

Towards Finite Rate Chemical Kinetics Modeling of Detonation Afterburn Using the BKW Equation of State

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1 Introduction

High fidelity numerical simulations of high explosive (HE) detonation product afterburn are especially challenging due to the extreme ranges of thermodynamic states and flow scales involved. Immediately following detonation, the detonation product gases are at very high densities and pressures (e.g., 1 g/cc and hundreds of thousands of atmospheres), and they rapidly expand to near-atmospheric pressure, while mixing and burning with available oxygen. When modeling high-pressure detonation physics (e.g., shock-to-detonation transition), it is common to use an equation of state (EOS) for the detonation products that does not explicitly account for the chemical species that are present [1], e.g., the Jones-Wilkins-Lee EOS [2]. With our emphasis on late-time mixing and afterburn, we desire a model which includes detailed species information and allows finite-rate chemical transformations therein. For this purpose we adopt the well known Becker-Kistiakowsky-Wilson (BKW) EOS [3], which is an empirical real-gas EOS historically used for detonation performance calculations [4]. The BKW EOS is built upon a multi-species ideal gas mixture, making it well-suited for coupling to a detailed finite rate chemical kinetics scheme to model afterburn combustion. In the sections below we detail important aspects of such a model and show extensive verification tests conducted in the high-fidelity research hydrodynamics code HyBurn developed at the University of Florida.

2 Real Gas Equation of State and Verification

The BKW EOS is an empirical real-gas EOS of the form [5]

$$pV = NRTZ, \quad Z = 1 + x \exp(\beta x), \quad x = \frac{\kappa N}{V(T + \theta)^\alpha} \sum_{i=1}^m \chi_i k_i, \quad (1)$$

where p is the pressure, V is the volume, N is the number of moles, R is the universal gas constant, T is the temperature, Z is the compressibility factor, m is the number of species, χ_i is the mole fraction of species i , k_i is the geometrical covolume of species i , and α , β , θ and κ are calibration constants. At large volumes or high temperatures x becomes small and Z approaches unity, so that ideal gas behavior is retained by the EOS. We use the General Limit Method [6] to compute properties of the real-gas mixture through so-called departure functions. Due to space limitations and our emphasis on the finite rate chemical kinetics formulation in the next section, we do not summarize the departure functions here — see the Chemkin Real Gas manual by the late Bob Schmitt for an excellent summary [5].

Table 1: Summary of constant states appearing in the solution of the Sod-like Riemann problem. The “Left” and “Right” states form the initial conditions, and the “Star Left” and “Star Right” states (in the nomenclature of Toro [7]) are those intermediate constant regions appearing for $t > 0$.

Region	Left	Star Left	Star Right	Right
p (GPa)	10	0.04544	0.04544	0.0001
ρ (g/cc)	1.500	0.1225	0.01060	0.001155
T (K)	2837	926.5	14739	300
u (mm/ μ s)	1.500	5.915	5.915	0
a (mm/ μ s)	4.616	0.7519	2.245	0.3483

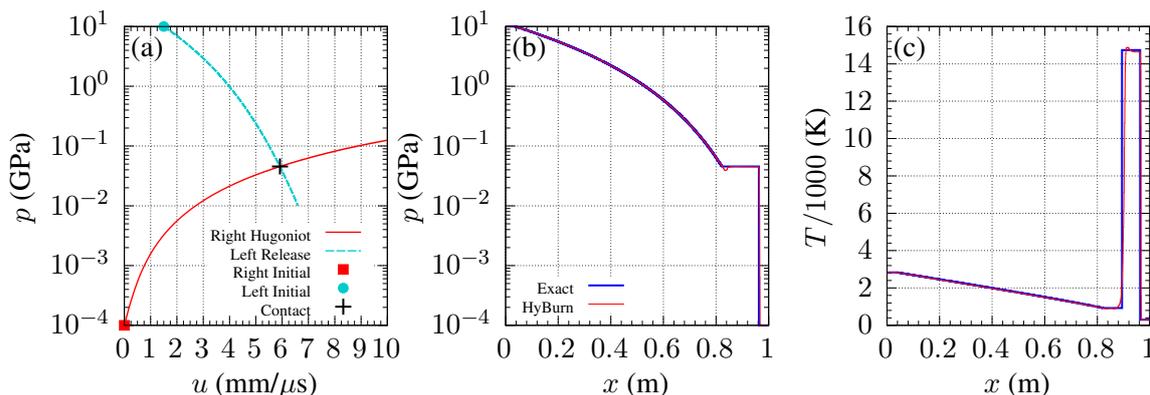


Figure 1: Exact and numerical solutions to Sod-like Riemann problem. Wave curves from TIGER used to compute the exact solution in frame (a). Pressure and temperature profiles in frames (b) and (c), respectively, after $t = 9.5 \times 10^{-5}$ s for an initial interface location $x = 0.33203125$ m.

To verify our implementation of the BKW EOS in HyBurn, we made extensive comparisons with the thermochemical equilibrium code TIGER developed by Sandia National Laboratories [4]. Point calculations for a mixture of CO_2 and O_2 over a wide range of (V, T) space encompassing regions with significant real-gas effects showed identical results between HyBurn and TIGER for energy, entropy, pressure, specific heat, Grüneisen parameter, sound speed, etc. To verify the EOS in the context of hydrodynamics, we again used TIGER to construct exact solutions to canonical 1-D Riemann problems, with left and right states that are relevant to HE detonation products expanding into air. For a Sod-like [7] Riemann problem, the chemical compositions are frozen, with $\chi_{\text{H}_2\text{O}} = 0.3$, $\chi_{\text{CO}_2} = 0.25$, $\chi_{\text{N}_2} = 0.25$, $\chi_{\text{CH}_4} = 0.1$, $\chi_{\text{H}_2} = 0.05$ and $\chi_{\text{CO}} = 0.05$ for the left state and $\chi_{\text{N}_2} = 0.79$ and $\chi_{\text{O}_2} = 0.21$ for the right state. The left, right and contact states for the Riemann problem are summarized in table 1, and a graphical solution to the Riemann problem using wave curves from TIGER is shown in frame (a) of figure 1. In frames (b) and (c) of figure 1 we compare the exact solution to HyBurn results computed using the HLLC Riemann solver with Einfeldt wave speed estimates, WENO5 reconstruction and a grid with 1024 cells in the direction normal to the interface. The results of these and other verification tests suggest the BKW EOS is implemented correctly and is properly integrated into the flow solver.

3 Finite Rate Chemical Kinetics Formulation

The elementary chemical reactions comprising a kinetics mechanism may be written as [8]



where m is the number of species M_i , ν'_i and ν''_i are the stoichiometric coefficients, and k_f and k_r are the forward and reverse reaction rate parameters, respectively. The net production rate for ideal gases is

commonly modeled with the law of mass action as

$$\frac{d\omega}{dt} = k_f \prod_{i=1}^m c_i^{\nu_i'} - k_r \prod_{i=1}^m c_i^{\nu_i''}, \quad (3)$$

where $c_i = N_i/V$ is the concentration of species M_i having N_i moles. The net production rate is zero at equilibrium, thus giving the following relation between the forward and reverse rate parameters

$$\frac{k_f}{k_r} = \prod_{i=1}^m c_i^{\nu_i'' - \nu_i'} = \prod_{i=1}^m c_i^{\Delta\nu_i}, \quad (4)$$

where $\Delta\nu_i = \nu_i'' - \nu_i'$ is the net stoichiometric coefficient for species M_i . When modeling non-ideal gases or mixtures, it may be more appropriate to evaluate kinetics rate expressions with activity concentrations instead of the standard concentrations appearing above [9]. Denoting the activity concentration $a_i = \gamma_i c_i$, with γ_i being the activity coefficient (discussed shortly), the net production rate is taken as

$$\frac{d\omega}{dt} = k_f \prod_{i=1}^m a_i^{\nu_i'} - k_r \prod_{i=1}^m a_i^{\nu_i''}, \quad (5)$$

and at equilibrium, we have

$$\frac{k_f}{k_r} = \prod_{i=1}^m a_i^{\Delta\nu_i}. \quad (6)$$

As we will see shortly, (6) is only a function of temperature and the stoichiometry of the reaction.

To ensure the finite rate kinetics scheme converges to the correct equilibrium, the reverse reaction rate parameter k_r is computed using k_f and the equilibrium constant on the right-hand-side of (6). The equilibrium constant is derived from the equation for chemical equilibrium $\sum_{i=1}^m \Delta\nu_i \mu_i = 0$, where μ_i is the chemical potential of species M_i . For real gases, the chemical potential is often written as [10]

$$\left. \begin{aligned} \mu_i &= \mu_i^0 + RT \log \left(\frac{f_i}{p_0} \right), \\ f_i/p_i &\rightarrow 1, \text{ as } p \rightarrow 0, \end{aligned} \right\} \quad (7)$$

where f_i is the fugacity of species M_i , p_0 is unit pressure, $\mu_i^0 = \mu_i^0(T)$ is the chemical potential of the pure species M_i at unit fugacity and is only a function of temperature, p is the pressure and $p_i = \chi_i p$ is the partial pressure of species M_i . Substituting in the fugacity coefficient $\phi_i = f_i/p_i$ and (1), we get

$$\mu_i = \mu_i^0 + RT \log \left(\frac{\phi_i Z c_i}{c_0} \right), \quad (8)$$

where $c_0 = N/V_0$ is the mixture concentration at the reference volume, i.e., the volume computed from $p_0 V_0 = NRT$, with $Z_0 = 1$ assumed for the reference state. The activity coefficient for species M_i is $\gamma_i = \phi_i Z$. Performing the sum for the condition of chemical equilibrium, we get

$$\sum_{i=1}^m \Delta\nu_i \mu_i^0 + RT \log \left[\prod_{i=1}^m \left(\frac{\phi_i Z c_i}{c_0} \right)^{\Delta\nu_i} \right] = 0. \quad (9)$$

Recalling that $a_i = \phi_i Z c_i$, we solve for the product of activity concentrations in (6) to get

$$\prod_{i=1}^m a_i^{\Delta\nu_i} = \exp \left(\frac{-\Delta g^0(T)}{RT} \right) c_0^{\sum_{i=1}^m \Delta\nu_i}, \quad \Delta g^0(T) \equiv \sum_{i=1}^m \Delta\nu_i \mu_i^0. \quad (10)$$

Hence, to compute one rate parameter given the other when kinetics are expressed in terms of activity concentrations, we only need to compute the standard equilibrium constant with which we are familiar. If the rates were, however, written with standard concentrations, the equilibrium constant appearing on the right-hand-side of (4) would be harder to compute, because its evaluation would require the activity coefficients (being functions of an unknown equilibrium state), and not solely the temperature.

While the equilibrium constant is relatively simple to compute, to evaluate the production rates we must compute the activity coefficients, i.e., the fugacity coefficients. See Schmitt *et al.* [5] for the fugacity coefficient for the BKW EOS. Once again, we verified our implementation by making comparisons to TIGER for a model system, where we found excellent agreement for the chemical potentials of individual species in a mixture over a wide enough range of pressure to include real-gas effects.

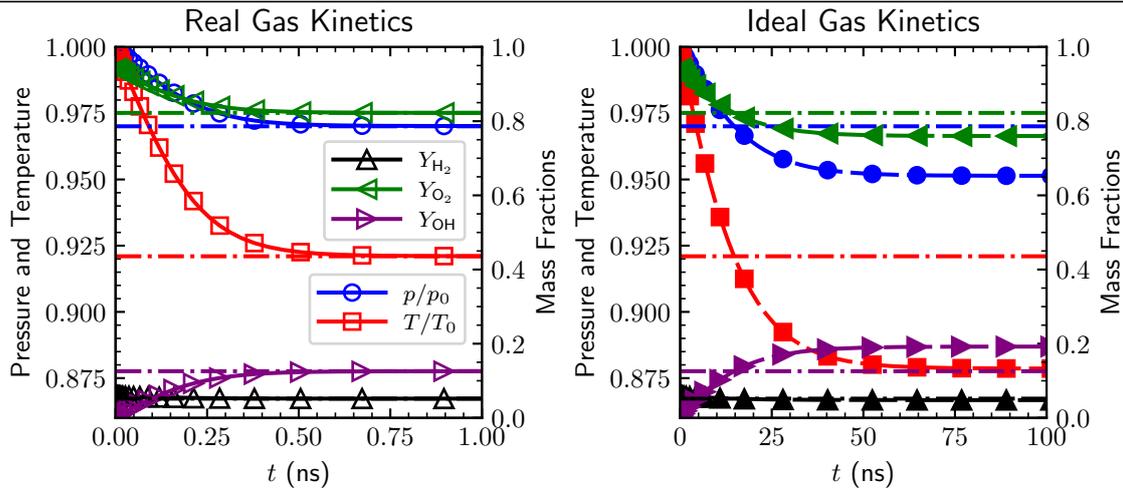


Figure 2: Plots of temperature, pressure and composition evolution for (left frame, open symbols) real-gas kinetics and (right frame, closed symbols) ideal-gas kinetics for the hydrogen-oxygen system. The horizontal dash-dotted lines are the equilibrium values from TIGER for the given quantity based on line color, e.g., blue for the pressure and purple for Y_{OH} .

4 Numerical Integration and Verification Tests

In HyBurn we need to integrate production equations like those shown in Section 3 at each time step to update the chemical composition. The code works with mass fractions Y_i instead of concentrations, and the system of m (the number of species) ordinary differential equations (ODEs) is

$$\frac{dY_i}{dt} = \frac{W_i}{\rho} \sum_{j=1}^r \nu_{ij} \frac{d\omega_j}{dt} = f_i, \quad i = 1, \dots, m, \quad (11)$$

where r is the number of reactions in the chemical mechanism, ν_{ij} is the net stoichiometric coefficient of the i^{th} species in the j^{th} reaction, W_i is the molecular weight of the i^{th} species, $d\omega_j/dt = \dot{\omega}_j$ is the production rate of the j^{th} reaction, which takes the same form as (5), but with an additional subscript j on the parameters to identify a particular reaction. To integrate the system (11) we use the YASS integrator, which is first-order accurate, very robust and precisely conserves mass without ad-hoc adjustments or corrections [11]. YASS requires the exact Jacobian $J_{ik} = (\partial f_i / \partial Y_k)_{e,v,Y_l \neq k}$, which we do not have space to summarize. We have also conducted integration tests with the VODE integrator [12] using an approximate Jacobian for additional verification of our formulation.

As an initial verification test of the kinetics formulation, we compute the evolution of an H_2 , O_2 and OH system governed by the reaction $\text{H}_2 + \text{O}_2 \rightleftharpoons 2 \text{OH}$. The forward rate parameter is of the modified Arrhenius form $k_f = aT^b \exp(-E/RT)$, where we arbitrarily take $a = 1 \times 10^{10} \text{ cm}^3/\text{mol}\cdot\text{s}$, $b = 0$ and $E = 1 \times 10^4 \text{ cal/mol}$. The initial mixture is equal parts H_2 and O_2 (by moles) at a temperature of 2000 K, and to ensure real-gas effects are not negligible, we set the initial pressure to 10000 atmospheres. We assume adiabatic and constant volume conditions for the reaction. The evolution of the system in HyBurn is shown in the left frame of figure 2, where we have included horizontal lines for the exact equilibrium solution computed by TIGER. To understand the importance of computing a reverse rate parameter that is consistent with equilibrium, in the right frame we show the evolution of the same system with “ideal gas kinetics”, i.e., equations (3) and (4), with the equilibrium constant (erroneously) taken as function of temperature only. This mimics what would happen in a code if the BKW EOS were substituted for the ideal gas equation of state, without any modification of the kinetics formulation. As we see in the right frame, the code converges to an incorrect equilibrium state at a very different rate.

To test the kinetics scheme in a hydrodynamic calculation, we simulate the development and propagation of a 1-D over-driven steady detonation in a reactive mixture. The initial conditions are a mixture of H_2 , O_2 and N_2 with mole fractions $\chi_{\text{H}_2} = 0.5$, $\chi_{\text{O}_2} = 0.25$ and $\chi_{\text{N}_2} = 0.25$. The initial pressure and temperature are 100 atm and 300 K, respectively. We constrain the system to only contain O, H, OH, HO_2 , H_2O_2 and H_2O , in addition to the H_2 , O_2 and N_2 forming the initial mixture. The evolution of the chemical state in HyBurn is governed by the mechanism used by Schmitt and Butler [13], but with elementary rates expressed in terms of activity concentrations. In HyBurn we set up a reverse impact problem with a rigid left boundary condition and an inflow boundary condition to the right. We found that an inflow particle velocity of 2.5 mm/ μs produced a steady detonation (another test at ~ 2.1 mm/ μs was longitudinally unstable). Our HyBurn simulation domain is ~ 40 μm long, and it is clear when viewing the solution in Visit that a nearly-steady wave is produced within the first, say, 5-10 μm of the domain. Using Visit, we extract profiles when the detonation is near the end of the domain and plot the results alongside the relevant Hugoniot loci computed with TIGER in frames (a) and (b) of figure 3. Aside from the first few points within the numerical shock profile, the solution through the wave falls directly on the Rayleigh line, giving confidence that the code is producing the correct steady-wave physics. In frames (c) and (d) we plot solution profiles along with the exact ZND profile obtained by integrating the necessary ODEs with VODE. The step-like appearance of the numerical profile (due to our oversampling of the data while making the Visit lineout), which reflects the grid resolution, gives us confidence that the reaction zone is resolved in this flow.

5 Conclusions

We have presented the core features of a model intended for high-fidelity simulations of detonation product afterburn. By adopting the BKW EOS, which has as its backbone an ideal gas mixture, we are able to capture the high density and pressure states relevant to detonation, while maintaining a detailed accounting of the species in the flow. The finite rate chemical kinetics scheme employed for our calculations uses activity concentrations in the rate expressions, which readily enables the code to converge to the correct equilibrium state. Results from extensive verification tests between HyBurn and the TIGER thermochemical equilibrium code indicate that the BKW EOS is implemented correctly and that the kinetics scheme approaches the correct equilibrium. Future work will focus on verifying the chemical production rates and conducting simulations of detonation product expansion and afterburn.

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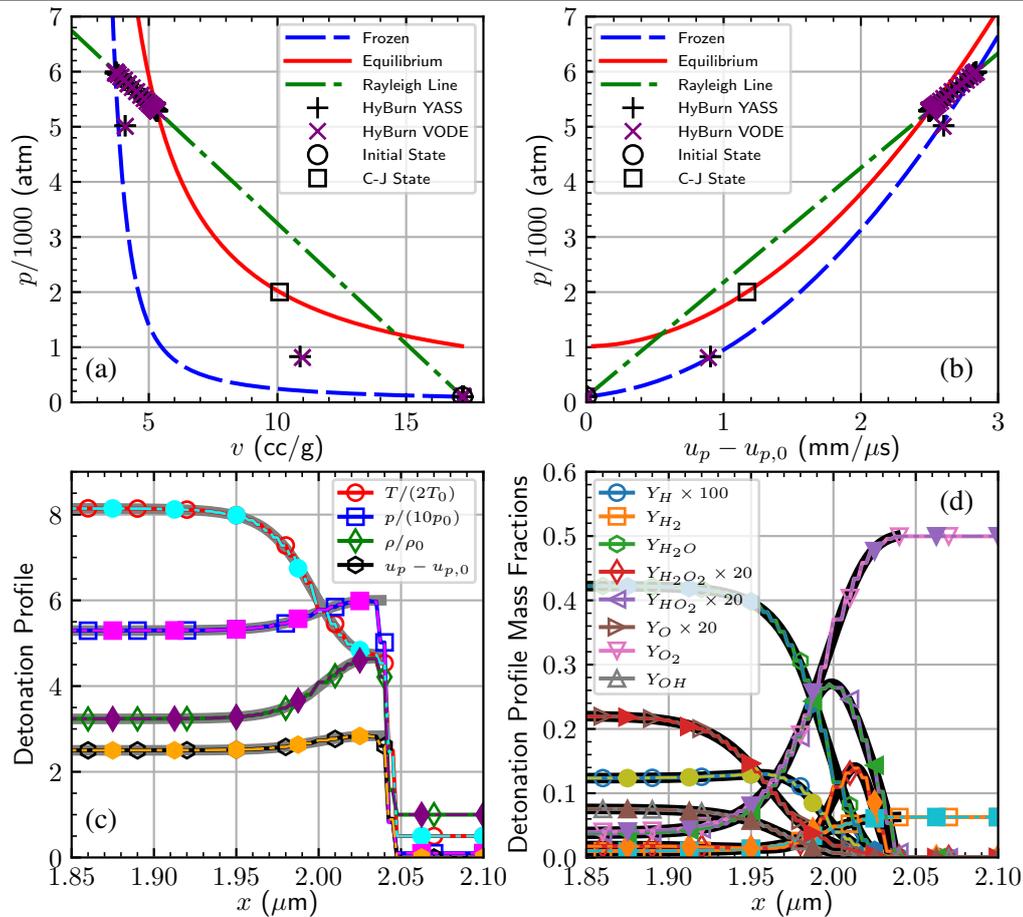


Figure 3: Thermodynamic loci and points relevant to steady wave analysis in the (v, p) plane in frame (a), and in the (u_p, p) plane in frame (b), using both the YASS and VODE integrators in HyBurn. Frozen (unreacted) and equilibrium (fully reacted) Hugoniot loci computed with TIGER. In frames (c) and (d), detonation profiles from HyBurn, with open symbols for simulations with YASS and closed symbols for simulations with VODE. Exact ZND solution starting from the von Neumann state shown with thick solid lines. Data extracted from simulations after the detonation has traveled approximately $40 \mu\text{m}$.

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