Equation of state for shock compression of distended solids

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Abstract. Shock Hugoniot data for full-density and porous compounds of boron carbide, silicon dioxide, tantalum pentoxide, uranium dioxide and playa alluvium are investigated for the purpose of equation-of-state representation of intense shock compression. Complications of multivalued Hugoniot behavior characteristic of highly distended solids are addressed through the application of enthalpy-based equations of state of the form originally proposed by Rice and Walsh in the late 1950’s. Additive measures of cold and thermal pressure intrinsic to the Mie-Gruneisen EOS framework is replaced by isobaric additive functions of the cold and thermal specific volume components in the enthalpy-based formulation. Additionally, experimental evidence reveals enhancement of shock-induced phase transformation on the Hugoniot with increasing levels of initial distension for silicon dioxide, uranium dioxide and possibly boron carbide. Methods for addressing this experimentally observed feature of the shock compression are incorporated into the EOS model.

1. Introduction
The present study is motivated by a requirement to describe the response of material mixtures, such as the compounds noted in the abstract, with water, air, possibly metals, or other solids, to intense shock wave loading. Constitutive modelling for computational simulation purposes involves, in comparable measures, volumetric compaction, deviatory strength, and equation of state. This paper is focused on the unique equation of state issues that have been motivated by the extreme effective distension of the mixtures and the concomitant material heating and volume expansion that complicate Hugoniot compaction of such material mixtures. Application requirements have found the Rice-Walsh enthalpy-based equation of state effective for such materials. Phase changes further complicate material modelling.

2. Equation of state
The term equation-of-state (EOS) in the shock compression community lacks rigor and is occasionally a source of confusion. The Murnaghan and Birch equations of state, for example, are analytic relations that describe the reference compression path of a material, usually under conditions of constant temperature or constant entropy. Such expressions are identified here as reference equations of state. Equation-of-state relations that provide the pressure as a function of specific volume and energy \(P(\nu, E)\) are not sufficient to describe the full thermo-elastic response of the material. Such partial...
equations of state are sufficient, however, for characterization of wave propagation properties of a material without strength, are adequate for many applications, and are appropriate for the present study. When combined with specific heat properties of the material, such partial equations of state fully characterize the thermo-elastic properties of materials without strength and can be solved for the complete energy equation of state or any of the equivalent free energies.

An isochoric Taylor expansion of the \( P(\nu,E) \) equation of state, and keeping only the linear term in the thermal energy, leads to the commonly used Gruneisen equation of state,

\[
P(\nu,E) = P'_r(\nu) + \frac{\gamma(\nu)}{\nu}(E - E'_r(\nu)),
\]

where \( P'_r(\nu) \) and \( E'_r(\nu) \) provide the reference state at which the Taylor expansion is centered.

Hugoniot states achieved in the intense shock compression of highly distended solids can render awkward application of the Mie-Gruneisen EOS. First, the shock Hugoniot can be multivalued on isochoric paths. Second, expanded shock Hugoniot states can correspond to tension states of the reference EOS. Both can complicate application of an isochoric equation of state such as the Mie-Gruneisen EOS.

Equations of state based on the isobaric superposition of the cold (reference) and thermal expansion volumes are less commonly used. Such equations of state are nonetheless attractive for dealing with shock compression complications noted above and are more conveniently couched in an enthalpy framework.

Rice and Walsh [1] proposed a high-pressure shock-wave equation of state for water based on the assumption that the enthalpy derivative of the specific volume \( \partial v/\partial H \big|_P = \eta(P) \) is a function of the pressure only. Integration yields the Rice-Walsh EOS,

\[
\nu(P,H) = \nu_r(P) + \eta(P)(H - H_r(P)),
\]

where \( \nu_r(P) \) and \( H_r(P) \) provide the reference compression and enthalpy of the material while \( \eta(P) \) characterizes the thermal expansion.

An alternative isobaric EOS follows from the study of Anderson [2] of thermal expansion properties of mineralogy of the Earth’s interior. Based on the observation of near constancy of the product of the isentropic bulk modulus and the thermal expansion \( K_s \alpha \), along with a Murnaghan description of the compressibility \( K_s = K_s + K'_s P \), the enthalpy based Anderson-Gruneisen EOS is obtained,

\[
\frac{\nu(P,H)}{\nu_r} = \left[ \left( \frac{\nu_r(P)}{\nu_r} \right)^{\frac{1}{\gamma}} - \frac{\gamma}{\eta(P)} \frac{\nu_r(P)}{K_s} (H - H_r(P)) \right]^{\frac{1}{\gamma}},
\]

where the Anderson-Gruneisen constant \( \gamma \) is reasonably approximated by \( K'_s \).

Over the intended range of application (pressures and temperatures of the Earth’s interior), the Anderson-Gruneisen EOS is found to be a modest improvement over the Rice-Walsh EOS. Over the energy extremes achieved in the intense shock compression of distended solids the Rice-Walsh EOS is determined to be more robust and is used in the EOS analysis described in the present work. Recognizing the phenomenological nature of this model, application is intended strictly for interpolation within the range of available experimental data. The model is benchmarked to available data and intended for interpolation within the range of the data. The range spans thermodynamic states.
where thermal and lattice energies are comparable. The model approximates thermal states within a region of material behavior were even detailed physics-based theories are challenged.

The Rice-Walsh equation of state follows from an isobaric Taylor expansion of the specific volume, truncated to the linear term in the specific enthalpy. Whether the Mie-Gruneisen EOS in equation (1) or the Rice-Walsh EOS in equation (2) has theoretical precedence over the range of shock-wave pressures and temperatures spanned by the range of distended compounds of interest in the present study is debatable. The Rice-Walsh equation of state has computational convenience in addressing the backward leaning and multivalued Hugoniot relations occurring in the shock compression of highly distended solids.

Construction of the Rice-Walsh EOS requires a reference EOS that provides the specific volume $v(P)$ and specific enthalpy $H_s(P)$ on some identified pressure path. Also necessary, is a thermal equation of state that is provided by a pressure-dependent relation for the Rice-Walsh (RW) factor $\eta(P)$ and accounts for thermal expansion on the specified isobar. The Rice-Walsh factor can be specified directly, or if the isentropic bulk modulus $K_s$ is known on the reference equation of state path, the RW factor is provided by the Gruneisen parameter $\Gamma$ and the bulk modulus through the thermodynamic identity, $\eta = \Gamma / K_s$.

In this study, equations of state are constructed to describe the shock Hugoniot properties of porous media that here include silicon dioxide, uranium dioxide, boron carbide, tantalum pentoxide and lastly, playa alluvium, a naturally occurring silicate mixture, for which appropriate shock Hugoniot data are available. Equation of state developments focus on the reference and the thermal equations of state, which are constructed to account for the observed shock Hugoniot response of increasingly distended samples of the porous compounds investigated.

The cold curve, the ambient isentrope or the Hugoniot of the fully-dense solid (the cold Hugoniot) are appropriate reference equations of state when constructing shock-wave equations of state for porous materials. Here the principal Hugoniot of the full-density solid is used as the reference EOS. Most analytic forms for the reference equation of state (Birch, Murnaghan or Rose-Vinet equations for example) are adequate for the present development. Here a particularly convenient form is used that results from a modification of the Murnaghan equation that follows from the assumption of a linear dependence on pressure of the inertial modulus [3],

\[ Z(P) = \rho K = \rho_o K_o + \rho_o (K_o' + 1) P, \]

leading to the relation,

\[ \upsilon_{ho}(P) = \upsilon_o \left[ 1 - \frac{1}{K_o'} \ln \left( 1 + \frac{P}{K_o} \right) \right], \]

where $\upsilon_{ho}(P)$ provides the pressure-dependence of the specific volume on the principal Hugoniot. The reference EOS for a material undergoing phase transformation on the Hugoniot is then formed through an additive mixing of the compression relations for the low-pressure and the high-pressure phases,

\[ \upsilon_{ho}(P) = (1 - \mu(P))\upsilon_{h1}(P) + \mu(P)\upsilon_{h2}(P), \]

where $\mu(P)$ is the Hugoniot phase transformation function and mass fraction of the high-pressure phase. The functional forms for $\upsilon_{h1}(P)$ and $\upsilon_{h2}(P)$ are provided by equation (5). The phase transformation function has the form,
\[ \mu(P) = 1 - e^{-(P/\sigma)^n}. \]  

The transformation pressure scale is provided by the scale parameter \( \sigma \). The shape parameter \( n \) determines the spread in transformation pressure. Although the form of Equation (7) could apply to aspects of non-equilibrium phase transformation, the present purpose is to address the spread in transformation brought about by heterogeneous pressure states on the granular scale common to the high-strength compounds of interest.

Thermal-elastic properties of the equation of state are modelled with the Rice-Walsh factor \( \eta = \Gamma / K_e \). In construction of the equation of state it is found that a constant Gruneisen parameter or a Gruneisen parameter that modestly decreases with pressure adequately represents the available data. A pressure dependent Gruneisen parameter of the exponential form,

\[ \Gamma(P) = \Gamma_o e^{-P/P_e}, \]  

is used in the equation-of-state description. When combined with pressure dependence of the bulk modulus, the necessary relation is provided for the thermodynamic Rice-Walsh factor. Equations (5), (6), (7) and (8) are joined with the Rice-Walsh EOS from equation (2) to provide a thermo-elastic description of the Hugoniot shock compression of the porous materials.

Hugoniot expressions for the distended materials are readily calculated from equation (2). Hugoniot enthalpy relations for the principal Hugoniot (full density initial state) and the distended media Hugoniot are,

\[ H_{ho}(P) = \frac{1}{2} P \left( v_o + v_{ho}(P) \right), \]  

\[ H_{h}(P) = \frac{1}{2} P \left( v_{oo} + v_h(P) \right), \]  

where \( v_o \) and \( v_{oo} \) are initial specific volumes of the full-density and distended material, respectively. Introducing the Hugoniot relations in equations (9) and (10) into (2) and solving yields,

\[ v_h(P) = v_{ho}(P) + \frac{\eta}{1 - \eta P/2} \left( \frac{1}{2} P (v_{oo} - v_o) \right), \]  

for the Hugoniot of the distended solid. The first term is the specific volume on the principal Hugoniot while the second term provides the excess isobaric thermal expansion brought about by shock heating due to compaction of the distended material at the Hugoniot pressure. Shock velocity and particle velocity corresponding to the Hugoniot state follow from,

\[ U_h(P) = \sqrt{\frac{P}{\rho_{oo}}} \left( 1 - \frac{v_h(P)}{v_{oo}} \right)^{-1}, \]  

\[ u_h(P) = \sqrt{\frac{P}{\rho_{oo}}} \left( 1 - \frac{v_h(P)}{v_{oo}} \right). \]  

3. Phase transformation

The compounds investigated in the present equation of state study are known to undergo shock-induced phase transformation or exhibit Hugoniot features that are indicative of phase transformation. Experimental Hugoniot data for these materials reveal phase transformation characteristics that are not
commonly associated with equilibrium thermodynamic behavior. Namely, increased levels of initial distension of the porous material leads to Hugoniot compression that indicate increased levels of phase transformation at lower pressures. This observation for silicon dioxide, uranium dioxide and possibly boron carbide is illustrated in figure 1 where, in each case, Hugoniot compression of higher initial distension material achieve Hugoniot segments residing at higher Hugoniot state density (lower specific volume) than the more modest distension material.

Several explanations for the observed behavior have been offered. Increased initial distension leads to increased inelastic deformation in the Hugoniot compaction process with attendant excessive plastic shear, stress and strain concentrations, and increased temperatures and temperature hot spots, all inducing enhanced phase transition through both equilibrium and kinetic mechanisms [4]. Feasibility of this mechanism has been demonstrated through molecular dynamics simulations of shock-induced phase transformation in porous silicon [5]. An alternative explanation has been proposed for silicon dioxide of equilibrium thermodynamic behavior with phase transition within the pressure and temperature region achieved in the Hugoniot compression governed by a negative Gruneisen parameter [6]. Supporting evidence for the latter is offered by features of silicate mineralogy in the Earth’s interior. Material strength on the Hugoniot may also play a role. Strength issues have been considered and judged to be an unlikely contributor to the observed anomalies [4,6].

Recognizing the uncertain physics governing phase transformation of the compounds investigated in this study, equation-of-state construction in the range of Hugoniot phase transformation is achieved by appropriate adjustment of the transformation function in equation (7) to account for differences in the initial distension densities.

![Figure 1](image.png)

**Figure 1.** Comparison of Hugoniot states for near-full-density material (solid points) and porous material (open points) illustrating increased compressibility and phase transformation at lower shock pressures for the more distended material. Third-order Birch equation of state representation of initial phase compressibility reveals increased Hugoniot densification and phase transformation for the three materials.

4. Shock equation of state of selected compounds

The materials selected for equation-of-state studies all have available high pressure shock Hugoniot data that span a substantial range of initial distension. The Rice-Walsh form of the equation of state, along with the features of the equation-of-state model proposed to account for deformation-augmented phase transformation and thermo-elastic properties are applied to each material. In general the equation-of-state model provides a satisfactory representation of the available shock Hugoniot data.

4.1. Silicon Dioxide

Shock Hugoniot data for full-density and a wide range of distended silicon dioxide materials are provided in the compendium of Trunin [7]. The $\alpha$-quartz to stishovite transition on the Hugoniot is
perhaps the most widely studied and best understood of the many solid-solid phase transformations known to occur under shock compression. The Hugoniot data shown in figure 1 provide evidence that enhanced deformation brought about by initial distension accelerates phase transformation on the Hugoniot. High-pressure compressibility of both the low-pressure (α-quartz) and the high-pressure (stishovite) phase of silicon dioxide are reasonably well known.

The extent to which initial distension of the material augments the phase transformation is not known. The constants \( \sigma \) and \( n \) in the equation (7) transformation function are selected for each of the different distension levels to provide a best agreement with the experimental Hugoniot data in the region of phase transformation.

Equation-of-state calculations for the distended material Hugoniot from equation (11) are compared with the shock Hugoniot data of Trunin [7] in figure 2. Initial distension of the porous material, often identified as the parameter \( \alpha = \rho_0 / \rho_{\infty} \), is identified for each Hugoniot in the plot.

![Figure 2. Rice-Walsh equation-of-state representation of shock Hugoniot data for porous silicon dioxide [7]. Distension levels are identified for the selected porosities for which Hugoniot data are plotted.](image)

A Gruneisen parameter that decreases modestly with pressure is, as with all of the materials examine, required to fit the experimental data [4]. Notable is the equation-of-state model predictions of enhanced phase transformation on the Hugoniot for increased distension materials. The Rice-Walsh equation of state also provided a reasonable description of the markedly hotter intermediate and large distension Hugoniot data.

4.2. Uranium Dioxide

High-pressure Hugoniot data for near full density and porous uranium dioxide is provided by the experimental study of Goplen [8] on a modestly porous (4-6%) sintered uranium dioxide ceramic and on uranium dioxide powder with three initial distension densities. Uranium dioxide undergoes shock-induced solid-solid phase transformation on the Hugoniot [9]. Again, the Rice-Walsh equation of state is constrained by and applied to the shock Hugoniot data. The influence of increased porosity on the Hugoniot phase transformation is most clearly seen in comparison of the Hugoniot characteristics of the sintered ceramic and the lowest distension uranium dioxide powder between about 10-30 GPa as shown in figure 1. Hugoniot data for the four uranium dioxide sample densities tested are plotted in figure 3 and shown with the Rice-Walsh equation-of-state description of the material.
The near-full-density ($\alpha = 1.06$) data of Goplen [8] is normalized to a crystal density ($\alpha = 1.00$) and provides the additional plot of the shock velocity particle velocity data on the left in figure 3. This later relation provides the reference equation of state.

4.3. Boron Carbide, Tantalum Oxide, Playa Alluvium
Comparable equation of state analysis is undertaken for boron carbide, tantalum oxide and playa alluvium. The results contribute further support for the occurrence of accelerated phase transformation brought about by compaction-induced deformation and/or equation-of-state effects in the Hugoniot compression process. The experimental data are comparably well represented by a Rice-Walsh equation-of-state description of the Hugoniot compression of the materials [4].

In particular the shock Hugoniot data for Nevada Test Site (NTS) playa alluvium [10] when joined with the present equation-of-state study, illuminate several issues critical to extreme-pressure equation-of-state modelling of granular mixtures. Alluvium is a silt, sand, and gravel composite. At the Nevada Test Site, alluvium is composed principally of oxide minerals. Approximately 70-75% silicon dioxide and 10-15% aluminum oxide with percentage levels of other oxides is representative of the NTS alluvium. Densities for the two alluvium samples tested are 1.54 and 1.80 g/cm$^3$. Accounting for the mineral mixture yields an average crystal density of about 2.80 g/cm$^3$ and initial distensions of approximately 1.56 and 1.82 for the two test series.

![Figure 3. Rice-Walsh equation-of-state representation of shock Hugoniot data for selected densities of uranium dioxide [8]. Distension levels are identified for the selected porosities for which Hugoniot data are plotted.](image)

Shock Hugoniot data for alluvium is plotted in figure 4 along with Hugoniot data for full-density quartz. Rice-Walsh equation-of-state predictions of the Hugoniot response of the mixture are shown. Predictions are based strictly on the equation-of-state properties determined for silicon dioxide and result in the Hugoniot representations displayed in figure 4. Although reasonable, the predictions exhibit modestly larger compressibility in both the shock velocity versus particle velocity and pressure versus specific volume plots of the data. This discrepancy is readily accounted for by the 10-15% aluminum oxide mineral in the mixture which does not undergo shock-induced phase transformation within the pressure range of the data. The present equation-of-state model leads naturally to the characterization of the extreme pressure equation-of-state of mixtures.

5. Closure
Central to the present study is the thermo-elastic equation-of-state description of the high-pressure shock compression of compounds and mixtures of compounds that occur in the initial state over a wide
range of initial distension. The less-commonly used Rice-Walsh form of the equation-of-state surface is applied in the present study. The Rice-Walsh equation of state exhibits features that lend its application to shock-wave compression of highly distended materials where often multi-valued Hugoniot compression curves are common.

The study also reveals that shock-induced phase transformation on the Hugoniot is common to many of the compounds of interest. Further, the extent of phase transformation is shown from the experimental Hugoniot data to be dependent on the initial distension of the test material. The present authors suggest that accelerated phase transition is a consequence of excessive deformation and stress heterogeneity brought about by the shock compaction of distended material [4]. Other workers have proposed that observations are indicative of range of Hugoniot behavior characterized by a negative thermodynamic Gruneisen parameter [5].

![Figure 4. Shock Hugoniot data for two sample densities of Nevada Test Site alluvium. Equation-of-state representation is based on equation-of-state constants for silicon dioxide.](image)

Dependence of phase transformation on the initial state of distension of the material is incorporated into the present Rice-Walsh equation-of-state model. Shock Hugoniot data available from the literature for near-full-density and porous silicon dioxide, boron carbide, uranium dioxide, tantalum pentoxide and playa alluvium are investigated with the present equation-of-state model. Generally, the wide-ranging Hugoniot data are sensibly represented by the Rice-Walsh equation of state accounting for phase transformation.

References
[1] Rice M H and Walsh J M 1957 J. Chem. Phys. 26 824
[2] Anderson O L 1967 J. Geophys. Res. 72 3661
[3] Grady D E 2012 AIP Conf. Proc. 1426 800
[4] Grady D E and Fenton G and Vogler T 2013 Int. J. Impact Eng. 56 19.
[5] Lane J M D and Vogler T J 2013 Am. Phys. Soc. March Mtn. (abstract only)
[6] Medvedev A B and Trunin R 2012 Physics Uspekhi 55 773
[7] Trunin R F et al. 2001 Experimental Data Shock Compression and Adiabatic Expansion of Condensed Matter (Sarov: RFNC-VNIIEF)
[8] Goplen B 1970 Los Alamos Scientific Laboratory Tech. Rep. LA-4319
[9] Gust W H 1982 J. Nuc. Materials 107 290
[10] McQueen R G and Marsh S P 1962 Los Alamos Scientific Laboratory Tech. Rep. LAMS-2760