A Mie-Grüneisen EOS with non-constant specific heat

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Abstract. A complete and consistent equation of state based on Mie-Grüneisen assumptions was developed. This EOS assumes constant Grüneisen coefficient, but a variable specific heat that is modeled using Einstein’s theory of heat capacities using two oscillators. The shock velocity particle velocity Hugoniot (U_s-u_p) was derived from density functional theory molecular dynamics (DFT-MD). The EOS was formatted as a tabular EOS and checked for consistency using one-dimensional impact simulations in CTH.

1. Introduction
Mesoscale simulations of explosive initiation and growth have increased in fidelity and use due to the desire of researchers to understand hot spot formation and growth at a more fundamental level. Researchers have employed this technique to investigate hot spot physics on several length scales, including single pores, several pores and/or particles, and domains on the scale of the run distance [1–4]. When attempting to model pore physics directly, the fidelity of the EOS is critical, because of the difficulty in measuring directly the state of nanometric sized collapsing pores and surrounding material.

Many reactive burn models for hydrocode simulation can accurately match certain properties inherent to heterogeneous materials, such as the run-to-detonation distance, reaction zone thickness, and corner turning [5–7]. The mesoscale description of a material, however, does not lend itself to intuitive application of these models when pores are modeled discretely. Reactive burn models that use basic physical principles, such as an Arrhenius reaction rate, use the material temperature to determine the rate of conversion from reactants to products, and so require accurate temperatures to be employed in a predictive sense. Mie-Grüneisen type EOS have been used in hydrocodes for decades, however the temperature is not usually the desired state variable, and is often calculated as an afterthought. Menikoff has outlined several approaches for complete EOS based on Mie-Grüneisen techniques [8,9]. The EOS discussed here is an attempt to provide more realistic temperatures for use in mesoscale models, and is derived from Mie-Grüneisen assumptions.
2. Equation of State

Arbitrary states present in the material are referenced from the Hugoniot, and so the jump equations,

\[ \mu = 1 - \frac{\rho_0}{\rho} = \frac{u_p}{U_s}, \]  
\[ P_H = P_0 + \rho_0 U_s u_p = \rho_0 \mu U_s^2, \]  
\[ E_H = E_0 + P_0 \frac{\mu + P}{2\rho_0} \]  

are listed for completeness. Initial pressure has been arbitrarily set to zero in the final statement of equation (2) and equation (3). Because we have chosen the Einstein model for specific heat, the reference energy \(E_0\) is naturally and analytically defined as

\[ E_0 = \int_{T_0}^{T} c_v(T) \, dT. \]  

The constants in the quadratic \(U_s-u_p\) relation,

\[ U_s = c_0 + s_1 u_p + \left( \frac{s_2}{c_0} \right) u_p^2, \]

are obtained through DFT-MD calculations that are discussed in [10]. The shock speed,

\[ U_s(\mu) = \frac{2c_0}{1 - s_1 \mu + \sqrt{(s_1 \mu - 1)^2 - 4s_2 \mu^2}}, \]

can also be expressed in terms of \(\mu\) for derivation of the sound speed along the Hugoniot. The temperature along the Hugoniot is determined iteratively from

\[ \int_{T_H}^{T} c_v(\hat{T}) \, d\hat{T} = \frac{(\mu U_s)^2}{2} + e^{\Gamma_0 \mu} E_0 - e^{\Gamma_0 \mu} \int_0^{\mu} \left( 1 - \frac{\Gamma_0 \hat{\mu}}{2} \right) \hat{\mu} U_s^2 e^{-\Gamma_0 \hat{\mu}} \, d\hat{\mu}. \]

The last term on the right is encountered throughout the derivation, and so is named \(I_1\). By invoking the Mie-Grüneisen assumption,

\[ \left( \frac{\partial p}{\partial E} \right)_\rho = \rho \Gamma = \rho_0 \Gamma_0, \]

an expression is obtained for arbitrary pressure,

\[ P(\mu, \epsilon) = P_H(\mu) + \rho_0 \Gamma_0 [E - E_H(\mu)]. \]

Arbitrary energy (or temperature through iterative solving),

\[ E(\mu, T) = E_H + \int_{T_H}^{T} c_v(\hat{T}) \, d\hat{T}, \]

is found by manipulating thermodynamic relations and referencing the cold curve. Finally, the entropy is derived from the definition of Helmholtz free energy and Gibbs relations,

\[ \eta(\mu, T) = \int_{T_0}^{T} \frac{c_v(\hat{T})}{\hat{T}} \, d\hat{T} - \frac{E_0 \Gamma_0 \mu}{T_0}. \]
Isentropic properties were also determined through manipulation of thermodynamic identities. The isentropic pressure,

\[ P_{\eta} = P_H \left( 1 - \frac{\Gamma_0 \mu}{2} \right) + \rho_0 \Gamma_0 I_1, \quad (12) \]

is determined by manipulation of the Gibbs relations. For energy along the isentrope,

\[ E_{\eta} = I_1 + E_0, \quad (13) \]

equation (9) is employed at the isentropic pressure. Finally, the isentropic temperature is found by employing equation (10) at the isentropic temperature, and combining the cold curve energy with equation (13) resulting in

\[ E_0 e^{\Gamma_0 \mu} = \int_0^{T_0} c_v dT, \quad (14) \]

which can be solved iteratively.

3. One-dimensional impact

Following the mathematical development of the EOS, the theory was employed to generate a tabular EOS for Hexanitrostilbene (HNS) using the SESAME \[12\] format. In order to verify correct implementation, and highlight the importance of proper EOS treatment, a series of one-dimensional impact studies were performed using CTH, a multi material, multidimensional Eulerian shock physics code \[11\]. The simulations consisted of PMMA flyers of varying velocities impacting a block of inert HNS. Figure 1 shows the results of the temporal and spatial grid resolution studies, resulting in a cell size choice of 50 \( \mu m \).

\[ \begin{array}{c}
\text{Hugoniot Temperature (K)} \\
\text{Hugoniot Pressure (GPa)}
\end{array} \]

\[ \begin{array}{c}
dt \leq 1e^{-07} s \\
dt \leq 1e^{-08} s \\
dt \leq 1e^{-09} s
\end{array} \]

**Figure 1.** Temporal and spatial grid resolution study corresponding to a flyer impact velocity of 4.7 km/s and Hugoniot pressure of approximately 21 GPa.

The CTH simulation results were compared to the analytical values, as well as to values from the BCAT code \[13\]. The \( P-v \) Hugoniot shown in figure 2 shows agreement between these separate methods that is typical for all of the state variables. Figure 3 also shows similar agreement between methods, but highlights the drastic difference in temperature due to the treatment of
It is important to note that at inert shock pressures typical of flyer-impact, the difference in temperature is on the order of 100-200 K. Although these temperatures seem modest, in reactive burn models that use temperature dependent kinetic schemes, the difference is critical. This EOS was developed for the purpose of more accurately capturing temperatures at extreme states for mesoscale models of initiation. The modest difference in temperature that is captured by assuming a variable \( c_v \) will greatly affect the reaction zone thickness, run-to-detonation distance, and initiation characteristics of these models. As these mesoscale models increase in accuracy, the results can be used in developing new classes of predictive continuum models.

\[ \begin{align*}
\text{Figure 2. } & P-v \text{ Hugoniot with variable and constant } c_v \text{ shown.} \\
\text{Figure 3. } & T \text{ along the Hugoniot with variable and constant } c_v \text{ shown.}
\end{align*} \]

4. Conclusion
An EOS for HNS was developed based on Mie-Grüneisen assumptions, and including the effects of a variable specific heat. In addition to mechanical state variables, temperature and entropy are also globally defined. This EOS is thermodynamically consistent and complete. The EOS was verified by comparing impact simulation results to analytical results, as well as results from other
codes. The more realistic temperatures are anticipated to make a large impact in the fidelity of mesoscale impact initiation studies. Further developments of this EOS are anticipated, such as treatment of the constant Grüneisen coefficient.

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