General shock wave equation of state for solids

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A theoretical shock wave equation of state has been derived based on the Morse potential function, known from classical spectroscopy. Using this potential function and an interstitial-electron model, a linear relation between the shock wave velocity and the mass displacement velocity can be found, analogous to the common empirical relation, but with parameters derived from easily accessible nonshock-wave data. The equation is applicable to a wide range of inorganic materials, as will be demonstrated in two forthcoming articles on metals and ceramics. Examples are shown for silver and copper. Calculations are within 5% average error between experimental data and the model. © 1995 American Institute of Physics.

I. INTRODUCTION

The application of shock waves in new production methods, such as shock wave compaction of powders¹ or shock synthesis,² requires extensive knowledge of the shock wave behavior of the materials involved. However, the science of material properties under shock wave conditions is a largely empirical field, and this is disadvantageous when dealing with new materials. The theoretical shock wave equation of state developed in the present article, which uses easily accessible data, is meant to increase the flexibility of the application of production methods, involving shock waves, to new materials.

In shock wave physics the most generally used equation of state is an empirical equation known as the Rankine-Hugoniot equation, or Hugoniot.³ This Hugoniot can be expressed as a linear relation between the velocity at which a shock wave travels, the shock wave velocity U , and the velocity at which the material moves directly after passage of the shock wave front, the mass displacement velocity u . The Hugoniot is then expressed as

$$U = C_0 + Su, \quad (1)$$

in which C_0 can be approximated with the bulk sound velocity and S is an empirically determined material constant, which can be approximated with⁴

$$S = \frac{1}{2}(1 + \Gamma), \quad (2)$$

in which Γ is the Grüneisen coefficient, which characterizes the ratio of the thermal pressure P_T , which is the pressure associated with the thermal motion⁵ of the atoms (and electrons), to the thermal energy E_T of the lattice,³

$$\Gamma = V \left(\frac{\partial P_T}{\partial E_T} \right)_V. \quad (3)$$

The approximation in Eq. (2), however, is valid only at low shock stresses.

When data over a very large stress range are available a second-order term is sometimes added to the Hugoniot. For many materials, however, a linear relationship fits the experimental data well.⁶

A number of approaches has been explored so far to predict the shock behavior of materials. Ross and Ree⁷ used the pair potential of gases, and scaled them in accordance with the "law of corresponding states" to predict the behavior of gases under shock conditions.

For solid materials Dandache,⁸ for example, derived an equation for the Grüneisen coefficient as a function of volume $[\Gamma(V)]$ for which the parameters can be calculated from the slope of the Hugoniot curve at $u=0$, and the Grüneisen coefficient at standard conditions Γ_0 . This $\Gamma(V)$ function can be combined with the Mie-Grüneisen equation of state⁴ to calculate shock wave conditions. Dandache⁸ used these equations to calculate the thermodynamic states of Al, Cu, and Pb under shock wave conditions.

The approach used by Dandache is like many other methods⁸ based on the Grüneisen coefficient. The Grüneisen coefficient at standard conditions Γ_0 can be determined with⁵

$$\Gamma_0 = \frac{\alpha_V}{C_V \kappa_0 \rho_0}, \quad (4)$$

in which α_V is the isobaric volume expansion coefficient at constant pressure, C_V is the heat capacity at constant volume, κ_0 is the isothermal compressibility at standard conditions ($T=300$ K, $P=0.1$ MPa), and ρ_0 is the density at standard conditions. The values of the parameters used to calculate Γ_0 with Eq. (4) can be determined experimentally. This would, however, require many experiments. Furthermore, for these experiments a dense sample would be needed, which is often rather difficult to obtain for new materials.

In this article it is shown that a linear shock wave equation of state can be derived using an interatomic potential with parameters that can be determined from infrared spectroscopic data.

Infrared spectroscopic data were chosen as a basis for our calculations because of their general availability, and because of the analogies between infrared spectroscopy, during

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which deformation of the bonds between the atoms by vibrations is measured, and a shock wave in which the bonds are compressed.

In classic spectroscopy one very well-known example of an equation describing the energy of atomic motion is the interatomic potential. In this equation the potential energy of a diatomic molecule is related to the deviation of the interatomic distance from its equilibrium value.

A well-known interatomic potential is the Morse potential⁹ [see Fig. 1(a)]. The Morse potential was chosen because of its successful, widespread use and its mathematical form. Its relatively simple mathematical structure makes it more attractive for calculations than potentials with multiple exponents. Furthermore, although increasing the number of parameters in a potential increases its accuracy, it also causes complications in their determination. The Morse potential is very often used in spectroscopy, and the required parameters are easily obtained. This makes this potential a suitable basis for a generally valid shock wave equation of state.

In the present model the parameters of a potential are used, which are obtained for a diatomic molecule in the gas phase, to describe the bonds that exist in a lattice. This is accomplished by the application of an interstitial-electron model.¹⁰ Bonds are assumed to exist between an atom and all atoms that border the nearest and next-nearest interstitial sites around it, with the exception of cases in which there is an atom on a straight line between them. Only bonds are assumed to exist between atoms that border adjacent interstitial sites, but no further. In practice this means that bonds are considered at interatomic distances up to slightly more than twice the nearest-neighbor distance (see Appendix C). This model is applicable to lattices with short-range atomic interaction, such as metals¹⁰ and covalent materials. For lattices with a strong ionic bond nature, the interstitial-electron model cannot be used to determine the bonds, due to the presence of long-range Coulombic interaction in these lattices.

The Morse potential describes the relation between the potential energy of atomic vibration ϕ and the deviation from the equilibrium distance r_0 between the atoms. The Morse potential can be written as

$$\phi(r) = D' [1 - e^{\alpha(r_0 - r)}]^2. \quad (5)$$

Here D' is the bond dissociation energy per mole, which is the energy difference between the ground state of a diatomic molecule in the gaseous phase with the atoms at equilibrium distance and with the atoms at infinite separation, α is the reciprocal vibration number, and $(r_0 - r)$ is the deviation from the equilibrium distance, with r being the actual distance. Both D' and r_0 can be obtained easily even for new compounds. The reciprocal vibration number α can be calculated from infrared spectral data with⁹

$$\alpha = 2\pi c_0 \omega_0 \sqrt{\mu/2D'}, \quad (6)$$

in which c_0 is the velocity of light in vacuum, μ is the reduced mass of the molecule, and ω_0 is the wave number (in m^{-1}) of the zeroth-order transition. The bond dissociation energy D' and the wave number ω_0 can be determined from

FIG. 1. (a) The Morse potential curve, the left-hand side of the curve for $r < r_0$ can be considered to represent isothermal compression of the bond. (b) By averaging over the maximum and minimum deviation of the potential curve, the isobaric expansion curve can be found. (c) The shock wave state is constructed by following the isotherm from $(r_0, E=0)$ to (r_c, E_c) , and then expanding along the isobar to $(r_s, E_{int} = E_c + E_T)$. (d) The construction of the Hugoniot as in (c) in a plot of stress σ against specific volume V .

the infrared spectrum.⁹ The Morse potential was originally derived for diatomic gases; in the current model, however, the potential is used to describe the interaction in a solid. The equilibrium distance or bond length between the atoms r_0 that is used in the model refers to the average equilibrium distance in the solid and can, therefore, be determined from x-ray data. The average equilibrium distance r_0 is discussed further in Sec. III describing effects of the lattice.

In the current model the adiabatic shock wave compression is calculated by dividing the shock process into two stages: first isothermal compression, and second isobaric expansion. Both processes can be described with equations that can easily be derived from the Morse potential.

The assumptions underlying the present derivation of a shock wave equation of state from a potential are as follows:

- (1) the translational motion of the atoms must be classical;
- (2) the thermal excitation of electrons is negligible;

FIG. 2. Effect of an external stress on the shape of the potential curve. Adding the extra potential energy due to the external stress (dashed line) results in a counterclockwise rotation. The change in the equilibrium distance is accounted for in the model, only the rotation was neglected. The shape of the potential curve in the lower regions, relevant for thermal excitation up to shock temperatures ($T < 10\,000$ K), is rather insensitive to this rotation.

- (3) thermal vibrations in the shock wave state can be approximated by the potential at standard conditions;
- (4) on the average there is no atomic motion lateral to the shock wave direction; and
- (5) the true interatomic potential can be approximated with the Morse potential.

At the stress conditions achieved by shock wave experiments the concentration of phonons is sufficiently high that the first assumption, that of classical motion, is clearly valid. Coffey and Toton¹¹ calculated that the phonon density at about 2×10^{11} Hz, in a low-amplitude compressive wave of 0.5 GPa, with a wave velocity of 2 km/s, would be approximately 10^{27} phonons/m³. The thermal equilibrium density at 2×10^{11} Hz at shock temperatures would typically¹¹ be less than 100 phonons/m³.

The second assumption is reasonable at lattice temperatures below 10 000 K, because the effect of thermal excitation of the electrons is small compared to the thermal vibrations of the atoms.³

The thermal vibrations at "low" stresses can be described accurately by the potential. The effect of a non-negligible external stress on the potential can be represented in a potential plot by adding a linear function of the bond length to the original potential, as is shown in Fig. 2. This transformation results in a smaller equilibrium distance and a counterclockwise rotation of the potential. The decrease in the equilibrium distance is accounted for in the model. The third assumption is based on the fact that the shape of the potential near its minimum is rather insensitive to rotation, as shown in Fig. 2.

The force balance between the atoms and their bonds in the shock wave state causes the bonds to attain a new equilibrium length, and because there is no overall mass transport perpendicular to the shock wave direction this means that the fourth assumption is valid for the average atom.

The Morse potential has been successfully applied to a

wide range of materials.¹² The conditions under which infrared spectroscopy is performed, however, are not as extreme as in a shock wave. At high compressive stresses, the true interatomic potential of materials with an extremely asymmetric interatomic potential might deviate from a Morse potential determined with infrared spectroscopy. Compounds with such an extremely asymmetric potential are few as will be shown in two following articles, in which a wide range of metals¹³ and ceramics¹⁴ will be discussed. The calculations in this article, and in the forthcoming articles, reveal that most materials obey the fifth condition.

The aim of this article is to develop a theoretical shock wave equation of state with well-known nonshock-wave parameters, which if not available can be determined beforehand without shock wave experiments.

In the following sections the basic shock wave equations are introduced: the three conservation laws of mass, momentum, and energy. After this an example of a generally used empirical shock wave equation of state is given, and after this short introduction a new theoretical shock wave equation of state is developed in seven stages.

In the first stage the shock wave compression is divided in two processes: first an isothermal, or cold compression, and second an isobaric, or thermal expansion. It should be borne in mind that this division is of course purely theoretical.

In the second and third stages the isothermal compression and isobaric expansion are related to the internal energy by using the potential.

In the fourth stage the shock wave compression is derived from combining the isothermal compression and the isobaric expansion. This yields a relation between the internal energy (distributed between isothermal compression, and isobaric expansion), and the bond length in the shock wave. This relation can be expressed in an equation in which the relative shock wave compression is a function of the shock wave velocity, the mass displacement velocity, and the relative amount of internal energy used for isothermal compression.

In the fifth stage a relation is determined between the bond length, the shock wave velocity, and the mass displacement velocity, using mass conservation.

In the sixth stage the equations found in the fourth and fifth stages are combined to eliminate the bond length from the equation. This yields an equation for the shock wave velocity as a function of the mass displacement velocity and the fraction of internal energy used for isothermal compression.

In the seventh and final stage the relative amount of internal energy used for isothermal compression is determined by a one-step iteration, and some approximations. This yields a shock wave equation of state with the shock velocity as a function of the mass displacement velocity.

After the derivation of this new linear shock wave equation of state the calculation of the relevant parameters is discussed. It is demonstrated how to calculate the average bond length in a metal. Finally, it is shown that the parameters of the model can be determined in a second way using the bulk sound velocity (which is sometimes considered to

be a shock wave parameter, but can be determined without shock wave experiments) as a key parameter.

II. THE MODEL

A. Shock equations

To calculate the shock wave state of a material three balance equations are available. The balance equations in shock wave physics are determined over the shock wave front, moving with the shock wave velocity U .

The mass conservation law over the shock front dictates that the mass entering the shock front with a velocity U is equal to the mass leaving the shock front with a velocity $U-u$. This gives

$$\rho_0 U = \rho(U-u), \quad (7)$$

in which ρ_0 is the density ahead of the shock wave and ρ the density directly behind the shock wave front.

The conservation of momentum yields

$$\sigma - \sigma_0 = \rho_0 U u, \quad (8)$$

in which σ is the shock stress, or force per unit surface. In shock wave physics the stress before arrival of the shock wave σ_0 is often considered to be negligible.

When we neglect viscosity effects and heat conduction effects, the internal energy change E_{int} is determined by

$$E_{\text{int}} = \frac{1}{2} \sigma \Delta V, \quad (9)$$

in which ΔV is the difference in specific volume before and after arrival of the shock wave.

With the use of Eqs. (7)–(9) the change in internal energy for the shock wave can also be written as

$$E_{\text{int}} = \frac{1}{2} u^2. \quad (10)$$

These three conservation laws, however, are not sufficient to calculate the shock wave state and, therefore, a fourth equation is needed. This fourth equation is called the shock wave equation of state, or Hugoniot. An example of such an equation was given earlier [Eq. (1)].

B. Division into two stages

In the following an equivalent fourth equation is derived. To this end the thermodynamic state reached after adiabatic shock compression is calculated in two steps.

First an isothermal compression process is considered, and second an isobaric expansion is considered in such a way that the same end state is reached as in a shock compression process. This construction is illustrated in Figs. 1(a)–1(d). In Fig. 1(a) the Morse potential is shown. The part of the curve for $r < r_0$ can also be interpreted as describing the internal energy increase in an isothermal compression. Figure 1(b) shows how for a certain energy level the isobaric expansion can be calculated from the Morse potential by averaging the maximum compression and expansion. In Fig. 1(c) these two steps are combined by considering the material to be compressed from $(r=r_0, E=0)$ to (r_c, E_c) , and then to expand along an isobar to $(r_s, E_c + E_T)$.

In Fig. 1(d) the processes in Fig. 1(c) are shown in an alternative plot of the stress σ against the specific volume V .

For the mathematical construction first the internal energy increase due to the shock wave E_{int} is divided into two parts: E_c , the isothermal, or cold compression energy increase, and E_T , the energy increase due to isobaric expansion (both per unit mass),

$$E_{\text{int}} = E_c + E_T. \quad (11)$$

By introducing the fraction f of isothermal energy over the total internal energy increase,

$$f \equiv \frac{E_c}{E_{\text{int}}}, \quad (12)$$

the internal energies can be written as a function of u ,

$$E_c = f \frac{1}{2} u^2 \quad \text{and} \quad E_T = (1-f) \frac{1}{2} u^2. \quad (13)$$

C. Isothermal compression

The relative isothermal compression $\epsilon_c [(r_c - r_0)/r_0]$ can be calculated from the isothermal energy increase, or cold compression energy E_c with the potential [Eq. (5)] rewritten to

$$E_c = D(1 - e^{-\alpha r_0 \epsilon_c})^2. \quad (14)$$

In the following the bond dissociation energy per unit mass D is used instead of the bond dissociation energy per mole D' . This is done in accordance to conventions in shock wave physics, where it is standard procedure to use energies per unit mass.

Rewriting Eq. (14) yields ϵ_c expressed as a function of the cold compression energy,

$$\epsilon_c = \frac{-1}{\alpha r_0} \ln \left[1 + \left(\frac{E_c}{D} \right)^{1/2} \right]. \quad (15)$$

D. Isobaric expansion

The isobaric expansion can be determined from the potential by determining the average deviation from the equilibrium radius, due to the asymmetry of the thermal vibration, as shown in Fig. 1(b). In the cold compressed state the thermal vibrations occur around the equilibrium distance in that state, $r_c [(1 + \epsilon_c)r_0]$. The thermal energy E_T is related to the maximum thermal deviation $x_T [(r_s - r_c)/r_c]$ by the potential

$$E_T = D(1 - e^{-\alpha r_c x_T})^2. \quad (16)$$

Rewriting Eq. (16) gives

$$x_T = \frac{-1}{\alpha r_c} \ln \left[1 \pm \left(\frac{E_T}{D} \right)^{1/2} \right]. \quad (17)$$

The average thermal expansion ϵ_T , which is the isobaric expansion, can be found from averaging x_T over expansion x_T^- and compression x_T^+ [shown in Fig. 1(b)],

$$\epsilon_T = \frac{x_T^+ + x_T^-}{2} = \frac{-1}{2\alpha r_0(1 + \epsilon_c)} \ln \left(1 - \frac{E_T}{D} \right). \quad (18)$$

E. Combination of stages

The equilibrium radius in the shock wave state r_s is calculated from the relative isothermal compression ϵ_c and the relative thermal expansion ϵ_T ,

$$r_s = (1 + \epsilon_c)(1 + \epsilon_T)r_0. \quad (19)$$

Substitution of Eqs. (15) and (18) in Eq. (19) gives

$$\frac{r_s}{r_0} = 1 - \frac{1}{\alpha r_0} \ln \left[\left(1 + \left(\frac{E_c}{D} \right)^{1/2} \right) \left(1 - \frac{E_T}{D} \right)^{1/2} \right]. \quad (20)$$

This yields a relation between the cold and thermal internal energies and the bond compression in the shock state. A schematic representation of this construction is shown in Fig. 1(c).

Substitution of Eq. (13) in Eq. (20) gives

$$\frac{r_s}{r_0} = 1 - \frac{1}{A} \ln \{ (1 + \sqrt{fBu}) \sqrt{1 - (1-f)B^2u^2} \}, \quad (21)$$

with

$$A = \alpha r_0 \quad \text{and} \quad B = \sqrt{1/2D}. \quad (22)$$

Combining Eq. (21) with a second relation between r_s , u and U will yield a relation between u and U , which is the aim of this work. This second relation can be obtained from the conservation of mass.

F. Application of mass conservation

Until now only the relations between the shock wave energy and the average bond length were considered. Changes in the average bond length, however, are also related directly to changes in the overall density. In the following the relations between the bond length and the overall density, as well as Eq. (7) resulting from the conservation of mass, are used to derive a second relation between the average equilibrium bond length in the shock state r_s , u , and U .

Because shock wave compression in a planar shock wave in solids is always anisotropical on the scale of atomic bonds, the effect of the angle between the interatomic bond and the shock wave should be carefully considered. There is no overall mass transport in lateral direction. Therefore, the average bond will remain uncompressed in directions perpendicular to the shock wave direction.

When these effects are taken into account the following equation results, as is demonstrated in Appendix A:

$$\frac{u}{U} = 3 \left(1 - \left\langle \frac{r_s}{r_0} \right\rangle \right) + \frac{9}{5} \left(1 - \left\langle \frac{r_s}{r_0} \right\rangle \right)^2 + 2\sqrt{5} \left(1 - \left\langle \frac{r_s}{r_0} \right\rangle \right)^3. \quad (23)$$

G. Elimination of bond length

Substitution of Eq. (21) in Eq. (23), and expanding to series yields an expression of U as a function of u and f ,

$$U = \frac{A}{3B\sqrt{f}} + \left(\frac{A}{6f} - \frac{1}{5} \right) u - \left(\frac{\sqrt{f}A}{9} + \frac{2\sqrt{5}f}{9A} - \frac{A}{12f^{3/2}} - \frac{3\sqrt{f}}{25A} \right) Bu^2. \quad (24)$$

H. Elimination of f

The ratio f of energy used in isothermal compression E_0 and total internal energy E_{int} can be calculated using the fact that the stress after isothermal compression equals the shock stress, because the expansion is an isobaric process. In Appendix B an equation for f is derived using this equality and the potential. After some approximations it is found that

$$f \approx 1 - \frac{A}{6} \frac{u}{U}. \quad (25)$$

By using an iteration with Eqs. (24) and (25) an expression for U as a function of u can be obtained. First f is solved by using a simple first-order expression with $f=1$ for U from Eq. (24), which is substituted in Eq. (25),

$$f \approx 1 - \frac{A}{6} \frac{u}{(A/3B) + [(A/6) - (1/5)]u}. \quad (26)$$

Substitution of Eq. (26) in Eq. (24), and discarding terms of second order and higher, yields an equation analogous to the empirical Hugoniot,

$$U = \frac{A}{3B} + \left(\frac{A}{4} - \frac{1}{5} \right) u, \quad (27)$$

in which the parameters A and B can be calculated from nonshock-wave data, with

$$A = \alpha r_0 \quad \text{and} \quad B = \sqrt{1/2D}. \quad (28)$$

In the above derivation terms of second order and higher were discarded for the following reasons:

- (1) it is common practice to use a linear equation of state, which also fits the experimental data very well for many materials,⁶ and
- (2) in view of some assumptions used in the model and some approximations applied in the derivation, the reliability of a second-order term would have been questionable.

It should be remembered that the linearity has no physical significance. In our calculations we found that if a second-order term had been included, its sign would have been negative.

III. INFLUENCE OF LATTICE

In the modern bond theory of metals¹⁰ they are considered to consist of a packing of positive ions with a maximum valence electron density in the interstitial sites. According to this theory the electrons are not moving around freely without preference. The electrons in the interstitial sites bind the positive ions together.

In our calculations bonds are assumed to exist between an ion and all ions that border the nearest and next-nearest interstitial sites around it. This means that bonds are assumed to exist between the ions of two adjacent interstitial sites. In this model the average bond length between the ions does not equal the nearest-neighbor distance, which is generally quoted as bond length,¹⁵ but the average distance between an ion, and the ions bordering the nearest and next-nearest interstitial sites around it.

TABLE I. The IR data necessary for the calculations with method 1.

Metal	Dissociation energy ^a D' (kJ/mol)	Mass of diatomic molecule ^a M (g/mol)	Nearest neighbor distance ^a R_0 (nm)	Lattice const ^b q	Wave number ^c ω_0 (10^3 m^{-1})
Ag (fcc)	163 ± 8	215.74	0.2889	1.73	20.70
Cu (fcc)	177 ± 2	127.10	0.2556	1.73	26.89

^aReference 15.^cReference 12.^bAppendix C.

This average bond length is especially important in a shock wave model, because the lattices in a macroscopic polycrystalline sample are anisotropically compacted, and not necessarily in the direction of one of the axes of the lattice. During shock compression of a macroscopic metal sample, which is not a single crystal, every ion bordering an interstitial site can be moved in the direction of every other ion bordering the same, or even the next interstitial site, because of their random orientation with respect to the shock wave direction (due to the polycrystalline nature of the sample). This means that, if the strength of the lattice is described with a bond model, bonds must be considered between all the ions bordering an interstitial site and those that border the adjacent interstitial sites. In Appendix C [Figs. 5(a)–5(d)] the bonds are determined for a fcc lattice.

The average bond length r_0 can be calculated from the lattice structure or packing and the nearest-neighbor distance. For the regular packings that apply to most metals a constant ratio q between the nearest-neighbor distance and the average bond length can be found applicable to all metals with the same packing.

This lattice ratio q is found by averaging the distances x ($x = r/R_0$ with R_0 the nearest-neighbor distance) between an ion and the ions bordering the interstitial sites around it, and those in a second layer around these over their number of occurrences n_i

$$q = \frac{\sum n_i x_i}{n_{\text{tot}}} \quad (29)$$

The bond length can be calculated from q and the nearest-neighbor distance R_0 in the lattice,

$$r_0 = qR_0. \quad (30)$$

The value of q for a fcc lattice is calculated in Appendix C.

IV. ALTERNATIVE CALCULATION OF EQUATION OF STATE

An alternative method is available for the calculation of the parameters of the linear equation of state. This method

uses the bulk sound velocity, which can be measured without shock wave experiments, e.g., with ultrasonics.

Analogous to the Hugoniot, the first term can be approximated with the bulk sound velocity C_0 . For very low mass displacement velocities ($u \downarrow 0$) the shock wave velocity U approaches the bulk sound velocity C_0 . This means that

$$U(u \downarrow 0) = \frac{A}{3B} \approx C_0. \quad (31)$$

This has an important consequence for the application of the equation of state [Eq. (27)], because it means that if the bulk sound velocity is known, and B can be calculated from other parameters, an alternative equation can be used,

$$U = C_{0,\text{expt}} + \left(\frac{3BC_{0,\text{expt}}}{4} - \frac{1}{5} \right) u. \quad (32)$$

V. CALCULATIONS

In Table I the necessary data to calculate the equation of state are presented for Ag and Cu, which both have a fcc-type lattice.

The calculated intercept ($C_{0,\text{calc}}$) and slope of the equation of state are shown in Table II, together with the range over which data were available, and the average error in the calculations compared to the data.

When not all the spectroscopic data are available a second method can be applied in which the bulk sound velocity is used to calculate the parameters of the equation of state [Eq. (32)]. In Table III the parameters are shown, which are necessary to calculate B from the experimental bulk sound velocity.

The intercept ($C_{0,\text{expt}}$) and the slope of the equation of state calculated with the experimental bulk sound velocity are shown in Table IV, together with the range over which data were available and the average error in the calculation compared to the data.

The linear shock wave equations of state calculated for Ag from infrared (IR) data and from the sound velocity are compared with literature data⁵ in Fig. 3.

TABLE II. Results of calculations with method 1 using spectroscopic data.

Metal	Data range ^a u (km/s)	Constant A [Eq. (28)]	Constant B [Eq. (28)] (s/km)	Calculated intercept $C_{0,\text{calc}}$ [Eq. (27)] (km/s)	Calculated slope S [Eq. (27)]	Average error in calculated shock wave velocity U (%)
Ag	0.5–2.1	7.93	0.814	3.25	1.78	5.0
Cu	0.2–4.2	6.72	0.600	3.73	1.48	2.7

^aReference 6.

TABLE III. The data necessary for the calculations of the constant B for method 2.

Metal	Experimental bulk sound velocity ^a $C_{0,\text{expt}}$ (km/s)	Dissociation energy ^b D' (kJ/mol)	Mass of diatomic molecule ^b M (g/mol)
Ag (fcc)	3.176	163 ± 8	215.74
Cu (fcc)	3.927	177 ± 2	127.10

^aReference 6.

^bReference 15.

VI. DISCUSSION

The calculated equations of state are within 5% average error. In Fig. 3 it can be seen that the accuracy of the calculations tends to decrease with increasing shock wave velocity. This might be due to the fact that higher-order terms were neglected. In this example the calculation with the IR data is less accurate than with the sound velocity; this is, however, a coincidence: In most cases^{13,14} the calculations with IR data are more accurate. For most metals the current model, when used with all spectroscopic data, calculates the shock wave velocity within 1%–10% average error, as is shown in Ref. 1.

When only the sound velocity and the dissociation energy are used the calculation for the two model materials is within 3% average error. In general,¹³ the second method is slightly less accurate because the bulk sound velocity is not exactly equal to the intercept of the shock wave curve. For most metals the current model, when used with only the bulk sound velocity, calculates the shock wave velocity within 2%–25% average error, as is shown in Ref. 1.

Before applying the present model one should first evaluate whether it is reasonable to assume that the compressive strength of the material can be described with an interatomic potential determined at low stress conditions. The conditions under which infrared spectroscopy are performed are not as extreme as in a shock wave. At high compressive stresses the true interatomic potential of materials with an extremely asymmetric interatomic potential might deviate from a Morse potential, which was determined with IR spectroscopy.

Materials that have potentials that are difficult to characterize with the Morse potential are usually recognizable for their low bond strength, or dissociation energy and high thermal-expansion coefficient.

The fact that the Morse potential is not applicable to some materials is not a shortcoming of the current model, but merely a result of the choice in potentials. It can be remedied by choosing a different potential, which is applicable to those materials.

The factors that determine the suitability of the model for different materials will be discussed further in two following articles, the first about metals,¹³ the second about ceramics.¹⁴ In these articles a large range of materials will be considered.

For the two materials Ag and Cu discussed here it appears that the compression in a shock wave can very well be characterized with the Morse interatomic potential.

VII. CONCLUSIONS

It has been shown that it is possible to derive a shock wave equation of state using the Morse potential function, known from infrared spectroscopy, and an interstitial-electron model. Two methods are demonstrated to calculate a linear shock wave equation of state.

The first method yields Eq. (27),

$$U = \frac{A}{3B} + \left(\frac{A}{4} - \frac{1}{5} \right) u,$$

in which A and B are material constants that can be determined from infrared spectroscopic and x-ray data: the dissociation energy D (from thermodynamic or IR spectroscopic measurements); the wave number of the zeroth order transition in the infrared spectrum ω_0 ; the atomic lattice (from x-ray data); and the nearest-neighbor distance R_0 , in the lattice (from x-ray data).

The second method, which is less accurate but uses fewer data, yields Eq. (32),

$$U = C_{0,\text{expt}} + \left(\frac{3BC_{0,\text{expt}}}{4} - \frac{1}{5} \right) u,$$

in which $C_{0,\text{expt}}$ is the bulk sound velocity and B can be determined from the dissociation energy D (from thermodynamic or IR spectroscopic measurements).

For the examples Ag and Cu calculations with method 1, using all data, are within 5% average error of experimental data. Calculations with method 2, using only the bulk sound velocity and the dissociation energy, are within 3% average error. This is sufficiently accurate for most shock wave applications.

TABLE IV. Results of calculations with method 2 using the experimental bulk sound velocity $C_{0,\text{expt}}$.

Metal	Data range ^a u (km/s)	Intercept (experimental bulk sound velocity ^a) $C_{0,\text{expt}}$ (km/s)	Constant B [Eq. (28)] (s/km)	Calculated slope S [Eq. (33)]	Average error in calculated shock wave velocity U (%)
Ag (fcc)	0.5–2.1	3.176	0.81	1.74	2.6
Cu (fcc)	0.2–4.2	3.927	0.60	1.57	2.6

^aReference 5.

FIG. 3. The linear shock wave equation of state for Ag calculated with IR data, and with the experimental bulk sound velocity compared with data from Marsh (see Ref. 6).

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APPENDIX A: EFFECT OF VOLUME CHANGE ON BOND LENGTH

In Fig. 4 the effect of the shock wave on the bond is represented schematically. In the figure the shock wave travels downward. The ratio a over b is a measure of the shock wave compression,

$$\frac{b}{a} = \frac{\rho_0}{\rho}. \quad (\text{A1})$$

Using the conservation of mass one obtains

$$\frac{b}{a} = \frac{\rho_0}{\rho} = \frac{U-u}{U}. \quad (\text{A2})$$

The bond remains uncompressed in lateral direction, hence, e is constant.

The bond before and after compression is represented by the diagonals, hence,

$$\frac{r_s}{r_0} = \frac{d}{c}. \quad (\text{A3})$$

In Fig. 4 it can be seen that

$$a = c \sin \beta \quad (\text{A4})$$

and

$$d = \left[\left(a \frac{b}{a} \right)^2 + (c \cos \beta)^2 \right]^{1/2}. \quad (\text{A5})$$

Substitution of Eq. (A4) in Eq. (A5) gives

FIG. 4. A schematic representation of bond compression by the shock wave. The shock wave travels downward parallel to a and b . The bond is represented by c before arrival of the shock wave and d during shock compression. The ratio of b over a is proportional to the overall compression. There is no overall compression perpendicular to the shock wave direction, the projection of the bond in the shock wave plane e , therefore, remains constant. The angle of the bond with the shock wave plane changes from γ to β , due to the arrival of the shock wave.

$$d = \left[\left(c \frac{b}{a} \sin \beta \right)^2 + (c \cos \beta)^2 \right]^{1/2} \quad (\text{A6})$$

or

$$\frac{d}{c} = \left\{ 1 + \left[\left(\frac{U-u}{U} \right)^2 - 1 \right] \sin^2 \beta \right\}^{1/2}. \quad (\text{A7})$$

Equation (A3) now becomes

$$\frac{r_s}{r_0} = \left\{ 1 + \left[\left(\frac{U-u}{U} \right)^2 - 1 \right] \sin^2 \beta \right\}^{1/2}. \quad (\text{A8})$$

When a macroscopic sample of a polycrystalline solid is considered in which the angle of the atomic bond can be considered to vary randomly with respect to the shock wave direction, the average bond can be approximated using a simple hemispherical model. From the position of an atom, atoms with which a bond exists in shock wave direction can then be considered to be distributed over the surface of a hemisphere with radius r_0 , centered around this position. It is assumed that the bound atoms are equally distributed over the surface of the hemisphere. With this assumption the average radius in the shock wave can be found from Eq. (A8) by averaging over β using

$$\left\langle \frac{r_s}{r_0} \right\rangle = \frac{\int_0^{\pi/2} 2\pi \cos \beta [r_s(\beta)/r_0] d\beta}{\int_0^{\pi/2} 2\pi \cos \beta d\beta}. \quad (\text{A9})$$

This yields

$$\left\langle \frac{r_s}{r_0} \right\rangle = \frac{1}{2} \left(1 - \frac{u}{U} + \frac{\arcsin\{1 - [1 - (u/U)^2]\}}{1 - [1 - (u/U)^2]} \right). \quad (\text{A10})$$

Expanding to series with a third-order approximation gives

$$\left\langle \frac{r_s}{r_0} \right\rangle = 1 - \frac{1}{3} \frac{u}{U} + \frac{1}{15} \left(\frac{u}{U} \right)^2 + \frac{1}{35} \left(\frac{u}{U} \right)^3. \quad (\text{A11})$$

The physical solution for u over U from Eq. (A11) can be approximated with

FIG. 5. Schematic representation of a fcc lattice. The ions in the vicinity of ion i are numbered in order of increasing distance. Ion IV is screened from ion i by I. Ion V is the furthest ion still bordering the next-nearest layer of interstitial sites [see also (d)]. Ion VI and those that are further away do not border one of the nearest or the next-nearest interstitial sites [see (b) and (d)] and are, therefore, considered screened. (b) Examples of the nearest and next-nearest layer of interstitial sites in the fcc lattice: a tetrahedral interstitial site in the nearest layer and an adjacent octahedral site in the next-nearest layer. The longest distance between the ions in these layers is between ion i and III. (c) Examples from the first layer of octahedral sites in the fcc lattice. The longest distance within this layer is found between the ions i and II. (d) Examples of connected nearest and next-nearest octahedral sites. The longest distance between ions in the first and second layer is found between the ions i and V.

$$\frac{u}{U} = 3 \left(1 - \left\langle \frac{r_s}{r_0} \right\rangle \right) + \frac{9}{5} \left(1 - \left\langle \frac{r_s}{r_0} \right\rangle \right)^2 + 2\sqrt{5} \left(1 - \left\langle \frac{r_s}{r_0} \right\rangle \right)^3. \quad (\text{A12})$$

APPENDIX B: CALCULATION OF f

The factor f is defined as the relative amount of energy used in isothermal compression compared to the total internal shock wave energy,

$$f \equiv \frac{E_c}{E_{\text{int}}}. \quad (\text{B1})$$

This ratio can be determined with sufficient accuracy by using some simple approximations.

Because the thermal expansion used in the current model is isobaric, the stress after isothermal compression σ_c is equal to the shock stress σ ,

$$\sigma = \sigma_c. \quad (\text{B2})$$

From energy conservation [Eq. (9)] it can be derived that

$$\sigma = \frac{2E_{\text{int}}}{V_0 - V}. \quad (\text{B3})$$

Using the Morse potential to describe isothermal compression yields³

$$\sigma_c = - \left(\frac{d\phi}{dV} \right) = \frac{dr_c}{dV} \frac{2A}{r_0} \frac{\exp\{A[1 - (r_c/r_0)]\}}{1 - \exp\{A[1 - (r_c/r_0)]\}} E_c. \quad (\text{B4})$$

Combining Eqs. (B1)–(B4) gives

$$f = - \frac{r_0}{A} \frac{dV}{dr_c} \frac{1}{V_0 - V} \left\{ \exp \left[-A \left(1 - \frac{r_c}{r_0} \right) \right] - 1 \right\}. \quad (\text{B5})$$

This equation can be solved using some approximations,

$$\frac{dV}{dr_c} = \frac{dV}{d\epsilon} \frac{d\epsilon}{dr_s} \frac{dr_s}{dr_c}, \quad (\text{B6})$$

in which

$$\epsilon = \frac{u}{U} = \frac{V_0 - V}{V}. \quad (\text{B7})$$

The first approximation that is used is based on Eq. (23),

$$\frac{r_s}{r_0} \approx 1 - \frac{\epsilon}{3}, \quad (\text{B8})$$

which yields

$$\frac{d\epsilon}{dr_s} = -\frac{3}{r_0}. \quad (\text{B9})$$

From Eq. (B7) it can be found that

$$\frac{dV}{d\epsilon} = -V_0, \quad (\text{B10})$$

while furthermore it is assumed that

$$\frac{dr_s}{dr_c} \approx 1. \quad (\text{B11})$$

Substitution of these approximations into Eq. (B5) gives

$$f \approx -\frac{3}{\epsilon A} \left[\exp\left(\frac{-A\epsilon}{3}\right) - 1 \right]. \quad (\text{B12})$$

Expanding to series yields in first-order approximation

$$f \approx 1 - \frac{A}{6} \frac{u}{U}. \quad (\text{B13})$$

APPENDIX C: CALCULATION OF LATTICE RATIO q

For the fcc packing [eight ions on the corners of a cube and six on the faces of the cube, shown in Fig. 5(a)] the lattice ratio q is calculated from the distances between ion i and the ions I–V [shown in Fig. 5(a)] as gathered in Table V. Using Eq. (30) this yields an average ratio q for a fcc packing of $q = 1.73$.

In Fig. 5(b) the adjacent tetrahedral and octahedral sites in the fcc lattice are shown that connect the ions of type i , I, and III. Within these two layers of interstitial sites, ions of type III are the most distant ions that are still considered for a bond. In Fig. 5(c) two octahedral sites in the nearest layer of interstitial sites are shown that border the ions of type i and II. In Fig. 5(d) examples of octahedral sites in the nearest

TABLE V. The distance between ions in a fcc packing x ($x = r/R_0$ with R_0 the nearest-neighbor distance), and their number of occurrences n for a single ion. The fcc packing is shown in Fig. 5(a). Ions at the opposite corners of the cubes face [such as ion IV in Fig. 5(a)] are considered to be screened by the ions on the cube face [such as ion I in Fig. 5(a)], and ions at distances $x > \sqrt{5}$ [such as ion VI in Fig. 5(a)] do not border the nearest or next-nearest layer of interstitial sites, and are, therefore, not considered for bonds.

Type of ion [Fig. 5(a)]	Distance to ion i x_i	Number of occurrences n_i
I	1	12
II	$\sqrt{2}$	12
III	$\sqrt{3}$	24
IV	2	0 (screened)
V	$\sqrt{5}$	24

and next-nearest layer are shown. The largest distance that can be covered with two layers of interstitial sites is found in this figure, between ions of type i and type V. The ions at the top and bottom of the octahedral site bordering ion V are at the same distance from i as ion III.

¹ P. Boogerd and A. C. Van der Steen, in *Shock Waves and High-Strain-Rate Phenomena in Materials—1990*, edited by M. A. Meyers, L. E. Murr, and K. P. Staudhammer (Dekker, New York, 1992), p. 443.

² N. N. Thadhani, *Prog. Mater. Sci.* **37**, 117 (1993).

³ Ya. B. Zeldovich, and Yu. P. Raizer, in *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*, edited by W. D. Hayes, and R. F. Probstein (Academic, New York, 1967), Vol. 2, p. 710.

⁴ M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6, p. 62.

⁵ Ya. B. Zeldovich and Yu. P. Raizer, in *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*, edited by W. D. Hayes and R. F. Probstein (Academic, New York, 1967), Vol. 2, p. 697.

⁶ *LASL Shock Hugoniot Data*, edited by S. P. Marsh (University of California Press, Berkeley, CA, 1980).

⁷ M. Ross and F. H. Ree, *J. Chem. Phys.* **73**, 6164 (1980).

⁸ H. Dandache, *Solid State Commun.* **69**, 667 (1989).

⁹ E. U. Condon and P. M. Morse, *Quantum Mechanics* (McGraw-Hill, New York, 1929), p. 163.

¹⁰ O. Johnson, *Bull. Chem. Soc. Jpn.* **45**, 1599 (1972).

¹¹ C. S. Coffey and E. T. Toton, *J. Chem. Phys.* **76**, 949 (1982).

¹² *Spectroscopic Data*, edited by S. N. Suchard and J. E. Melzer (IFI/Plenum Data Company, New York, 1976), Vol. 2.

¹³ P. Boogerd, H. J. Verbeek, M. Stuiyinga, A. C. van der Steen, P. J. van der Put, and J. Schoonman (unpublished).

¹⁴ P. Boogerd, H. J. Verbeek, M. Stuiyinga, A. C. van der Steen, P. J. van der Put, and J. Schoonman (unpublished).

¹⁵ *CRC Handbook of Chemistry and Physics*, 73rd ed., edited by D. R. Lide (CRC, London, 1992).