the zero-temperature isotherm of three metals up to pressures of 10 TPa

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A generalized form of the Grüneisen function for condensed media has been proposed. The function found, together with Slater's relation, makes it possible to write expressions for the pressure and energy on the zero-temperature isotherm in the form of polynomials in powers of the compression. It has been demonstrated in the example of metals that the analytical relations derived are in qualitative and quantitative agreement with the widely accepted results at both small (of the order of gigapascals) and large (of the order of terapascals) pressures. © *1995 American Institute of Physics.*

It is well known (see, for example, Ref. 1) that determination of the dependence of the Grüneisen parameter γ on the volume V is one of the central problems in writing the equation of state of a solid. This problem has been the subject of a large number of studies, particularly studies which relied on the laws of shock-wave compression,[2-4] in which the Grüneisen parameter was measured with at least a twofold change in the volume of the solid. However, in this case the dependence of γ on V could be specified only in tabular form. At the same time, a general analytic expression of the Grüneisen parameter as a function of the volume, which holds true over a broad range of compressions, can be revealed on the basis of the laws of shock-wave propagation in monolithic materials at different initial temperatures.

Now we shall establish the form of the Grüneisen function $\gamma(V)$. Let a material with a volume expansion coefficient β obey a Mie–Grüneisen equation of state in the form $P - P_x = (E - E_x)\gamma/V$, where P and E are the pressure and the specific internal energy, P_x and E_x are the same quantities on the zero-temperature isotherm at a volume V, and $\gamma = \gamma(V)$ is the Grüneisen parameter, which is a function of only the volume V. We consider the relation between two shock adiabats of this material at different initial temperatures.

Let the shock adiabat P_1^H for the initial values V_0 and T_0 of the specific volume and the temperature be known (see curve *1* in Fig. 1). Then the shock adiabat for the same material with an initial specific volume $V_1 = V_0[1 + \beta(T_1 - T_0)]$ and an initial temperature T_1 will be specified by curve 2, along which the pressure equals

$$P_2^H = \frac{P_1^H(1 - 0.5\,\eta_1 V_0 \gamma/V) + (E_2^0 - E_1^0)\gamma/V}{1 - 0.5\,\eta_2 V_1 \gamma/V}, \qquad (1)$$

where $\eta_1 = 1 - V/V_0$, $\eta_2 = 1 - V/V_1$, and E_1^0 and E_2^0 are the initial values of the internal energy of the material at the points (T_0, V_0) and (T_0, V_1), respectively. The derivation of Eq. (1) and its form are similar to those for the shock adiabat of a metastable phase of quartz in Ref. 5.

We note that at the point $\eta = \eta_m = 1 - V_1/V_0 = -\beta(T_1 - T_0)$ (i.e., at $V = V_1$, see Fig. 1) the value of the pressure on shock adiabat *1* has a certain magnitude P_m^H,

while the value of P_2^H at this point is equal to zero. Let the shock adiabat for a material with an initial temperature T_0 be assigned in the form of a linear relation between the shock-wave velocity D and the mass velocity u, i.e., $D = C_0 + S_0 u$, where C_0 and S_0 are constants. Then the value of P_m^H is specified as

$$P_m^H = \frac{C_0^2 \eta_m}{V_0(1 - S_0 \eta_m)^2}.$$

Taking this into account and setting the numerator in (1) equal to zero, we obtain an expression for $\gamma(\eta_m)$:

$$\gamma(\eta_m) = \frac{1 - \eta_m}{\eta_m/2 - (E_2^0 - E_1^0)(1 - S_0\eta_m)^2/C_0^2 - \eta_m}. \qquad (2)$$

Now let T_1 differ slightly from T_0, i.e., let $T_1 \cong T_0$. In this case the amplitudes of the shock waves P_m^H are small. However, it is a well known fact that shock waves of small amplitude propagate with the (adiabatic) velocity of sound C.[6] This may formally signify that at low pressures the coefficient S_0 in the relation $D = C_0 + S_0 u$ decreases, vanishing in the limit of acoustic waves, and that the shock-wave velocity together with the coefficient C_0 tends to the velocity of sound C. On this basis, without distinguishing between the longitudinal and transverse velocities of sound, we assume that at small η_m in (2) $S_0 = 0$ and $C_0 = C$.

We note that in (2)

$$E_2^0 - E_1^0 = -P_{x0}(V_1 - V_0) + C_V(T_1 - T_0),$$

where

$$P_{x0} = P_x(V_0, T_0) = -\left(\frac{\partial E_x}{\partial V}\right)_T,$$

$$C_V = C_V(V_0, T_0) = -\left(\frac{\partial E_t}{\partial T}\right)_V$$

E_t is the thermal energy. For metals $C_V = C_{Vl} + C_{Ve}$, i.e., it is the sum of the lattice (C_{Vl}) and electronic (C_{Ve}) contributions. Taking into account the assumptions made and assuming that V_1 is the variable V, we write (2) at small η_m (i.e., at small deviations V from V_0) in the form
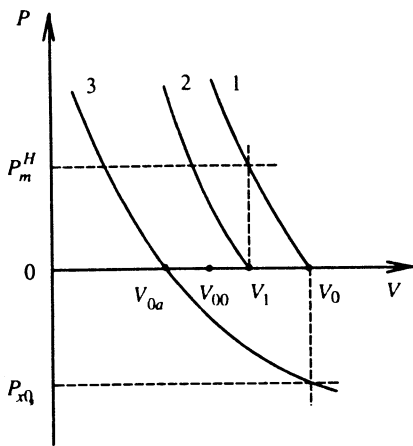
FIG. 1. Schematic arrangement of the shock adiabats of the same material at different initial temperatures, viz., T_0 (curve 1) and T_1 (curve 2), and the zero-temperature isotherm (curve 3); P is the pressure, V is the specific volume, V_0 is the specific volume under normal initial conditions, V_{00} is the specific volume at $T=0$ K increased due to the zero-point vibrations, and V_{0a} is the specific volume of the unstretched material at $T=0$ K.

FIG. 2. Dependence of the Grüneisen parameter on the volume calculated from Eq. (4) for copper and lead under normal initial conditions (1) and from the analytical fitting equation in Ref. 8 (2), as well as data from Ref. 7 (3) and Ref. 9 (4).

$$\gamma(V,V_0,T_0) = -\frac{2(V/V_0)}{V/V_0 - (1+2/\gamma_0 - 2P_{x0}/K_0)}. \qquad (3)$$

The notation $\gamma_0 = \beta C^2/C_V$ and the adiabatic bulk compressibility modulus $K_0 = C^2/V_0$ under the initial conditions (V_0, T_0) have been introduced in (3).

We next assume that the functional form (3) for γ is valid not only at small $\eta = 1 - V/V_0$ comparable with the thermal expansion, but also at values of V which are achieved, for example, in powerful shock waves. However, as is widely known (see, for example, Refs. 1 and 6), in the limit of strong compressions the Grüneisen parameter should tend to a value of 2/3. Equation (3) does not satisfy this requirement: when $V=0$, it gives a zero value for γ. Therefore, we "correct" relation (3) so that it would have the correct asymptote in the limit of large compressions. For this purpose, we add 2/3 to the right-hand side of (3). At the same time, in order for this equation to also remain valid under the initial conditions, we subtract 2/3 from the value of γ_0 in the denominator, i.e., we "force" (3) into the form

$$\gamma(V,V_0,T_0) = -\frac{2(V/V_0)}{V/V_0 - a} + \frac{2}{3}, \qquad (4)$$

where $a = 1 + 2/(\gamma_0 - 2/3) - 2P_{x0}/K_0$.

Relation (4) is the dependence sought of the Grüneisen parameter on the volume.

We note that Eq. (4), the basis equation for the present work, contains only general fundamental characteristics of the material and, therefore, claims to provide general results for condensed media. However, the final conclusion (4) is, of course, still heuristic; therefore, its value and validity will be determined by how and in what ranges of the thermodynamic variables it characterizes experimental data. As will be shown below in the case of metals, in this sense relation (4) provides satisfactory results.
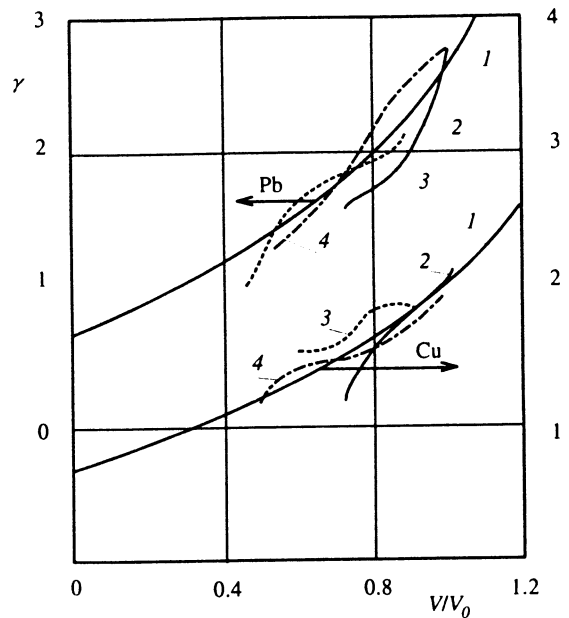
Let us discuss the reasonableness of Eq. (4) and its corollaries in comparison with the results of other investigations. We henceforth restrict ourselves to the range of volumes smaller than aV_{0a}.

The plot of function (4) has the form of a curve (see Fig. 2), near which the plots of the dependence of the Grüneisen parameter on the volume obtained in Refs. 7–9 for $0.5 < V/V_0 < 1$ cluster. The difference between the results of the calculation based on Eq. (4) and those obtained in Refs. 7–9, for example, for copper and lead, does not exceed 10%. Function (4) also gives acceptable results when the zero-temperature isotherm of a solid is calculated. For example, setting (4) at a zero initial temperature equal to Slater's relation[10] and integrating the equality obtained

$$-\frac{2}{3} - \frac{x}{2}\frac{\partial^2 P_x/\partial x^2}{\partial P_x/\partial x} = -\frac{2x}{x-a} + \frac{2}{3} \qquad (5)$$

in the region $x < a$ under appropriate initial conditions, we can find expressions for the pressure $P_x(x)$ and then for the energy $E_x(x)$ along the zero-temperature isotherm:

$$P_x(x) = -K_{00}g[F(x) - F(X_0)] - P_{t0}, \qquad (6)$$

$$E_x(x) = V_{0a}K_{00}g[H(x) - H(X_{0a}) - F(X_0)(x - X_{0a})]$$
$$+ V_{0a}P_{t0}(x - X_{0a}), \qquad (7)$$

where

$$F(x)=3\left(-\frac{1}{5}\,a^4x^{-5/3}+2a^3x^{-2/3}+6a^2x^{1/3}-ax^{4/3}\right.$$

$$\left.+\frac{1}{7}x^{7/3}\right),$$

$$H(x)=9\left(\frac{1}{10}\,a^4x^{-2/3}+2a^3x^{1/3}+\frac{3}{2}\,a^2x^{4/3}-\frac{1}{7}\,ax^{7/3}\right.$$

$$\left.+\frac{1}{70}x^{10/3}\right),$$

$X_0=V_0/V_{0a}$, $X_{0a}=V_{0a}/V_{0a}$, V_0 is the specific volume under normal conditions,

$$g=X_{00}^{5/3}/(X_{00}-a)^4,\qquad X_{00}=V_{00}/V_{0a},$$

the specific volume V_{00} and the bulk compressibility modulus K_{00} are taken at $T=0$ and atmospheric pressure, and $P_{t0}=-P_{x0}$ is the sum of the theoretically calculated (see, for example, Ref. 1) thermal lattice and electronic pressures at atmospheric pressure and room temperature T_0.

In (5)–(7) the notation x has been adopted for the relative specific volume $x=V/V_{0a}$, where V is the current volume and V_{0a} is the volume at which the pressure on the zero-temperature isotherm equals zero (see Fig. 1). Accordingly, the value of a is specified by the expression $a=1+2/(\gamma_{0a}-2/3)$, where, in accordance with (4), γ_{0a} is the isothermal Grüneisen parameter under the conditions $V=V_{0a}$ and $T=0$, since at absolute zero the isentrope is simultaneously the isotherm and P_{x0} equals zero.

The practical use of relations (6) and (7) requires knowledge of only one quantity, viz., V_{0a}, since the value of a can then be found as the root of the equation $P_x(1)=0$, which is obtained as a result of setting the pressure on the zero-temperature isotherm (6) equal to zero at the value of the specific volume $V=V_{0a}$.

Let us discuss one of the possible approaches for finding V_{0a}. The experimentally determined volume V_{00} exceeds V_{0a} due to the expansion of the crystal lattice caused by the zero-point vibrations. As we know, an approximate estimate of this effect is given by the formula (see, for example, Ref. 11) $V_{0a}=V_{00}(1-P_{n0}/K_{00})$, where P_{n0} is the pressure of the zero-point vibrations at $T=0$ K. However, in view of the fact that the expression for V_{0a} is approximate, as well as the fact that errors are possible in the experimental value of V_{00}, for V_{00} we shall use $V_{00}=V_{0k}/s$, where V_{0k} is the published value of the specific volume at zero temperature and atmospheric pressure and $1/s$ is a correction factor, which must be selected so as to most accurately describe the experimental data.

We illustrate the effectiveness of Eqs. (6) and (7). For this purpose, we utilize the values of s and the other parameters appearing in (6) and (7) which are presented in Table I for aluminum, copper, and lead.

Figure 3 shows the zero-temperature isotherm $P_x(V/V_0)$ for aluminum, which was calculated from Eq. (6) with the values of the correction factor $s=1.0$ (curve 1) and $s=0.999923$ (curve 2), as well as the zero-temperature isotherm (curve 3) obtained on the basis of treatment of the shock-wave experiments in Ref. 7. Figure 3 reveals that good

Parameter	Al	Pb	Cu
s	0.999923	0.999575	1.0006576
ρ_{0k}, g/cm^3	2.765	11.586	9.019
ρ_{0a}, g/cm^3	2.789414	11.609162	9.075238
ρ_0, g/cm^3	2.73	11.34	8.93
γ_{0a}	1.798175	2.583821	2.421139
K_{00}, GPa	88.0	48.77	142.0
K_0, GPa	76.3	44.7	137.1
P_{t0}, GPa	1.8809	1.087	2.2616
β, 10^{-6} K^{-1}	69.9	85.5	50.1
β_0, 10^{-10} kJ/g·K^2	500	144.8	113.3
A_V	26.98	207.2	63.546

agreement with the experimental data can be achieved by adjusting s or, equivalently, by adjusting V_{0a}, since curves 2 and 3 nearly coincide. At the same time, Fig. 3 indicates that for pressures greater than 4 GPa the value of V_{0a} must be determined with an accuracy at least of the order of thousandths of a percent.

The next figure (Fig. 4) compares the zero-temperature isotherms of copper and aluminum calculated from Eq. (6) up to $V/V_0=0.4$ with the results of various investigators. It is seen that the results of the present work are in good agreement with the widely accepted results in Refs. 7, 8, and 12 for copper and aluminum when Eq. (6) is used with the parameters in Table I. Similar agreement is observed for lead. Figure 4 also shows that the calculation of the zero-temperature isotherm of aluminum using Eq. (6) is in agree-
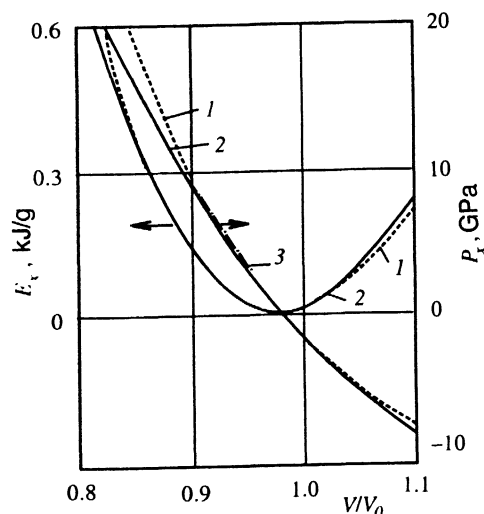

FIG. 3. Influence of the correction factor s on the course of the zero-temperature isotherm $P_x(x)$ and the potential energy $E_x(x)$, where $x=V/V_0$. Dashed curves 1—$s=1.0$; solid curves 2—$s=0.999923$; dot-dashed curve 3—zero-temperature isotherm of aluminum from Ref. 7.
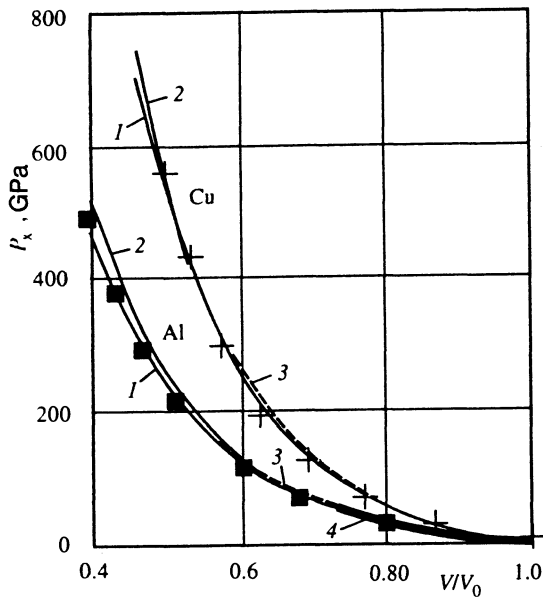
FIG. 4. Zero-temperature isotherms of P_x for copper and aluminum up to $V/V_0=0.4$: 1) calculation using Eq. (6); 2) calculation using polynomials from Ref. 13; 3) data from Ref. 7; 4) data from Ref. 8+—data from Ref. 12 for copper, ■—theoretical data for aluminum from Ref. 14.

ment with the theoretical calculations in Ref. 13 and with the recent calculation of this curve in Ref. 14 for the range of pressures considered in Fig. 4.

As for higher pressures, similar calculations using Eq. (6) give curves which smoothly join the zero-temperature isotherms presented in Refs. 15–18 for the metals under consideration at 3–10 TPa. This is seen in Fig. 5(a), in which the data from the present work, for example, for copper, nearly coincide with the results in Ref. 15, and the data for aluminum nearly coincide with the results in Ref. 17 up to 10 TPa. The plots of Eq. (6) for copper coincide with the results in Ref. 18 up to 2 TPa; in this case the similarity not only of the functions, but also of their derivatives should be noted. The same situation is also observed for the relative arrangement of the zero-temperature isotherms calculated from Eq. (6) and the results in Ref. 16 for lead. A significant deviation of the results of the calculation using (6), as well as of the data in Refs. 15 and 18, is observed only for copper when a com-

parison is made with the zero-temperature isotherms of this metal from Refs. 16 and 17.

According to an opinion held among specialists, the correctness of the calculations in Ref. 16 at large compressions is not questionable. Therefore, taking the results in Ref. 16 as a reliable criterion, we can discuss to what extent the zero-temperature isotherms calculated from (6) differ from the results obtained in Ref. 16 [see Fig. 5(b)].

Figure 5(b) reveals that the calculation of zero-temperature isotherms using Eq. (6) at pressures exceeding 10 TPa yields results which are in qualitative agreement with the calculations based on the Thomas–Fermi model with the corrections in Ref. 16. In fact, the plots of Eq. (6) [Fig. 5(b)] have the same form and relative positions as do the plots constructed on the basis of the data in Ref. 16. However, at pressures above 10 TPa Eq. (6) gives values of the pressure which are smaller than those in Ref. 16. For example, at a density of 1500 g/cm^3 the calculations using (6) give pressures for Al which are three times smaller, pressures for Cu which are four times smaller, and pressures for Pb which are 11 times smaller than the values in Ref. 16. Thus, an upper limit for the proposed zero-temperature isotherms can be specified on the basis of this figure. Although this limit is different for each metal, it is fairly high, i.e., at the level of pressures of the order of 10 TPa.

In conclusion, we give a graphic interpretation of the function $\gamma(V/V_0)$ according to (4). For this purpose, we note that the first term on the right-hand side of (4) is the sum of a decreasing infinite geometric progression with the common ratio x/a under the condition $x<a$, where $x=V/V_0$. Therefore, for $x<a$ Eq. (4) can be represented identically as

$$\gamma(x,T_0) = \frac{2}{3} + 2\left[\frac{x}{a} + \left(\frac{x}{a}\right)^2 + \left(\frac{x}{a}\right)^3 + \left(\frac{x}{a}\right)^4 + \ldots\right], \qquad (8)$$

i.e., the functional dependence of the Grüneisen parameter on the volume found is the infinite power series (8) in powers of the relative specific volume x normalized to a. Thus, Eqs. (4) or (8) is a generalization of the widely used linear approximation of $\gamma(V)$.

Summing up the results of the present for the case of metals, we may state that functions (4) and (6) are qualitatively correct and interpret the forces of elastic interaction in solids up to pressures of the order of 10 TPa with acceptable accuracy.
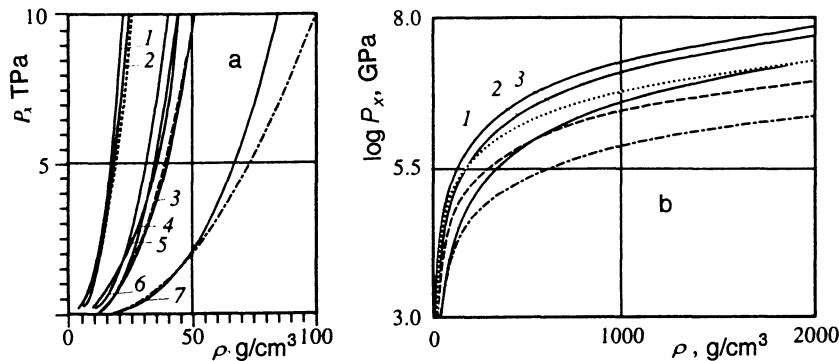

FIG. 5. a) Zero-temperature isotherms of $P_x(\rho)$ (ρ is the density) up to a pressure of 10 TPa for aluminum (1—Ref. 15, 2—Ref. 17) for copper (3—Ref. 15, 4—Ref. 18, 5—Ref. 16, 6—Ref. 17), and for lead (7—Ref. 16); calculations using Eq. (6) for aluminum (dotted line), copper (dashed line), and lead (dot–dashed line). b) Deviation from calculations based on the Thomas–Fermi model with corrections[16] at pressures of the order of 10^4 TPa for Al (1), Cu (2), and Pb (3);[16] calculation using Eq. (6) for Al (dotted line), Cu (dashed line), and Pb (dot–dashed line).

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Translated by P. Shelnitz