The objective of this work is to improve the robustness and accuracy of numerical simulations of both ideal and non-ideal explosives by introducing temperature dependence in mechanical equations of state for reactants and products.

To this end, we modify existing mechanical equations of state to appropriately approximate the temperature in the reaction zone. Mechanical equations of state of Mie-Grüneisen form are developed with extensions, which allow the temperature to be evaluated appropriately, and the temperature equilibrium condition to be applied robustly. Furthermore the snow plow model is used to capture the effect of porosity on the reactants equation of state.

We apply the methodology to predict the velocity of compliantly confined detonation waves. Once reaction rates are calibrated for unconfined detonation velocities, simulations of confined rate sticks and slabs are performed, and the experimental detonation velocities are matched without further parameter alteration, demonstrating the predictive capability of our simulations. We apply the same methodology to both ideal (PBX9502, a high explosive with principal ingredient TATB) and non-ideal (EM120D, an ANE or ammonium nitrate based emulsion) explosives.

I. INTRODUCTION

This work is concerned with the numerical simulation of detonation waves propagating in confined non-ideal explosives, which exhibit velocities of detonation (VoD) lower than the ones predicted by the Zeldovich-Von Neumann-Döring (ZND) theory. Accurate calculation of the VoD for a broad range of confining materials is important for industrial applications such as mining, where a priori knowledge of the performance of the explosive is necessary in order to optimize blasting operations.

Numerical simulation is useful only if it is genuinely predictive. In the context of mining this means that once the computational model is calibrated for a particular explosive using unconfined detonation data, it can then be used to predict VoD curves for other confiners, without any further parameter adjustment. The material properties and the behavior of an explosive are captured in a mathematical model by means of the equations of state (EoS) for the reactants and the products and the reaction rate law. Although they are both important in characterizing an explosive, in this work we focus on improving the EoS models.

Commonly used EoS models are in Mie-Grüneisen form (such as the JWL EoS\(^1,2\)) for the detonation products and the shock Mie-Grüneisen EoS for the reactants\(^2,3\)) and they relate pressure, volume and energy. These EoS models are considered to be incomplete because they do not involve the temperature. However, there are strong motivations for using a temperature capable EoS, not least because these are necessary for temperature-dependent reaction rate laws. Even if a pressure-based rate law is used, we have found that in comparison to incomplete EoS models these allow for more robust implementations of reduced multi-phase formulations\(^4-6\) which employ a temperature equilibrium condition between reactants and products which coexist in the reaction zone. Moreover, to ensure the existence of physical solutions to the temperature equilibrium equation, we require EoS models with which to recover temperatures.

Important previous work on this topic includes the paper by Wescott et al.\(^7\) (referred to as the WSD model), which presented temperature capable EoS models for modeling the reactants and products of PBX9502. Those formulations consist of a mechanical EoS of Mie-Grüneisen form with an additional temperature reference curve. In particular they use the relationship between the Grüneisen gamma and the variation in temperature along the reference curve of the Mie-Grüneisen EoS, a relationship which only holds if the reference curve is isentropic\(^7-9\).

An alternative approach for calculating temperatures is presented by Menikoff\(^10\) using a thermal model derived from a vibrational spectrum from Raman scattering. Temperatures calculated in this way have also been leveraged for EoS calibration by Aslam\(^11\). Kittell and Yarrington\(^12\), on the other hand, derive an expression for post-shock temperatures using a multi-term Einstein oscillator model for the specific heat capacity. In either case, the approach is reliant on data which for many explosives are unavailable.

Similar to the works referenced above, the objective of the present work is to improve the robustness and accuracy of numerical simulations by introducing temperature dependence in mechanical EoS models for reactants and products. We focus on EoS models applicable to both ideal and non-ideal explosives. We use the ANFO based emulsion EM120D as an example of a non-ideal explosive; the VoD in narrow rate sticks can deviate from
The evolution of the fluid is calculated using forces arising from gradients in the pressure field, so an equation of state (EoS) relating the pressure, $p$, to the conserved variables is required, such that

$$ p = f(v, e), $$

where $v$ is the specific volume, and $e$ is the specific internal energy.

A standard form for this purpose is the Mie-Grüneisen EoS\textsuperscript{14} given as

$$ p - p_{\text{REF}}(v) = \frac{\Gamma(v)}{v} (e - e_{\text{REF}}(v)). $$

EoS models of Mie-Grüneisen form use reference functions, $p_{\text{REF}}(v)$ and $e_{\text{REF}}(v)$, of arbitrary form and complexity to encode the behavior of the material at hand. The reference curves specify a one dimensional path through the (two dimensional) EoS. States which are off the reference curve are approximated with what is effectively a first order Taylor expansion of the state at constant volume, which relates the deviation in pressure from the reference curve with the deviation in specific internal energy. This is done using the Grüneisen gamma, $\Gamma$, defined as

$$ \Gamma(v) = v \left( \frac{\partial p}{\partial e} \right)_v. $$

The Grüneisen gamma is in general a function of volume and entropy. However, equations of state of Mie-Grüneisen form approximate it as a function of the specific volume only. This approximation means that the EoS will only be valid for states that are relatively close to the reference curve. The reference curve should therefore be chosen to be a locus of states which are representative of the expected evolution of the material.

For the reactants, the commonly used shock Mie-Grüneisen EoS\textsuperscript{2,3} uses the Hugoniot curve as the reference curve, so that the state will remain on or close to the reference curve when the material is shocked. Its form is based on the assumption that the shock propagation velocity, $D$, is linearly related to the flow velocity behind the shock, $u$, such that

$$ D = a + bu, $$

where $a$ is the ambient speed of sound, and $b$ is a constant fitted to experimental data. This approximation fits experimental data well for most solids. It cannot however
where $\rho$ is the density and $\Gamma_0$ is the value at ambient density, $\rho_0$. This is a crude approximation, and thus the EoS is of limited use for modeling phenomena where the state deviates significantly from the reference curve.

The detonation products will expand adiabatically in a rarefaction wave after the chemical reaction is completed. A typical choice for the reference curve in the product EoS is therefore the adiabat corresponding to the rarefaction following an ideal detonation wave - the so-called ‘principal’ isentrope. Note that the adiabat is not necessarily isentropic, since the gaseous mixture may continue to react or undergo phase changes within the rarefaction. However, by taking the adiabat to be the isentrope of the detonation products, any further reactions or phase changes are implicitly accounted for in the product EoS. Cylinder tests can be used to measure the form of the principal adiabat (henceforth called the principal isentrope) in pressure-volume space experimentally.

The commonly used EoS for detonation products is the JWL (Jones-Wilkins-Lee) EoS, which fits the principal isentrope data to curves using a combination of one or two exponential terms and a power law in the volume.

Since no information is available for states away from the isentrope, a constant value for the Grüneisen gamma is assumed. This is not strictly valid, but it is the best approximation that can be made when using cylinder test data. Further problems with the JWL EoS are presented by Braithwaite et al. Using empirical EoS models for each of the product chemicals and mixture rules, an EoS for the product mixture can be constructed. An ideal detonation code (IDEX) can be used for this purpose. This code uses fluid EoS based on an intermolecular Buckingham alpha exponential 6 potential.

### A. Temperature

As discussed in the introduction, many formulations use a temperature equilibrium condition to allow for the mixing of materials governed by distinct EoS models. If this equilibrium condition is to be implemented, mechanical EoS models need to be extended so that the temperature of the materials can be approximated.

One approach to extend mechanical EoS models of Mie-Grüneisen form, is to supplement them with a reference function for temperature, $T_{\text{REF}}$, analogous to the standard reference functions for pressure and energy. The temperature reference function is closely linked to the Grüneisen gamma since

$$\Gamma = v \left( \frac{\partial p}{\partial S} \right)_v \left( \frac{\partial S}{\partial e} \right)_v = -v \frac{T}{T} \left( \frac{\partial T}{\partial v} \right)_S,$$

where use has been made of one of Maxwell’s relations

$$\frac{\partial^2 e}{\partial S \partial v} = -\left( \frac{\partial p}{\partial S} \right)_v \left( \frac{\partial T}{\partial v} \right)_S. \quad (7)$$

Note that the partial derivative in (6) is a derivative at constant entropy, $S$. The use of this relationship therefore relies on the reference curve being an isentrope.

Temperature values for states which deviate from the reference curve can be approximated by relating the temperature change with the change in specific internal energy using the specific heat capacity at constant volume, $c_v$,

$$T - T_{\text{REF}}(v) = \frac{e - e_{\text{REF}}(v)}{c_v}. \quad (8)$$

This approach defines an EoS with temperature without having to explicitly calculate any entropies. The fundamental assumption made here is that any changes in entropy (at constant volume) can be modeled using entropy-independent values for the Grüneisen gamma and specific heat capacities. Thus, the validity of these approximations relies on the entropy changes being small.

Note that in the present work the specific heat capacity at constant volume, $c_v$, is assumed to be constant. This assumption has been shown to be incorrect in some cases. An avenue for future investigation is to evaluate whether a volume-dependent or temperature-dependent specific heat capacity would lead to a significant improvement in the capability of the model.

### B. Products

Cylinder test experiments only provide data for the pressure and energy reference curves of the EoS. Hence, data must be leveraged from elsewhere if a complimentary reference function for the temperature is to be constructed. An ideal detonation code (IDEX) such as that presented by Braithwaite et al. can be used for this purpose. This code uses fluid EoS based on an intermolecular Buckingham alpha exponential 6 potential.

The program uses the chemical composition of an explosive to find the configuration of molecules which minimizes the Helmholtz free energy for a given temperature and volume. This also requires knowledge of the energy content of the explosive. If in practice the energy content is not known accurately, it can be reverse engineered using an experimental value for the ideal detonation velocity. Using empirical EoS models for each of the product chemicals and mixture rules, an EoS for the product mixture can be constructed. However, it is cumbersome to use such an EoS directly in hydrocodes. So instead the code is used to output pressure, energy and temperature data for the principal isentrope, which is used to calibrate numerical expressions for the reference functions.
Reference functions of the following form
\[ \rho = a v^b + c \exp(-dv) \]  
\[ e(v) = -\frac{a}{b + 1} v^{b+1} + \frac{c}{d} \exp(-dv) - Q \]
\[ T(v) = a_T v^{b_T} + c_T \exp(-d_T v), \]

where \( S_{CJ} \) represents the entropy of the CJ state which lies on the principal isentrope are then fit to the data. The energy reference function is obtained by integrating the pressure reference function, with integration constant \( Q \) representing the specific energy in the large volume limit. The value of the constant is arbitrary, but is by convention chosen to be the specific energy release associated with the conversion of material from reactants to products. The specific energy of the reactants in the large volume limit is set to zero. The energy release associated with the reaction from reactants to products is thus accounted for directly in the EoS.

The fitting process is done by fitting the high volume data to a power law first, and then adding the exponential term as a correction such as to also fit the low volume data and to satisfy the CJ criterion. In the large volume limit, where the exponential term goes to zero, the presence of the power law means that the isentrope approximately takes on the properties of an ideal gas and is well behaved even at volumes far larger than the volume range of the data used for the fitting.

In order to accurately reproduce the CJ pressure and ideal VoD it is important that the value and the derivative of the pressure reference function are exactly reproduced at the CJ state\(^{19,20}\). To this end, the parameters \( c \) and \( d \) are fixed in terms of \( a \) and \( b \) using
\[ p_{CJ} = av_c^b + c \exp(-dv_{CJ}) \]
\[ \frac{\partial p}{\partial v}_{S,v=v_{CJ}} = abv_{CJ}^{b-1} - cd \exp(-dv_{CJ}) \]
\[ d = \frac{abv_{CJ}^{b-1} - \frac{\partial p}{\partial v}_{S,v=v_{CJ}}}{p_{CJ} - av_c^b} \]
\[ c = \exp(dv_{CJ})(p_{CJ} - av_c^b). \]

The form of the function for the Gruneisen gamma is derived from (6) and (11). The chosen form for \( T_{S,CJ} \) is shown to be suitable in Figure 1 which demonstrates that for the products of PBX9502 the Gruneisen gamma is well behaved across the whole range of volumes - it never diverges, nor does it go negative or close to zero. This takes the form:
\[ \Gamma(v) = -\frac{a_T b_T v^{b_T-1} - c_T d_T \exp(-d_T v)}{a_T v^{b_T} + c_T \exp(-d_T v)}. \]

The physical interpretation of the parameters is discussed further in Section II C since the same form is used for the reactants.

We calibrated EoS models for the products of the two explosives PBX9502 and EM120D. The parameters are presented in Table I. Note that for PBX9502, the ideal detonation velocity of 7755 m s\(^{-1}\) from Jackson and Short\(^{21}\) was used to calibrate the heat of reaction, since \( IDeX \) predicts a slightly higher ideal detonation velocity of 7933 m s\(^{-1}\). For EM120D, on the other hand, the ideal detonation velocity is taken to be the one which is predicted by \( IDeX \). Figures 2 and 3 show the reference curves along with the constituent exponential and power law terms. This is to show that the presented fitting parameters are such that the power law is the dominant term, especially in the large volume limit.

Having calibrated the EoS to fit the principal isentrope, it cannot be assumed that the EoS will accu-
FIG. 2. A fit to the principal isentrope from IDeX for PBX9502. The principal isentrope data are given as blue dots. The fit (red) is the sum of the power law (cyan) and the exponential curve (green). The energy reference curve also includes a non-zero constant, $Q$, corresponding to the energy content of the explosive.

FIG. 3. A fit to the principal isentrope from IDeX for EM120D.

FIG. 4. The EoS calibrated using the ideal detonation code data is used to calculate the Crussard curve for PBX9502. It matches the experimental data from Tang et al.\textsuperscript{22} reasonably well. The CJ state is at the intersection of the Crussard curve with the Rayleigh line.

C. Reactants

A methodology presented by Davis\textsuperscript{9} can be used to construct an EoS for explosive reactants using an isentropic reference curve. An equation for the isentrope pressure is derived using the assumption of a linear $D,u$ relationship (4) as is used in the shock Mie-Grüneisen
\[ D = a + bu \]  
\[ p_{\text{REF}}(v) = \frac{\rho_0 a^2}{4b} \left[ \exp(4b(1 - v/v_0)) - 1 \right] \]  
\[ e_{\text{REF}}(v) = \left( \frac{a}{4b} \right)^2 \left[ \exp(4b(1 - v/v_0)) - 1 \right] + \frac{\rho_0 a^2}{4b} \left( v - v_0 \right) \]

Note that these expressions for the pressure and energy reference curves do not diverge in the limit of small volumes, but grow sufficiently quickly to avoid potential practical issues.

Data for the volume and pressure on the Hugoniot curve can be used to calibrate the Grüneisen gamma. Across a shock wave the entropy increases, and thus states on the Hugoniot curve lie above the reference curve which is an isentrope. The deviation between the Hugoniot curve and the isentrope is related to the Grüneisen gamma. Note, however, that in practice this calibration process is somewhat ill-conditioned. Small relative errors in pressure measurements for Hugoniot states be

The Grüneisen gamma must not diverge or go negative for a thermodynamically stable EoS\(^{23}\). To ensure that this is the case, we fit it with the same form that was used for the products EoS. The reference temperature is defined as a power law with a correcting exponential at small volumes \((11)\). The parameters of \( T_{1/3} \) are restricted to ensure that the EoS behaves normally: \( a_T, c_T \) and \( d_T \) are set to be positive, while \( b_T \) must be negative. The values of the parameters can be further constrained by observing that \(-b_T \) is the Grüneisen gamma in the limit of large volumes, where the EoS begins to behave like an ideal gas. As such we expect \(-b_T \) to have a value close to the ambient Grüneisen gamma, \( \Gamma_0 \),

\[ \Gamma_0 = \frac{\beta c^2}{c_p} \]  

where \( \beta \) is the ambient coefficient of thermal expansion, \( c \) is the ambient frozen sound speed and \( c_p \) is the ambient specific heat capacity at constant pressure. Furthermore we choose initial values for the fitting process such that the power law is the dominant term. As a result, the EoS will approach ideal gas-like behavior in the large volume limit.

1. Porosity Model

For porous materials of total specific volume, \( v_0 \), we define the crushing specific volume, \( v_{00} \), to be the specific volume of the matrix material - the material excluding the pores. Compression of the material at low densities requires little work, since it principally leads to closing of the pores, while the density of the matrix material remains largely unchanged. Compression at higher density, on the other hand, leads to compression of the matrix material and requires more work.

The leading shock at the front of a detonation wave compresses the material to volumes significantly smaller than the crushing volume. As such it is adequate to adapt the reference curves of the reactant EoS following the snow plow model\(^{24,25}\). The compressibility of the material at volumes larger than the crushing specific volume is taken to be infinity. In other words, it is assumed that the integral of pressure with respect to volume, which represents the work done compressing the material, is entirely due to the work done for compression beyond the crushing volume. The reference pressure on the isentrope is thus taken to be zero for larger volumes.

It is possible to calibrate the EoS such as to match the volume-pressure experimental data for the Hugoniot curve even without employing any porosity model. However the temperature and \( D,u \) relationship is significantly affected by the explosive porosity. Figure 5 shows how the temperature of the Hugoniot path is increased if the porosity of the reactants is captured using the method presented here. The explosive modeled is PBX9502 with an initial density of 1886 kgm\(^{-3}\). The density corresponding to the crushing specific volume\(^{26}\) is taken to be 1942 kgm\(^{-3}\).

It has been noted before that the \( D,u \) relationship for PBX9502 is not linear across all shock velocities\(^2\). Figure 6 shows however that an EoS constructed using a linear fit for the \( D,u \) relationship and extended with a porosity model will match the experimental data for moderate as well as strong shocks. Use of the porosity model here means a simple linear fit of the \( D,u \) data in the strong shock regime is sufficient to model a wide range of shock strengths. The WSD model\(^7\), on the other hand, uses a nonlinear fit to the \( D,u \) data.

Modeling porosity in this way can be problematic in the weak shock regime. The speed of sound in the porous reactants under ambient conditions is unphysical. This is because the compressibility of the porous material is of course finite, but we have assumed it to be infinite. Furthermore the predicted shock velocity is unphysical for weak shocks. Figure 6 shows that the Hugoniot curve in the \( D,u \) space curves towards zero in the limit of small \( u \). As such the snow plow model must be improved upon if for example ignition is to be modeled.

More complex models of porous materials, such as the \( P-\alpha \) model capture the effect of porosity for weak shocks much more accurately\(^ {27-30} \).

The curved shape of the \( D,u \) Hugoniot arising from the snow plow model matches that presented by Lambourn and Handley\(^ {31} \), Menikoff\(^ {15} \), and Schoch\(^ {32} \) (Appendix G) where the porosity is modeled explicitly using a multiphase model. In the multiphase model, the matrix material is represented by the shock Mie-Grüneisen EoS which is calibrated using data for the non-porous explosive. The
2. Temperature of Reactants in the Expansion Regime

The modeling of explosive reactants poses difficulties when states in the expansion regime occur\textsuperscript{23}. The data available for calibration relate exclusively to states under compression - which is the regime of interest for modeling shock waves. However states in the expansion regime can occur in the context of direct numerical simulation of detonation waves. The usual location of these states is far behind the detonation wave where the detonation products have rarefied and depressurised to ambient conditions. If the loss of pressure is fast, the explosive may stop burning while a small amount of reactants is still present. The pressure in these cells must be found by applying the usual pressure and temperature closure conditions. The EoS models must therefore be suitable for finding pressure equilibrium and temperature equilibrium under these conditions, even though the state has much less energy than typical cells in the reaction zone.

Other authors have also encountered this problem. Arienti et al.\textsuperscript{34} developed an approach for dealing with large volume states when using the shock Mie-Grüneisen EoS. Menikoff\textsuperscript{10} also introduces a work-around specifically for the expansion regime. Since states in the expansion regime will only occur far from the front of the detonation wave, outside the detonation driving zone, the handling of these states will not influence the predicted VoD. It is only required to ensure that the model can be applied robustly across the entire domain of the simulation.

Given the porosity model discussed above, the pressure reference curve is chosen to be exactly zero for volumes above $v_0$. It is clearly not isentropic in this regime, as such an additional term (which increases with volume) must be added to the temperature reference curve for large volumes. This ensures that the coefficient of thermal expansion,

\begin{equation}
\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p ,
\end{equation}

is positive for all volumes, including the expansion regime. This is essential for robust solution of the thermal equilibrium equations.

The form of this additional term required by the temperature reference curve in the expansion regime is calculated by considering the difference between the new $p_{REF}$ which has been set to zero for the purpose of modeling the porosity and the original form, $\tilde{p}_{REF}$,

\begin{equation}
 p_{REF} - \tilde{p}_{REF} = \rho \Gamma(v) \frac{T_{REF} - \tilde{T}_{REF}}{c_v} .
\end{equation}
The formulation of Michael and Nikiforakis (MiNi16) requires careful attention. In one dimension, the governing equations for the evolution of the three materials are

\[
\frac{\partial}{\partial t} \begin{pmatrix} z \rho_1 \\ (1-z) \rho_2 \\ \rho u \end{pmatrix} + \frac{\partial}{\partial x} \begin{pmatrix} z \rho_1 u \\ (1-z) \rho_2 u \\ \rho u^2 + p \end{pmatrix} = \begin{cases} 0 & \text{for } u \geq v_{99} \\ \frac{\rho_1}{\rho_\alpha} + \frac{1 - \lambda}{\rho_\beta} & \text{for } \rho \geq \rho_1 \\ \frac{\rho u^2}{\rho_\alpha} + z \rho_1 e_1 + (1-z) \rho_2 e_2 & \text{for } k \in \{1, \alpha, \beta\} \\ \rho_k - \rho_k \text{REF}(v_k) = \rho_k \Gamma_k(v_k)(e_k - e_k \text{REF}(v_k)) & \text{for } k \in \{1, \alpha, \beta\} 
\end{cases}
\]

The three materials correspond to the confiner (labeled 1), the reactants (\(\alpha\)) and the products (\(\beta\)). In addition, the reactants and products collectively form the explosive which is referred to as the second phase (labeled 2). Variables without subscript labels refer to the properties of the three material mixture. There is a single value for the flow velocity, \(u\), and the pressure, \(p\). The conversion from reactants to products is encoded in the reaction rate,

\[
K = \frac{\partial \lambda}{\partial t}.
\]

The mixing rules for the three materials are presented here along with a general EoS of Mie-Grüneisen form

\[
ρ = z \rho_1 + (1-z) \rho_2
\]  \hspace{1cm} (30)

\[
1 - \lambda = \frac{\rho_\alpha}{\rho_\beta} + \frac{1 - \lambda}{\rho_\beta}
\]  \hspace{1cm} (31)

\[
ρ E = \frac{1}{2} \rho u^2 + z \rho_1 e_1 + (1-z) \rho_2 e_2
\]  \hspace{1cm} (32)

\[
e_2 = \lambda e_\alpha + (1 - \lambda) e_\beta
\]  \hspace{1cm} (33)

\[
p_k - p_k \text{REF}(v_k) = \rho_k \Gamma_k(v_k)(e_k - e_k \text{REF}(v_k)) \quad \text{for } k \in \{1, \alpha, \beta\}
\]  \hspace{1cm} (34)

The summarized equations for the reactant EoS are

\[
\hat{\rho}_\text{REF}(v) = \frac{\rho_0 a^2}{4b} \left[ \exp (4b(1 - v/v_{99})) - 1 \right] - 1
\]  \hspace{1cm} (23)

\[
\hat{c}_\text{REF}(v) = \left( \frac{a}{4b} \right)^2 \left[ \exp (4b(1 - v/v_{99})) - 1 \right] + \frac{\rho_0 a^2}{4b} (v - v_{99})
\]  \hspace{1cm} (24)

\[
\hat{T}_\text{REF}(v) = a T v^{b_T} + c_T \exp (-d_T v)
\]  \hspace{1cm} (25)

\[
\hat{p}_\text{REF}(v) = \hat{p}_\text{REF}(v)
\]  \hspace{1cm} (26)

\[
\hat{c}_\text{REF}(v) = \hat{c}_\text{REF}(v)
\]  \hspace{1cm} (27)

\[
\hat{T}_\text{REF}(v) = \hat{T}_\text{REF}(v)
\]  \hspace{1cm} (28)

\[
\hat{p}_\text{REF}(v) = \hat{p}_\text{REF}(v)
\]  \hspace{1cm} (29)

\[
\hat{c}_\text{REF}(v) = \hat{c}_\text{REF}(v)
\]  \hspace{1cm} (30)

\[
\hat{T}_\text{REF}(v) = \hat{T}_\text{REF}(v)
\]  \hspace{1cm} (31)

\[
p_k - p_k \text{REF}(v_k) = \rho_k \Gamma_k(v_k)(e_k - e_k \text{REF}(v_k)) \quad \text{for } k \in \{1, \alpha, \beta\}
\]  \hspace{1cm} (32)

The equation for the Grüneisen gamma is the same as for the products EoS (16). Note that volume-pressure data for the Hugoniot curve are required to calibrate for the temperature reference curve of the EoS above. For the emulsion explosive EM120D, these data are not available. We therefore use the Hugoniot curve as calculated by Schoch\textsuperscript{32}, where the shock response of the porous material is modeled using a multiphase model. The parameters for the reactants of both explosives are presented in Table II.

### Table II. Parameters for the reactant EoS models for PBX9502 and EM120D.

|   | PBX9502 | EM120D |
|---|---------|--------|
| \(a\) | 2970 ms\(^{-1}\) | 2170 ms\(^{-1}\) |
| \(b\) | 1.81 | 1.82 |
| \(a_T\) | 5.141 | 2.073 |
| \(b_T\) | -0.5371 | -0.6867 |
| \(c_T\) | 258020 K | 22805 K |
| \(d_T\) | 19960 kgm\(^{-3}\) | 10660 kgm\(^{-3}\) |
| \(\rho_0\) | 1942 kgm\(^{-3}\) | 1400 kgm\(^{-3}\) |
| \(\rho_o\) | 1886 kgm\(^{-3}\) | 1210 kgm\(^{-3}\) |
| \(c_v\) | 1000 JK\(^{-1}\)kg\(^{-1}\) | 1000 JK\(^{-1}\)kg\(^{-1}\) |

D. Closure Rules for Coexistence of Materials

Modeling of non-ideal detonation waves requires resolution of the DDZ (detonation driving zone) — only cells in this zone play a role in determining the velocity of detonation. This zone includes part of the reaction zone in which the chemical reaction occurs. Since the reactants and products are modeled using independent EoS models, the coexistence of both materials in the reaction zone requires careful attention.

The mathematical formulation used in this work is the formulation of Michael and Nikiforakis (MiNi16)\textsuperscript{4}. In one dimension, the governing equations for the evolution of pressure and temperature equilibrium are applied. Thus
Unfortunately the closure conditions of pressure and temperature equilibrium, which are introduced to remove the degrees of freedom associated with space and energy distribution, do not permit a closed form expression for the pressure. The new equation (35) for the pressure is derived by substituting the component EoS models into the energy equation (32)

$$
\rho(E - \frac{1}{2}u^2) = p\left(\frac{z}{\Gamma_1(v_1)} + \frac{(1-z)\rho_2\lambda}{\rho_\alpha \Gamma_\alpha(v_\alpha)} + \frac{(1-z)\rho_2(1-\lambda)}{\rho_\beta \Gamma_\beta(v_\beta)}\right) + z\rho_1 \text{REF}_1 + (1-z)\rho_2 \text{REF}_\alpha + (1-z)\rho_2(1-\lambda) \text{REF}_\beta,
$$

where

$$
\text{REF}_k = \frac{-p_k,\text{REF}(v_k)}{\rho_k \Gamma_k(v_k)} + c_{k,\text{REF}}(v_k) \quad \text{for } k \in \{1, \alpha, \beta\}.
$$

In other words the mass of material \( \alpha \) in the cell cannot exceed the total amount of mass in the cell. If \( \rho_\alpha \) violates this restriction the result for \( \rho_\beta \) will be negative. This is easily understood when it is considered that equation (31) is an addition of volumes, each of which must necessarily be positive.

This is the fundamental reason that the set of equations is not guaranteed to have solutions. If equation (36) is considered on its own (assuming the pressure has some fixed value) without any restrictions on the densities, then it is guaranteed to have solutions for well behaved EoS models.

As the density of a material approaches zero, the temperature will also approach zero. In doing so the density of the other material will increase, and its temperature will accordingly increase. At some point these temperature curves are bound to cross; this is the point of temperature equilibrium. However this crossing point may be in the region that has been excluded by the restrictions on density (37).

It is thus not realistic to guarantee that the problem will have solutions for an arbitrary state. We can however ensure that the equations will have a solution for all realizable states by ensuring the thermodynamically consistent behavior of the EoS models in the limits of large and small volumes.

Firstly, the Gr"uneisen gamma must be positive and bounded for all possible volumes accessed by the simulation. The form of the fitting function chosen for \( T_{\text{REF}} \) ensures that this is the case as shown in Figure 1 which demonstrates that the limiting behavior of the Gr"uneisen gamma is appropriate for large volumes as well as large densities.

Secondly, the temperature must increase monotonically with volume at any fixed pressure. In other words the coefficient of thermal expansion (21) must be positive. This can be verified for given EoS parameters before running the simulation. For the product EoS the isobars were found to increase monotonically across all volumes, while for the reactants the isobars were found to have a minimum, but at sufficiently low volumes to play no role.
in the simulation. To ensure that anomalous roots at these unphysically small volumes do not appear, smaller volumes are explicitly excluded from the search domain.

III. MODELING OF DETONATION WAVES IN 1D

The equations of MiNi16 comprise a system of hyperbolic partial differential equations. The equations are solved numerically using a conservative finite volume method. By defining the flux with the Godunov scheme, the problem is reduced to solving a Riemann problem at each cell interface. The Harten, Lax and van Leer, Contact (HLLC) approximate Riemann solver is used. It was first presented by Toro, Spruce and Spears and is an extension of the HLL method. This is extended to second order using MUSCL-Hancock with the van Leer limiter.

The methods described above are implemented in a code developed at the Laboratory of Scientific Computing at the University of Cambridge. This code is capable of adaptive mesh refinement (AMR) and parallel execution through subdivision of the domain. Simulations of rate stick detonations can be greatly accelerated with adaptive mesh refinement, because the detonation wave has a complex structure, which is very narrow in comparison to the domain. A high resolution is required to resolve the detonation wave, but it is impractical to use the fine resolution for the whole domain.

The ZND model for the structure of one-dimensional detonation waves can be used to calculate the Rayleigh line, the von Neumann spike, the CJ state and the principal isentrope of the rarefaction wave. This can be done using solely the EoS models of the reactants and products, and the Rankine-Hugoniot conditions. Figure 7 shows the ZND wave for PBX9502 and compares the numerical simulation of a one-dimensional detonation wave with the calculated Rayleigh line and the principal isentrope from the ideal detonation code.

The blue markers indicate the evolution of the state in the explosive as a whole. The ambient depressurised state is in the bottom right. Across the shock wave (approximately three cells) the state approaches the predicted von Neumann spike (top left). As the explosive burns, the state of the explosive (blue) follows the Rayleigh line towards the CJ state. During this stage, the explosive is a mixture of reactants and products, which are at pressure equilibrium but have different specific volumes. The green and black markers represent the states of each material. Following the CJ state, the explosive consists entirely of products and rarefies following the principal isentrope.

The blue markers lie on the Rayleigh line as expected, and the rarefaction of the detonation products follows the principal isentrope as used for the calibration. This demonstrates that the calibration process is working as expected. Furthermore the speed of propagation of the wave is observed to be as predicted by the Rankine-Hugoniot equations.

Note that even in the reaction zone the state of the products lies roughly on the principal isentrope. This indicates that there is not much heat transfer between reactants and products in the reaction zone. The isentropic closure law could therefore be applied in place of temperature equilibrium leading to similar results.

However, this is not true in general. Figure 8 shows the equivalent plot for the emulsion EM120D. The product density at the front of the reaction zone places the state above the principal isentrope. This shows that in the first stage of the burning the temperature equilibrium constraint causes heat to transfer from products to reactants, and the reactants compress to a higher density than that corresponding to the von Neumann spike.

The extent to which heat transfer between reactants and products occurs is dependent on the temperature at the von Neumann spike as predicted by the EoS of the reactants, and how that temperature compares to the temperatures on the principal isentrope of the product EoS. To illustrate this dependence, Figure 9 shows the ZND wave for the emulsion EM120D but with the specific heat capacity of the reactants arbitrarily increased from 1000 J K\(^{-1}\)kg\(^{-1}\) to 1500 J K\(^{-1}\)kg\(^{-1}\). This change reduces the von Neumann spike temperature in the reactants and alters the behavior to be analogous to what is observed in the ideal explosive PBX9502. Depending on the heat capacities and other parameters which are known with little precision, the difference between a thermal equilibrium condition and an isentropic closure law may be of little significance. It is thus not possible to conclude definitively whether the thermal equilibrium condition is physically justified or otherwise.
It is currently impractical to model the chemistry of the reaction directly. A one-step reaction model is used to calculate the rate at which reactants transition to products. The parameters for this model must be calibrated using experimental VoD measurements. This does not preclude the ability to be predictive. It was found that in practice only a few measurements are required for the calibration of the parameters, and that these same parameters can be used to predict detonation velocities in a different context.

For the ideal explosive, PBX9502, the reaction rate is calibrated using VoD data for rate sticks of multiple radii. The resulting parameters are used to predict the VoD in slabs of varying thickness. For the less ideal explosive EM120D, data for unconfined rate sticks (air confinement) are used for the calibration. Predictions are then made for rate sticks confined by concrete and steel.

The simulation of rate sticks is carried out in two dimensions using the assumption of rotational symmetry about the axis of the rate stick. This requires the use of a geometric source term4.

The detonation wave is initiated using a booster - an area of high pressure gas which shocks the explosive, initiating the reaction. After the start of the simulation, the detonation wave must be modeled for some time to allow it to settle to its steady speed. After the wave has converged, the speed can be measured by simply observing the distance covered in some time interval. The measurement of the position of the shock wave introduces an error related to the discretisation of the grid. However the error in the speed measurement can be reduced by measuring the speed over longer time intervals.

For unconfined rate sticks and slabs, the confining air is modeled with a polytropic EoS with an adiabatic gamma of 1.4. For rate sticks of EM120D with solid confinement, the shock Mie-Grüneisen EoS is used with the same parameters as Schoch et al.42. Note that while the mathematical formulation uses a temperature equilibrium condition between reactants and products, only pressure equilibrium is used between the explosive and confiner4. As such, temperatures in the confiner are inconsequential and use of the shock Mie-Grüneisen EoS is appropriate.

A linear fit of experimental data for the shock speed provides the parameters $a$ and $b$ (4). The reference curves are

\[ p_{\text{REF}} = \frac{\rho_0 \chi a^2}{(1 - b \chi)^2} \]

\[ \epsilon_{\text{REF}} = \frac{1}{2} (v_0 - v) p_{\text{REF}} \]

\[ \rho \Gamma = \rho_0 \Gamma_0. \]

where $\Gamma_0$ is the ambient Grüneisen gamma, $\rho_0 = 1/v_0$ is the initial density and $\chi$ is defined as

\[ \chi = 1 - \frac{\rho_0}{\rho}. \]

The parameters are given in Table III.
The reaction rate is very difficult to measure experimentally or to evaluate on the basis of chemical arguments. In reality the explosive does not transition directly from reactants to products but undergoes many intermediate reactions associated with varying amounts of energy. For the purposes of the simulation, these processes are combined into a single pressure-dependent expression, $K$, for the reaction rate as is used by Schoch et al.\textsuperscript{42},

$$K = \frac{d\lambda}{dt} = -\lambda^{indx} \left( \frac{1 - a_h}{\tau_s} \right) + H (p - p_h) \frac{a_h}{\tau_h} \left( \frac{p [\text{Pa}]}{10^9} \right)^{N_p} \times 10^9, \quad (42)$$

where

$$a_h = \exp \left( - \left( \frac{1 - \lambda}{\omega_h} \right)^{N_a} \right).$$

The leading coefficient causes the reaction rate to slow as the reaction nears completion. The regression index of the reaction is $indx$. The second term represents the hotspot reaction, where $H(x)$ is a Heaviside function, and $p_h$ is the critical pressure required for ignition. The first term is a bulk burning term which determines the reaction rate once the explosive is fully ignited. The parameter $a_h$ is initially 1, causing the hotspot reaction term to dominate. As the reaction progresses, $a_h$ approaches zero, and the equation becomes dominated by the bulk burning term.

$\omega_h$ determines the degree to which the hotspot process consumes the available explosive. $\tau_s$ and $\tau_h$ determine the time scales of the reaction, and the constant $N_a$ controls the speed at which the hotspots transition to a bulk burning process. Note that it is the pressure in GPa which is raised to the power of $N_p$.

The calibration was carried out using data from Dremin\textsuperscript{45} (which is also used by Schoch et al.\textsuperscript{42}) for the weakly confined rate sticks. It is then demonstrated that the same parameters allow for predictions to be made for confined detonation waves. The only input required for the predictions is the EoS of the confining material.

It was found that the principal parameters affecting the VoD were $\tau_h$ and $N_p$. The other parameters were assigned the same values as were used by Schoch et al.\textsuperscript{42}. Since there were only two degrees of freedom in the calibration process, only two data points were required to fully constrain the system. These were chosen to be the detonation velocities for 20 mm and 30 mm rate sticks which were 4920 m s$^{-1}$ and 5470 m s$^{-1}$ respectively\textsuperscript{45}.

A two-dimensional implementation of the secant method was applied to minimize the discrepancy between the numerical results and the experimental data. For each radius three evaluations of the velocity with different parameters are required to construct a two-dimensional plane in three dimensional space relating the values of the parameters with the VoD. The intersection of this plane with the experimental VoD constitutes a line through the two-dimensional parameter space. The final step is to find the intersection between this line and a similarly calculated line for the second value of the radius.

This process is repeated iteratively until good agreement with the experimental EoS is found. The results of the calibration along with the other parameters are presented in Table IV.

$$D = D_{CJ} \left( 1 - \frac{A}{R - R_C} \right). \quad (43)$$

The resulting values for $A$ and $R_C$ are in Table V.

Table IV. Parameters for the reaction rate model for EM120D. See equation (42).

| $\tau_h$ | 13 $\mu$s GPa |
|---------|---------------|
| $\tau_s$ | 20 $\mu$s GPa |
| $p_h$ | 1.51 GPa |
| $indx$ | 0.667 |
| $\omega_h$ | 0.95 |
| $N_a$ | 9.0 |
| $N_p$ | 1.11 |

Table V. Parameters for the fits of the radial dependence of the VoD with rate stick radius for EM120D, with ideal VoD $D_{CJ} = 6.3895$ m s$^{-1}$.

| Confiner | $A$ [mm] | $R_C$ [mm] |
|----------|---------|----------|
| Air      | 3.73    | 3.5      |
| Concrete | 3.61    | -0.6     |
| Steel    | 1.94    | -2.8     |
The plot shows the radial dependence of the VoD for rate sticks of EM120D. The lines interpolate the numerical results (square markers) using Eyring fits. The circular markers with error bars are the experimental data. The experimental data for unconfined rate sticks that were used for the calibration are highlighted with magenta markers.

The fact that the calibration was successful using just two parameters and two data points demonstrates that the physics of the detonation waves is being captured well by the EoS models and the MiNi16 formulation. It also suggests that it may be possible to use an expression much simpler than (42) for the reaction rate and achieve the same predictive capability.

B. Calibration of Reaction Rate for PBX9502

For PBX9502 we use a simplified version of the ignition and growth model presented by Tarver and McGuire and used by Wescott et al. We calibrate the reaction rate model using VoD data for unconfined rate sticks. The model is used to predict the VoD in slabs of varying thickness. The predictions are then compared with experimental data.

The form of the reaction rate was chosen to be

$$K = r_{DG} S_G(\lambda),$$

where

$$r_{DG} = k_{DG} (1 - \lambda)^{1/3} \lambda^{N_A},$$

$$S_G = \frac{1}{2} (1 - \tanh(30(0.1 - \lambda))).$$

However we believe that the results presented here are compatible with a pressure dependent model. This could be achieved through modification of the form of the reaction rate or adjustment of the exponents.

The calibration was carried out using the same methodology as was applied for the emulsion in the previous section. In this case the two free parameters are $k_{DG}$ and $N_A$. The final value for $k_{DG}$ was 60.65 $\mu$s$^{-1}$, while $N_A$ was 1.56.

The results are shown in Figure 11. The parameters for the Eyring fits are given in Table VI.

V. CONCLUSIONS

The objective of this work is to improve the robustness and accuracy of simulations of ideal and non-ideal explosives by introducing temperature dependence in mechanical EoS models for the reactants and products. A methodology for constructing a model for generic explosives has been presented. This is summarized in Figure 12, which lays out the experimental data required and outlines the steps involved in the methodology’s application.

The reactant EoS was developed following Davis and is calibrated using experimental data for the Hugoniot curve, thus reproducing the desired shock-response behavior. The temperatures are derived solely from the Hugoniot data and the thermodynamics of the explosive.
in ambient conditions, since there is very limited thermal data available for explosive reactants. The EoS explicitly accounts for the influence of porosity on the post-shock temperatures using the snow plow model.

The product EoS is an adaptation of the JWL EoS which accommodates evaluation of the temperature. The reference curves are calibrated to data for the principal isentrope from the ideal detonation code IDeX\textsuperscript{13}. The ideal detonation code requires the chemical composition of the explosive as well as the energy content of the explosive in comparison to the detonation products. Note that if the energy content is unknown, then an experimental measurement of the ideal VoD can be used instead.

Use of the ideal detonation code not only permits the calculation of temperatures but more accurate values for a volume-dependent Grüneisen gamma. This is important, since in non-ideal detonation waves the state of the products is expected to lie below the reference curve of the EoS. Away from the reference curve, the validity of the EoS relies on an accurate expression for the Grüneisen gamma.

The methodology was applied to the non-ideal explosive emulsion EM120D and the ideal TATB based explosive PBX9502. The resulting models for the explosives were used in the context of the MiNi16 formulation\textsuperscript{4} to perform direct numerical simulation of the detonation wave and its interaction with the confiner. Results demonstrate that the solution of the nonlinear temperature equilibrium equation can be found robustly.

For EM120D, the predictive capability demonstrated by Schoch et al.\textsuperscript{32} was successfully reproduced. The methodology was shown to be capable of predicting the effect of strong confinement on the VoD, despite using only data for weakly confined rate sticks in the calibration process. For PBX9502, the methodology was applied to predict the dependence of the VoD on the geometry. The model was calibrated using rate stick data, and used to predict the VoD in a slab geometry. In each case, the predictions were verified using experimental data.

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Specific Volume [cm$^3$/g]

Pressure [GPa]

- Numerical ZND path
- Numerical reactant path
- Numerical product path
- Predicted Principal Isentrope
- Predicted Hugoniot curve
- Predicted Rayleigh line
Specific Volume \( [\text{cm}^3/\text{g}] \)

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