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

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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]:

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

where $P$, $\phi$, $\gamma$, $U_s$, 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

$$F = \phi(V) + F_s + F^*(T) . \tag{2}$$

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

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

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

(ii) The vibrational free energy $F_s$ is given by

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

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

In the case of the fourth-order approximation, the $\omega_j$ 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:

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

where the derivatives are calculated in the unstrained state.

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

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

and

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

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 $\gamma_{ij}$ is defined in its tensorial expression as

$$\gamma_{ij} = -\tfrac{1}{2} F_{ip} \frac{\partial \ln \bar{\omega}^2}{\partial A_{pq}} F_{qj} , \tag{8}$$

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 $\omega_j$, by their spectral mean $\bar{\omega}$.

(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 $\delta_{ij}$ is the Kronecker $\delta$]. Using Eq. (2), which has been previously detailed, the fourth-order anharmonic equation of state can be written



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

where

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

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

$\lambda$ is the strain derivative of Grüneisen's tensor in the unstrained state, and $\gamma'$ is Grüneisen's ratio in the unstrained state.[5]

The solution, by iteration, of the set of five anharmonic equations[5] gives the constants $V'$, $K'$, $\gamma'$, $\Gamma$, and $\lambda$. 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 $T = T_0 = 300\,^\circ\mathrm{K}$); thermal-expansion coefficient $\alpha_0$; 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 $V'$, $K'$, $\gamma'$, $\Gamma$, $\lambda$, and $\Lambda$ do not depend on the deformed state. However, $\Lambda$ depends on the second pressure derivative of the isothermal compressibility calculated in the zero state, $(\partial^2 K^T/\partial P^2)_T|_0$, which is not known and cannot be determined experimentally at the present time. To evaluate $\Lambda$, the Hugoniot expression[6] might be used. The general form of the Hugoniot equation is

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

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

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

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

$$U_H = \phi(V_H) + U_s(V_H, T). \quad (12)$$

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

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

with

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

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

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

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

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

## 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

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

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

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

where $3N_s$ is the total number of normal modes, $\Theta_D$ 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 $(\Theta_D/T)$ 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]