SAND2019-8672C

An Improved Temperature-Dependent Specific Heat Model for Unreacted Explosive Equations of State

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Abstract. The any Mie-Grüneisen Equation of State (AMEOS) model in CTH was calibrated for four unreacted homogeneous explosives in temperature-volume space: HMX, TATB, PETN, and RDX. AMEOS employs a multi-term Einstein oscillator function, which is used to fit the specific heat over a range of temperature values. Here, this model is used to calculate a family of Hugoniot temperature curves that are much lower than for a constant specific heat approximation. Moreover, there is limited thermal EOS data which is extrapolated to the classic Dulong-Petit limit. Mesoscale simulations with Arrhenius burn models require this type of thermodynamically complete EOS for accurate temperature-based reaction rates. The improvements with temperature dependent versus constant specific heat are discussed, in addition to the Einstein oscillator coefficient fits for the four different homogeneous explosives considered.

INTRODUCTION

Accurate temperature predictions, including those made along the principal shock Hugoniot, are critical to the energetics community for several reasons. When studying the shock loading of high explosives, these reasons may include: (1) the simulation of hot spot formation and growth, (2) predicting the sub-detonation response of heterogeneous explosives, and (3) simulating the shock to detonation transition (SDT) in mesoscale simulations that include explicit chemistry. Unfortunately, Hugoniot temperatures (as well as some of the off-Hugoniot states) are inherently difficult to calculate in the shock regime. They depend on the Equation of State (EOS), and a thermodynamically complete EOS is needed to provide the most accurate predictions of the Hugoniot temperature. Currently, there is limited thermal EOS data available at elevated temperatures for explosives (chemical decomposition prevents the elevated-temperature measurements). Oftentimes, this limited thermal data must be extrapolated to the Dulong-Petit limit, which is an estimate for the maximum heat capacity based on the number of molecular degrees of freedom. In addition, mesoscale simulations with Arrhenius burn models (or explicit chemistry) require thermodynamically complete Equations of State for predicting accurate temperature-based reaction rates. In this study, we leverage a new EOS model in CTH [1] called AMEOS [2], which incorporates Cv(T) data from Baer [3]. AMEOS uses the thermal data, together with the experimental shock-particle Hugoniot data, to form a complete EOS for a single-phase, homogeneous material. In this work, AMEOS was calibrated for four unreacted homogenous explosives (HMX, PETN, RDX, and TATB) in temperature-volume space. Hugoniot temperatures are then predicted by the AMEOS model, and they are compared to those predicted using the standard Mie-Grüneisen EOS in CTH (i.e. MGR).

AMEOS

Currently, the AMEOS model is a beta capability in CTH version 12.1. This model was partly conceptualized in a paper by Kittell and Yarrington [4], although some improvements have been made since the original publication. It

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is a generalized framework for constructing any Mie-Grüneisen EOS utilizing three sub-models. These sub-models include input for a Grüneisen parameter (GEQ), reference curve (REQ), and a specific heat model (CEQ). The three independent sub-models are combined in a way that is both thermodynamically consistent and numerically efficient. Here, Eqs. 1-3 describe the sub-models used in this study (GEQ, REQ, and CEQ respectively). However, the AMEOS framework can accept several alternative forms for Eqs. 1-3 that are found throughout the literature. The sub-model equations are given by,

$$\Gamma(v) = \Gamma_0 \left(\frac{v}{v_0} \right)^m \quad \text{where m=1,} \tag{1}$$

$$U_s = C_s + S_1 u_p + \left(\frac{S_2}{C_s} \right) u_p^2, \tag{2}$$

and

$$C_v(v_0, T) = \sum_{i=1}^{N} C_{vi} E_i \left(\frac{\Theta_i}{T} \right) \quad \text{where} \quad E_i(x_i) = \frac{x_i^2 e^{x_i}}{\left(e^{x_i} - 1 \right)^2}. \tag{3}$$

METHODS

The experimental heat capacity data used in this work comes from a wide survey of the literature, and was compiled by M. R. Baer over the years working at Sandia [3]. This data primarily corresponds to experiments that measured specific heat at constant pressure, Cp(T), up to the thermal decomposition temperature. A conversion is needed to use the data for parameterizing the CEQ model in AMEOS; specific heat at constant volume, Cv(T), is calculated using the Cp(T) data along with the Grüneisen parameter and coefficient of thermal expansion. The conversion formula is given by,

$$\frac{Cp}{Cv} = 1 + \Gamma_0 \left(\frac{\rho_0}{\rho} \right) (\alpha_v T), \tag{4}$$

where α_v is the volume coefficient of thermal expansion and Γ_0 is the value of the Grüneisen parameter at the reference density. This conversion was made for all the materials compiled by Baer [3], including many elemental metals and homogeneous explosives; however, this work is focused on HMX, PETN, RDX, and TATB. The specific heat data for high explosives is currently available for relatively low temperatures (<500 K) due to the limitations imposed by thermal decomposition. However, molecular dynamics (MD) simulations and density functional theory (DFT) results may be included to augment the experimental data (e.g., available MD results for HMX extend the temperature range up to 3000 K). Fig. 1 shows the converted literature data (circles) as well as the parameterized multi-term Einstein oscillator sub-model (lines).

In summary of Fig. 1, the CEQ model is based on a multi-term Einstein oscillator function (see Eq. 3) that has been tuned to fit the available data, as well as the classical limit using as few terms as possible. In most cases, the data is fit using only 2 terms; however, some materials require additional terms, while for a few materials a single term is sufficient. AMEOS is then used to combine the CEQ parameterization with additional Hugoniot data to give a thermodynamically complete EOS. Table 1 shows the Cv_i coefficients and Θ_i terms used in Equation 3 in CTH base units for each explosive studied (these units are erg/gram/eV and eV, respectively). Note: 1 eV corresponds to 11604.5 K for all temperature conversions in CTH.

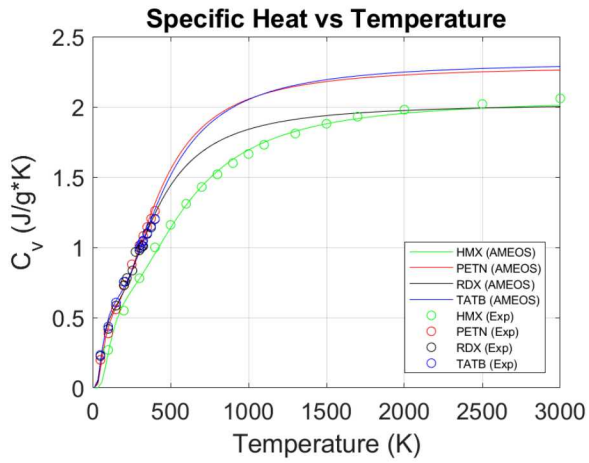

FIGURE 1. Hugoniot temperature as a function of specific volume for four explosives, including collected data and curve fits.

TABLE 1. Coefficients for four explosives for use in CEQ equation.

Explosive	Cv1	Theta 1	Cv2	Theta 2
HMX	9.64E10	3.49E-2	1.43E11	1.77E-1
PETN	7.99E10	2.09E-2	1.86E11	1.19E-1
RDX	7.7E10	1.79E-2	1.58E11	1.13E-1
TATB	8.53E10	1.93E-2	1.84E11	1.29E-1

RESULTS AND DISCUSSION

Hugoniot temperatures were calculated using both the AMEOS model and the standard Mie-Grüneisen model in CTH, and the results are shown in Fig. 2. For each explosive studied, the AMEOS and MGR results are shown as the blue and orange curves, respectively. While each of the four materials has a slightly different reference density, all temperature calculations between the range of specific volumes of 0.45 to 0.55 cm^3/g (or 1.82 to 2.22 g/cm^3 in density space) are very similar between AMEOS and MGR. The largest temperature deviations occur near 0.4 cm^3/g and above, where MGR tends to overpredict the Hugoniot temperature compared to AMEOS.

In general, it is true that the standard Mie-Grüneisen model with a constant specific heat overpredicts the Hugoniot temperature for a given shock pressure. While the difference between the two EOS models is relatively small near the reference volume (i.e. origin of the Hugoniot), even a difference of 50 to 100 K is enough to dramatically affect the Arrhenius kinetics of a reactive flow simulation, or a mesoscale simulation with explicit chemistry. However, as the specific volume decreases, this difference grows and the standard Mie-Grüneisen EOS increasingly overpredicts the Hugoniot temperature in the explosive; this will contribute to even larger errors using a Arrhenis-type rate law.

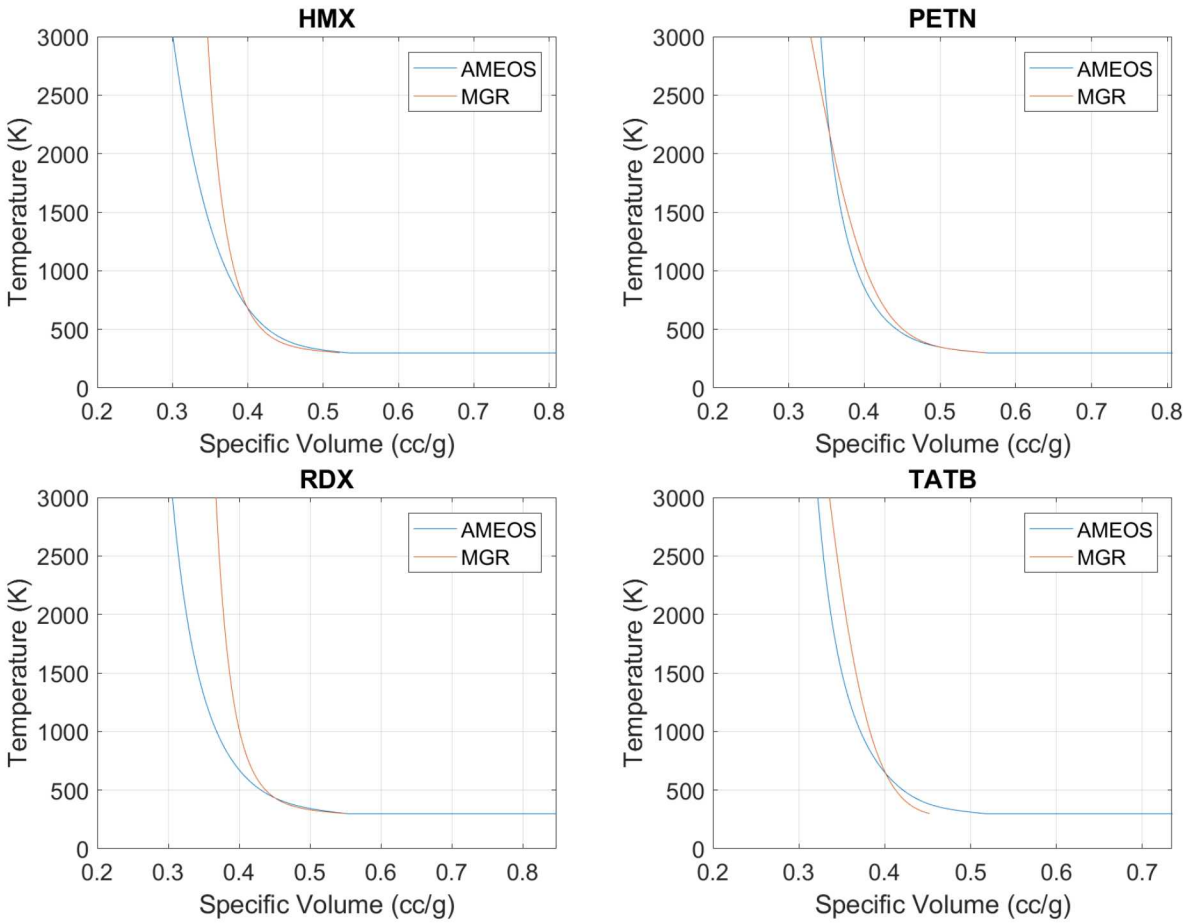

FIGURE 2. Hugoniot temperature vs. specific volume for four homogeneous explosives shown in (a)-(d), corresponding to HMX, PETN, RDX, and TATB, respectively. Results from AMEOS (blue) and MGR (orange) are shown in the same plot.

Table 2 gives quantitative differences between the two Equations of State for each explosive at a given specific volume.

TABLE 2. Comparison of predicted Hugoniot temperatures between AMEOS and the standard Mie-Grüneisen EOS for four explosives.

Explosive	Specific Volume (cc/g)	AMEOS Temperature (K)	Standard MGR Temperature (K)	Temperature Difference (K)
HMX	0.36098	1173.3	1833.2	659.9
PETN	0.375035	1334.4	1576	241.6
RDX	0.400961	667	995.82	328.82
TATB	0.350408	1491.2	2196.8	705.6

CONCLUSIONS

It has been shown that AMEOS can be used to take empirical specific heat data and Hugoniots to describe a thermally complete EOS. This EOS is more physically based for temperature than the standard Mie-Grüneisen EOS

that is in CTH. This difference between the two Equations of State can be seen in their Hugoniot temperature predictions for four common high explosives (HMX, PETN, RDX, and TATB). Both AMEOS and a standard Mie-Grüneisen EOS models were used to calculate Hugoniot temperature as a function of specific volume. In general, AMEOS predicts a lower Hugoniot temperature for a given shock pressure. The overprediction of the standard Mie-Grüneisen EOS could be upwards of 700 K. This difference in prediction could have a significant effect on a model's kinetics for example.

ACKNOWLEDGMENTS

The authors would like to thank M. R. Baer for allowing the use of his specific heat data for this work. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S .Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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