DELA-M-72-1334

PHYSICAL REVIEW B VOLUME 6, NUMBER 10 15 NOVEMBER 1972

Application of the Fourth-Order Anharmonic Theory to Shock Waves and the Derivation of the Temperature along the Hugoniot Curves

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(Received 22 May 1972)

The fourth-order anharmonic equation of state combined with the Hugoniot relation is used to describe the thermodynamic response of a solid subject to shock-wave compression. There is a quasiabsolute agreement in volume-ratio range $1 \geq V_H/V_0 \geq 0.8$ for the five materials considered: aluminum, copper, silver, sodium, and periclase. This agreement seems to be independent of the nature and the compressibility of the species. It is possible, therefore, to calculate the temperature along the obtained curves using the fourth-order anharmonic theory. There is a discrepancy of less than 1% between our results and the other published results.

I. INTRODUCTION

It has been shown[1-3] that the fourth-order anharmonic theory leads to the interpretation of the experimental data obtained from shock-wave-compression measurements on materials with cubic crystal structure. The fourth-order anharmonic approximation modifies the Mie–Grüneisen equation of state[4]:

$$P = -\frac{d\phi}{dV} + \gamma \frac{U_s}{V}, \qquad (1)$$

where P, ϕ, γ, U_s, and V are the external pressure, the potential energy of the crystal, Grüneisen's ratio, the vibrational contribution to the internal energy, and the specific volume of the material, respectively.

At the fourth order, the free energy is given by

$$F = \phi(V) + F_s + F^*(T). \qquad (2)$$

Here (i) the potential energy can be expanded into a Taylor series (omitting the terms higher than fourth order) with respect to the components of the Lagrangian strain tensor A. In this case, $\phi(V)$, the potential energy, is given by

$$\phi(V) = \phi' + \frac{V'}{2!} C'_{\alpha\beta} A_\alpha A_\beta + \frac{V'}{3!} C'_{\alpha\beta\tau} A_\alpha A_\beta A_\tau + \frac{V'}{4!} C'_{\alpha\beta\tau\pi} A_\alpha A_\beta A_\tau A_\pi, \qquad (3)$$

using the Voigt notation. The unstrained state is denoted by the primes.

(ii) The vibrational free energy F_s is given by

$$F_s = \textstyle\sum_j \left[\frac{1}{2}\hbar\omega_j + kT \ln(1 - e^{-\hbar\omega_j/kT})\right], \qquad (4)$$

where ω_j are the eigenfrequencies of the solid summed over the j vibrational eigenfrequencies, $\hbar$ is the Planck constant divided by 2π, k is the Boltzmann constant, and T is the absolute temperature.

In the case of the fourth-order approximation, the ω_j are of the second order with respect to the strain components A_{ij}; therefore it is sufficient to expand F_s up to the second order:

$$F_s = F'_s(T) + \left[\left(\frac{\partial F_s}{\partial A_{ij}}\right)_T\right]' A_{ij} + \frac{1}{2!}\left[\left(\frac{\partial^2 F_s}{\partial A_{ij}\,\partial A_{pq}}\right)_T\right]' A_{ij} A_{pq}, \qquad (5)$$

where the derivatives are calculated in the unstrained state.

After Leibfried and Ludwig[4] and Thomsen,[5]

$$\left[\left(\frac{\partial F_s}{\partial A_{ij}}\right)_T\right]' = -\gamma'_{ij} U'_s \qquad (6)$$

and

$$\left[\left(\frac{\partial^2 F_s}{\partial A_{ij}\,\partial A_{pq}}\right)_T\right]' = -\left(\frac{\partial \gamma_{ij}}{\partial A_{pq}}\right)' U'_s + \gamma'_{ij}\,\gamma'_{pq}(U'_s - TC'_v), \qquad (7)$$

where U'_s and C'_v are the internal vibrational energy and specific heat at constant volume of the solid in the unstrained state. Grüneisen's ratio γ_{ij} is defined in its tensorial expression as

$$\gamma_{ij} = -\tfrac{1}{2} F_{ip} \frac{\partial \ln \overline{\omega}^2}{\partial A_{pq}} F_{qj}, \qquad (8)$$

if $A_{ij} = \frac{1}{2}(F_{pi}F_{pj} - \delta_{ij})$ where F is the tensor gradient of the Lagrangian strain coordinates.

In Eqs. (6)–(8), the Grüneisen approximation is applied, which consists of the replacement of the eigenfrequencies ω_j, by their spectral mean $\overline{\omega}$.

(iii) $F^*(T)$ is the anharmonic contribution of the free energy in Eq. (2), depending upon the absolute temperature only.

In the case of cubic crystals, the equation of state is given by $P = -(\partial F/\partial V)_T$ and the Lagrangian strain tensor is spherical [i.e., $A_{ij} = A\delta_{ij}$, where $A = \frac{1}{2}((V/V')^{2/3} - 1)$ and δ_{ij} is the Kronecker δ]. Using Eq. (2), which has been previously detailed, the fourth-order anharmonic equation of state can be written

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$$P(V,T) = -3K'(V/V')^{-1/3}\big(A - \tfrac{3}{2}\Gamma A^2 + \tfrac{3}{2}\Lambda A^3 - (U_s'/V'K')\{\tfrac{1}{3}\gamma' + [\lambda - \gamma'^2(1 - TC_v'/U_s')]A\}\big), \tag{9}$$

where

$$K' = \frac{1}{3^2}\sum_{\alpha,\beta} C'_{\alpha\beta}, \qquad \Gamma = \frac{1}{3^3K'}\sum_{\alpha,\beta,\tau} C'_{\alpha\beta\tau},$$

$$\Lambda = \frac{1}{3^4K'}\sum_{\alpha,\beta,\tau,\pi} C'_{\alpha\beta\tau\pi}, \quad \lambda = \frac{1}{3^2}\sum_{\alpha,\beta}\left(\frac{\partial\gamma_\alpha}{\partial A_\beta}\right)',$$

λ is the strain derivative of Grüneisen's tensor in the unstrained state, and γ' is Grüneisen's ratio in the unstrained state.[5]

The solution, by iteration, of the set of five anharmonic equations[5] gives the constants V', K', γ', Γ, and λ. These are expressed in terms of five experimental data: volume of the zero state, V_0 (the zero state is defined by $P = 0$ and $T = T_0 = 300\,^\circ$K); thermal-expansion coefficient α_0; adiabatic compressibility $K_{0'}^s$; pressure derivative of the isothermal compressibility calculated in the zero state, $(\partial K^T/\partial P)_T|_0$, and temperature derivative of the adiabatic compressibility calculated in the zero state, $(\partial K^S/\partial T)_P|_0$. It has to be emphasized that V', K', γ', Γ, λ, and Λ do not depend on the deformed state. However, Λ depends on the second pressure derivative of the isothermal compressibility calculated in the zero state, $(\partial^2K^T/\partial P^2)_T|_0$, which is not known and cannot be determined experimentally at the present time. To evaluate Λ, the Hugoniot expression[6] might be used. The general form of the Hugoniot equation is

$$U_H - U_0 = \tfrac{1}{2}(P_H + P_0)(V_0 - V_H), \tag{10}$$

where U_0, U_H, V_0, V_H, P_0, and P_H are specific internal energies, volumes, and pressures ahead of and behind the shock wave, respectively. Taking $P_0 = 0$ the Hugoniot equation will be

$$U_H - U_0 = \tfrac{1}{2}P_H(V_0 - V_H). \tag{11}$$

According to the fourth-order anharmonic theory, U_H may be given by

$$U_H = \phi(V_H) + U_s(V_H, T). \tag{12}$$

Substituting (11) and (12) into Eq. (1) we get

$$P_H = -\left.\frac{d\phi}{dV}\right|_H + \gamma(V_H)\left[\tfrac{1}{2}P_H\left(\frac{V_0}{V_H} - 1\right) - \frac{\phi(V_H)}{V_H} + \frac{V_0}{V_H}\right], \tag{13}$$

with

$$-\left.\frac{d\phi}{dV}\right|_H = -3K'\left(\frac{V}{V'}\right)^{-1/3}(A - \tfrac{3}{2}\Gamma A^2 + \tfrac{3}{2}\Lambda A^3).$$

For a cubic crystal one can derive from Eq. (8), using the definitions of γ' and λ given in Eq. (9), that the volume dependence of the Grüneisen parameter γ is given by

$$\gamma(V) = (V/V')^{2/3}(\gamma' + 3\lambda A). \tag{14}$$

At a single Hugoniot point (P_H, V_H) Eq. (13) has only one unknown Λ, which is determined thereby. Knowing Λ, Eq. (13) might be rearranged to give

$$P_4 = \left[-\left.\frac{d\phi}{dV}\right|_H + \gamma(V_H)\left(\frac{U_0 - \phi(V_H)}{V_H}\right)\right] \bigg/ \left[1 - \frac{\gamma(V_H)}{2}\left(\frac{V_0}{V_H} - 1\right)\right]. \tag{15}$$

II. COMPARISON OF HUGONIOT CURVES WITH FOURTH-ORDER CURVES

Using Eq. (15), fourth-order curves H_4 (P_4, V_H locus) have been calculated for five solids,[2] four metals (aluminum, copper, silver, sodium), and one mineral (periclase). The calculated curves compared with the experimental Hugoniot curves[7] are shown in Figs. 1(a)–1(e). It can be seen that for the five materials considered there is practically no difference between the H_4 and the Hugoniot curves in the range of volume ratio of $1 \geq V_H/V_0 \geq 0.825$. Therefore, within these limits, it seems that the agreement between these curves does not depend (a) on the nature of the considered materials (the results are obviously very similar for copper and silver on the one hand, and for periclase on the other hand) or (b) on the compressibility of the considered solid (it is clear that the sodium is more compressible than the other four solids). Finally, a good agreement between theory and experience can be observed in a relatively extended pressure range. For instance, there is a close fit of the curves up to 300 kbar for aluminum and up to 580 kbar for copper and periclase.

III. DETERMINATION OF TEMPERATURE ALONG FOURTH-ORDER CURVES

In the range of agreement between the fourth-order curve and the Hugoniot curve, P_4 satisfies Eq. (1); therefore we have

$$P_H = -\left.\frac{d\phi}{dV}\right|_H + \gamma(V_H)\frac{U_s(V_H, T)}{V_H}. \tag{16}$$

In the right-hand side of the expression, the absolute temperature T figures in U_s only. The internal vibrational energy is given by

$$U_s(T, V_H) = T(U/T)_{\text{Debye}} + \tfrac{9}{8}N_s k\Theta_D, \tag{17}$$

where $3N_s$ is the total number of normal modes, Θ_D is the Debye temperature and $\frac{9}{8}N_s k\Theta_D$ is the limiting expression of $U_s(T, V_H)$ when $T \to 0$.[4] The numerical table of Gray,[8] where $(U/T)_{\text{Debye}}$ vs (Θ_D/T) is given, was used to compute the temperature in the range of agreement of the Hugoniot and H_4 curves. The results of these calculations are shown in Figs. 2(a)–2(e) and are compared with previous data.[6,9]

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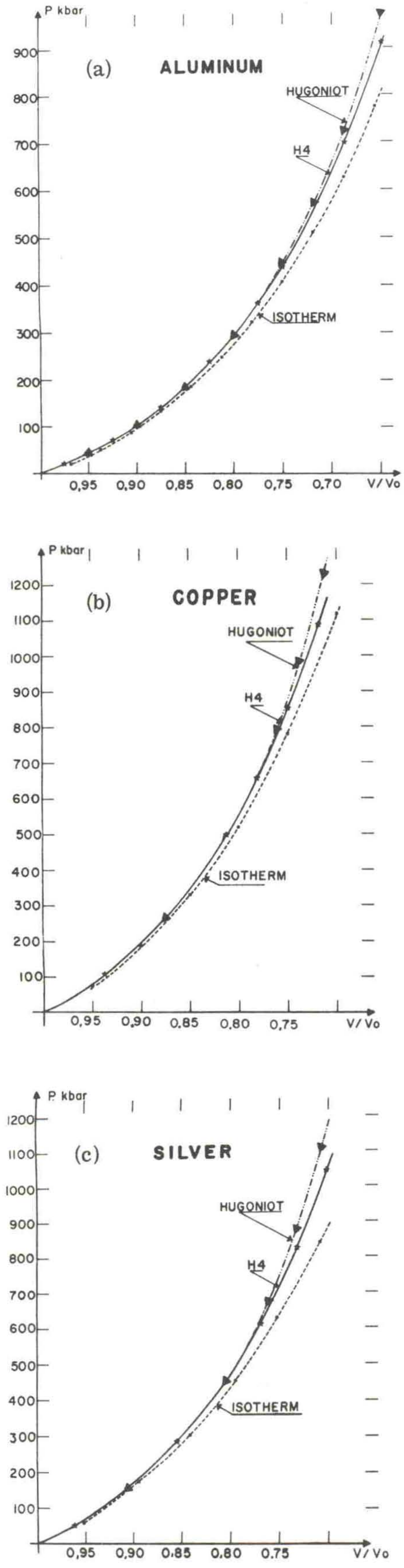
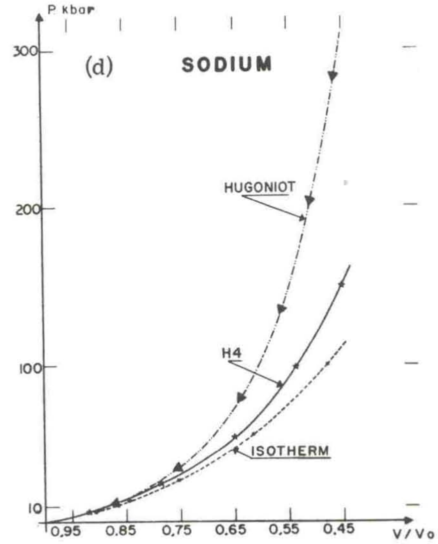




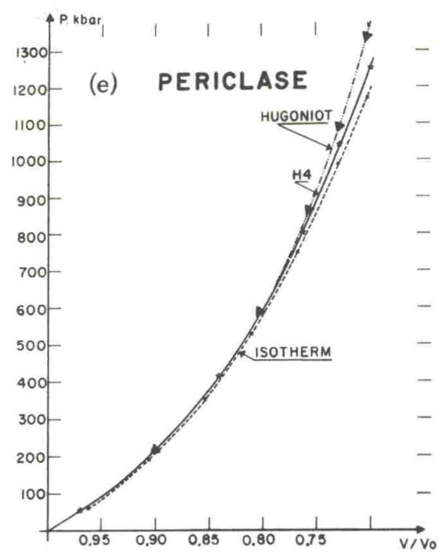
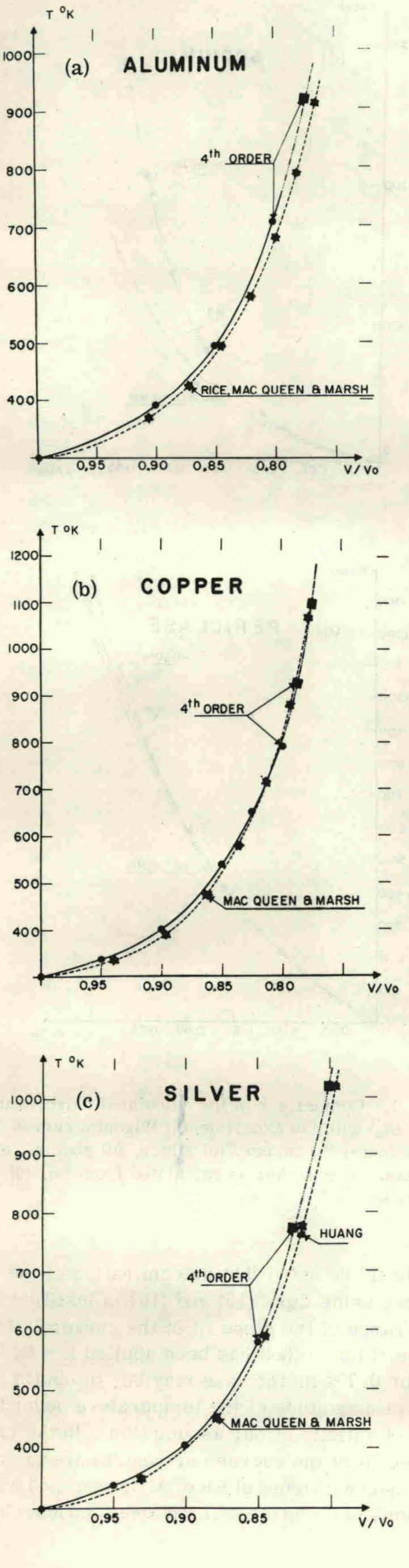


FIG. 1. Comparison of the calculated fourth-order curves (H_4) with the experimental Hugoniot curves for (a) aluminum, (b) copper, (c) silver, (d) sodium, and (e) periclase. The isotherms calculated from Eq. (9) are also shown for $T = 300\,^{\circ}\mathrm{K}$.

It should be noted that determination of the temperature using Eqs. (15) and (16) is justified only in the range of the close fit of the curves. Nevertheless, this method has been applied for $V_H/V_0 = 0.8$ or 0.775 as the case may be, to obtain an order of magnitude of the temperature beyond the range of validity of our assumption. In the range of close fit of the curves our results are in good agreement with those of Rice, McQueen, and Walsh[6] for aluminum, and those of McQueen and Marsh[9] for



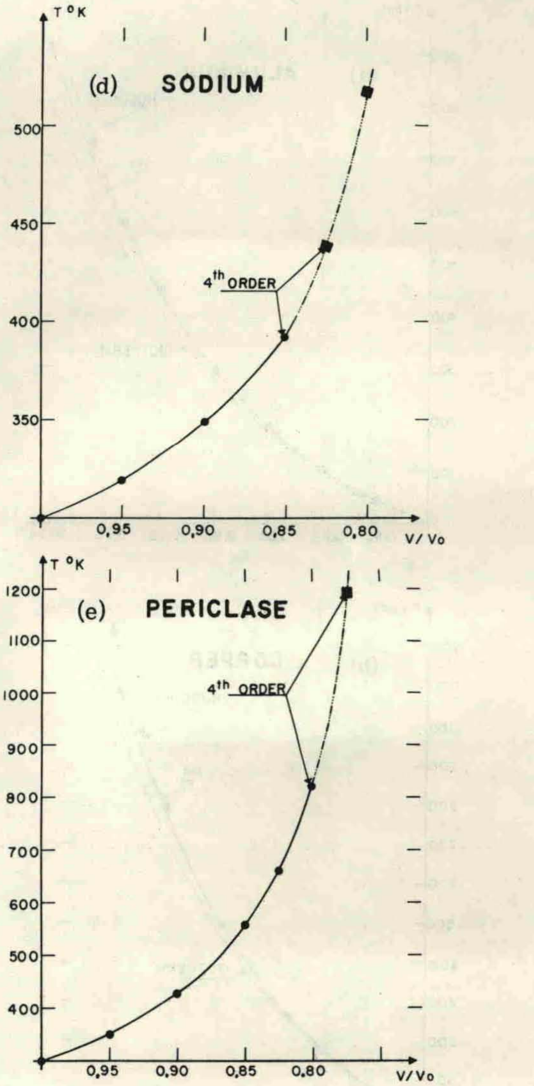


FIG. 2. Comparison of the calculated temperature (fourth-order) curves in the range of agreement of the Hugoniot and H_4 curves with the data determined by Rice, McQueen, and Walsh (Ref. 6) and by McQueen and Marsh (Ref. 9) for (a) aluminum, (b) copper, (c) silver, (d) sodium, and (e) periclase.

copper and silver.

The method of Rice and McQueen[6] consists of drawing adiabats and deriving the temperature at any point neighboring the Hugoniot curve from thermodynamic identities. To explain the slight discrepancy (1%) between our results and those reported in the literature,[6,9] we should note that these authors applied the Mie–Grüneisen expression in the form of

$$P_H = (\gamma / V_H)\,[U_H - U_0(V)]\,, \tag{18}$$

where $U_0(V)$ is the specific internal energy as a function of volume along the particular reference curve defined by $P = 0$. The essential differences between the method of Rice and McQueen and ours, are (a) that they used the Mie–Grüneisen equation (18) without considering the volume dependence of the potential energy while we took it into consideration as it is given by Eq. (3). (b) Furthermore these authors used the Dugdale–McDonald[10] relation to describe the volume dependence of Grüneisen's ratio, introducing additional hypotheses, while we are using the explicit expression given by (14). (c) It should be taken into account that the Mie–Grüneisen equation cannot be used in a large range of volume ratios, but only for $1 \geq V_H/V_0 \geq 0.8$, as it was shown in the Sec. II. In fact, only the assumptions required to develop the fourth-order anharmonic equation of state were used, and this equation has been applied only in its range of validity. Huang[11] studied silver by a method similar to the one of McQueen, using Slater's expression[12] for $\gamma(V)$, giving only a single point of comparison, and this is in agreement with our results.

Unfortunately, there are no elements of comparison for materials such as sodium and periclase which have physical properties very different from the other considered solids and which would have allowed us to formulate a more general conclusion. However, we hope to extend this work to other solids having cubic crystal structure in order to generalize the applicability of the fourth-order anharmonic theory.

ACKNOWLEDGMENT

The authors would like to thank Dr. B. A. Lombos of the George Williams University for helpful discussions concerning this work and for reading the manuscript.

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