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Adding Kinetics and Hydrodynamics to the CHEETAH Thermochemical Code

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Adding Kinetics and Hydrodynamics to the CHEETAH Thermochemical Code

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Abstract

In FY96 we released CHEETAH 1.40, which made extensive improvements on the stability and user-friendliness of the code. CHEETAH now has over 175 users in government, academia, and industry. Efforts have also been focused on adding new advanced features to CHEETAH 2.0, which is scheduled for release in FY97. We have added a new chemical kinetics capability to CHEETAH. In the past, CHEETAH assumed complete thermodynamic equilibrium and independence of time. The addition of a chemical kinetic framework will allow for modeling of time-dependent phenomena, such as partial combustion and detonation in composite explosives with large reaction zones. We have implemented a Wood-Kirkwood detonation framework in CHEETAH, which allows for the treatment of nonideal detonations and explosive failure. A second major effort in the project this year has been linking CHEETAH to hydrodynamic codes to yield an improved HE product equation of state. We have linked CHEETAH to 1- and 2-D hydrodynamic codes, and have compared the code to experimental data.

Overview: Kinetics in CHEETAH

There is a continuing need in the energetic materials field for reliable predictions of detonation velocity and energy delivery. This traditionally has been accomplished through the use of thermochemical codes, which implement Chapman-Jouget thermodynamic detonation theory. Chapman-Jouget detonation theory assumes that thermodynamic equilibrium of the detonation products is reached instantaneously.

So-called “nonideal” explosives, (e.g., heterogeneous composites) are often poorly modeled by Chapman-Jouget theory. The poor performance of thermochemical codes when applied to these problems is usually attributed to the relatively long reaction times of these materials (microsecond timescales) as compared to most homogeneous condensed explosives (20-nanosecond timescale). In this case, the Chapman-Jouget assumption of instantaneous thermodynamic equilibrium breaks down.

We are therefore forced to consider the interaction of chemical kinetics with the detonation wave in order to reach an acceptable representation of detonation in nonideal

explosives. Zeldovich, Von Neumann, and Doring[1] independently arrived at the "ZND" theory of detonation in the 1940s. In ZND theory a plane wave detonation is considered. The state of the system proceeds from the intersection of the unreacted shock Hugoniot with the Rayleigh line to the CJ state as the chemistry proceeds. ZND theory correctly predicts the existence of a high pressure transient preceding the CJ state. The plane wave nature of the system considered, however, guarantees that the CJ state is always reached; another consequence is that the detonation velocity in ZND theory is always the same as that of CJ theory.

It is found experimentally, however, that the detonation velocity of nonideal explosives varies sharply from the CJ value. Moreover, the detonation velocity in nonideal explosives is observed to be a strong function of charge diameter. Wood and Kirkwood (WK)[2] proposed a two-dimensional steady state kinetic detonation theory that solves many of the limitations of ZND theory. Wood and Kirkwood theory considered a cylindrical charge of infinite length. They solved the hydrodynamic Euler equations in the steady state limit along the central streamline of the cylinder. Radial expansion was treated as a source term in the 1-D flow along the streamline.

We have implemented three kinetic calculation types in the CHEETAH thermochemical code. The first type is general purpose kinetics. In this type of problem, the calculation is assumed to be at a fixed thermodynamic state (e.g., fixed P,T or fixed V,E). General-purpose kinetics are not specific to detonation and can be used to treat other sorts of problems, such as deflagration and nondetonating explosions. The second type of calculation is ZND theory. The third calculation type is WK theory, which includes the effect of radial expansion on the detonation velocity. CHEETAH implements ZND theory as a special case of WK theory where the radial expansion has been set to zero.

General-Purpose Kinetics

CHEETAH can model a wide variety of chemical processes using its general-purpose kinetics capability. In general-purpose kinetics, CHEETAH describes a spatially homogeneous reaction cell. Some people familiar with hydrodynamic codes like to think of this cell as a zone in a hydrodynamic simulation, but there is really no concept of the size of the cell. This cell is held at a *constant thermodynamic state*. The constant thermodynamic state is defined by holding any two thermodynamic variables that CHEETAH recognizes (e.g., P, V, T, E, H, A, G, S) constant. A wide variety of problems can be modeled with this framework. For instance, combustion in a bomb calorimeter is described by holding V and E constant. Combustion in an idealized internal combustion engine is described by holding P and H constant.

The second important concept in the kinetics capability is the partitioning of reactions into a *fast* subgroup and a *slow* subgroup. This partitioning is used in recognition of the fact that chemical reaction rates at high pressures and temperatures are largely unknown. It is therefore very difficult, if not impossible, to create a valid kinetic description of every reaction occurring in the reaction cell. It is often the case, however, that a few very slow reactions can be identified. For instance, the precipitation of solid products or the combustion of a solid

particle can be modeled with simple transport-limited models that should work well even in the high-pressure regime.

For each rate specified, we give a stoichiometric equation:

$$\sum A_i x_i \leftrightarrow \sum B_i y_i \ . \tag{1}$$

Here, the A_i are the stoichiometric coefficients of the reactant species x_i, while the B_i are the stoichiometric coefficients of the product species y_i. As an example, a reaction rate for the consumption of the HE molecule HMX may be specified as:

$$HMX \leftrightarrow 4CO + 4H_2 + 4N_2 + 2O_2 \ . \tag{2}$$

In a typical application, we would choose only HMX to be kinetically controlled, since its consumption controls the detonation process. The gas molecules CO, H_2, N_2, and O_2 are assumed to undergo rapid chemical reactions that maintain instantaneous chemical equilibrium with other product molecules in the calculation (e.g. CH_4).

Kinetic CHEETAH supports multiple reaction rate laws. We have implemented in the code a simple constant reaction rate:

$$\frac{dF}{dt} = A(1-F) \ . \tag{3}$$

Here F is the reaction coordinate, which varies from 0 (all reactant) to 1 (all product).

We have also implemented simple Arrhenius kinetics:

$$\frac{dF}{dt} = A\exp(-T^* / T)(1-F) \ , \tag{4}$$

as well as a pressure-dependent rate law describing surface controlled reactions:

$$\frac{dF}{dt} = AP^a (1-F)^b F^c \ . \tag{5}$$

Finally, we have implemented the hot spot model of Johnson, Tang, and Forrest.[3]

In Cheetah's kinetic module only forward reactions are specified. The backward reaction is calculated through the detailed balance condition

$$R_b = \exp(\Delta\mu / RT) R_f \ . \tag{6}$$

The reaction affinity $\Delta\mu$ is the chemical potential difference between the reactants and the products:

$$\Delta\mu = \sum a_i \mu_i \ . \tag{7}$$

The μ is calculated at fixed concentration with Cheetah's thermodynamic capabilities. The use of the detailed balance condition ensures that a system evolving kinetically at a fixed thermodynamic state (e.g., fixed P,T) always proceeds at long times to the same thermal equilibrium that CHEETAH would ordinarily predict. In other words, kinetics can be specified independently of thermodynamics when the detailed balance relation is used.

The user must specify only the slow reactions. The fast reactions are generated implicitly by the code. Slow reactions are specified by giving stoichiometric coefficients, a reaction rate law, and parameters for that law. The CHEETAH kinetics framework supports the implementation of multiple reaction rate laws. As an example, we consider the transformation of Al + 0.75 O2 -> Al2O3. We must specify to the framework which species are *kinetically controlled* and which are *thermodynamically controlled*. Kinetically controlled species do not take part in any fast reactions. Thermodynamically controlled species, on the other hand, are assumed to take part in fast reactions that maintain thermodynamic equilibrium. In this example we will assume that the Al is kinetically controlled. The O2 and Al2O3 will be thermodynamically controlled; their concentrations will be kept at equilibrium with the evolving mix of species. In effect, the calculation will release Al into the reacting mix as time proceeds. As a reaction rate law, we will use the simple exponential decay: d[Al]/dt = -a [Al].

The input deck that accomplishes this is the following:

```
comp, petn, 80, al, 20
fix con, *al, 7.40, mole
point, p, 1000.0, t, 4000.0
kinetics
reaction, *al, -1.0, o2, -0.75, al2o3, 0.5
law, exp decay, 0.1
slow, *al, 7.40
point, v, , e,
time, 0.0, 2.0, 20
end, kinetics
```

In this calculation, a mix of 80% PETN/20% Al by weight is treated. We start with an initial Al concentration of 7.40 mole/kg. The initial pressure is 1000 atm, while the initial temperature is 4000 K. The volume and energy of the reaction cell are fixed at their values at 1000 atm and 4000 K. The reaction rate is specified as 0.1/ms. The kinetics module will integrate from 0.0 ms to 2.0 ms, taking 20 steps.

Here is the output of the kinetics calculation:

```
Chemical Kinetic Run:
Reactions defined:
*al 0.75o2 -> 0.5al2o3
     Kinetic law:Simple exponential decay with rate   0.10000
Initial concentrations of kinetically controlled constituents:
         *al 7.4000 mol/kg
All other constituents will be kept at equilibrium
The kinetics will be run from t = 0.000 to t = 2.000 in 20 steps
The thermodynamic point command is point, v,, e,
The freezing command is :freeze , *al
```

Time(us)	T(K)	P(atm)	V(CC/GM)	E(CAL/G)	*al
0.00	4000.0	1000.0	10.6124	511.16	7.40000
0.11	4016.0	1004.0	10.6124	511.16	7.32251
0.21	4031.9	1007.9	10.6124	511.16	7.24584
0.32	4047.7	1011.9	10.6124	511.16	7.16997
0.42	4063.4	1015.8	10.6124	511.16	7.09489
0.53	4079.0	1019.6	10.6124	511.16	7.02060
0.63	4094.5	1023.5	10.6124	511.16	6.94708
0.74	4109.9	1027.3	10.6124	511.16	6.87434
0.84	4125.2	1031.2	10.6124	511.16	6.80236
0.95	4140.4	1034.9	10.6124	511.16	6.73113
1.05	4155.5	1038.7	10.6124	511.16	6.66065
1.16	4170.6	1042.5	10.6124	511.16	6.59090
1.26	4185.5	1046.2	10.6124	511.16	6.52189
1.37	4200.3	1049.9	10.6124	511.16	6.45360
1.47	4215.1	1053.6	10.6124	511.16	6.38602
1.58	4229.7	1057.3	10.6124	511.16	6.31915
1.68	4244.3	1060.9	10.6124	511.16	6.25298
1.79	4258.8	1064.5	10.6124	511.16	6.18751
1.89	4273.2	1068.1	10.6124	511.16	6.12272
2.00	4287.5	1071.7	10.6124	511.16	6.05861

As we can see, temperature and pressure increase with time, while the Al concentration decreases with time. In Figure 1 we show the variation of P with time in this run.

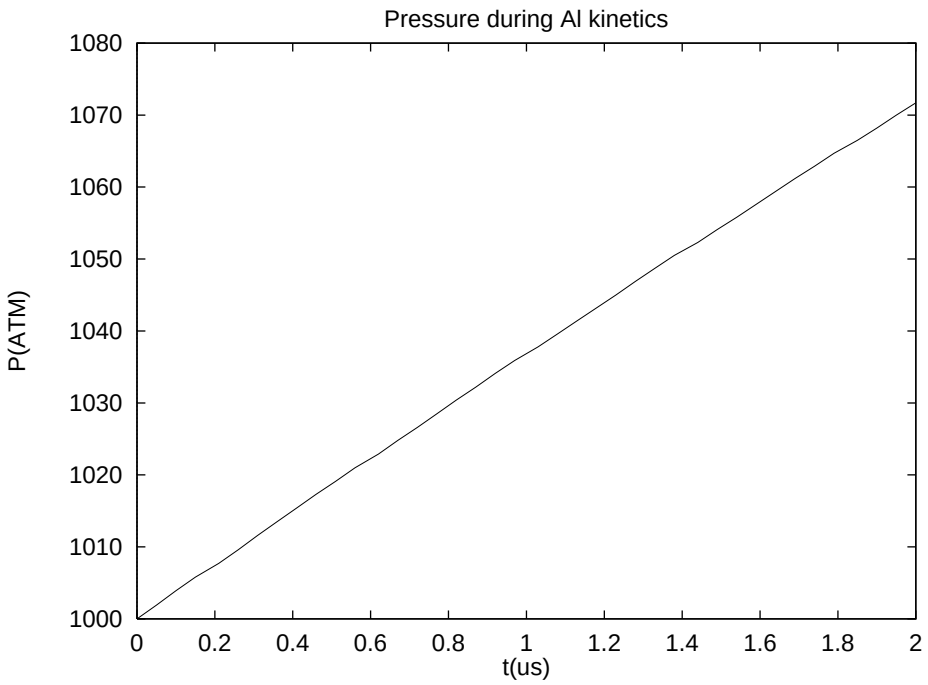

Figure 1. **The variation of pressure during constant (V,E) Al combustion**.

The thermodynamic state defining the reference cell has a determining effect on which quantities vary and the rate of variation. We repeat the above calculation, but this time with P and H fixed. Now the volume of the cell increases as P is held fixed. The energy of the cell decreases as the cell performs PV work on the environment. In Figure 2, we show the variation of V with time for this calculation.

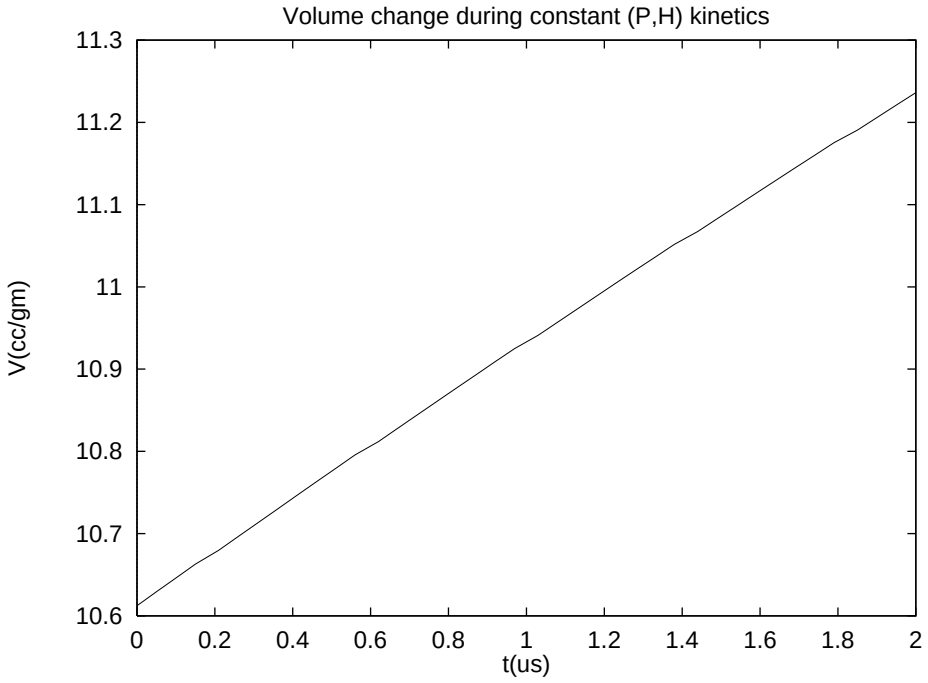

Figure 2. The variation of volume during constant (P,H) Al combustion.

Shock Kinetics

CHEETAH has the capability to perform kinetic detonation calculations. Kinetic detonation theory was first proposed (independently) in the early 1940s by Zeldovich, Von Neumann, and Doering.[1] The theory was generalized to multiple arbitrary chemical reactions by Wood and Kirkwood[2] in the 1950s. Further explication of the theory and its implications occurred in the 1960s.[4] Despite its age, kinetic detonation theory is still not widely understood by most practical explosives scientists and engineers. This is partly because the predictions of kinetic detonation theory are often difficult to measure directly, and partly because most hydrocode simulations do not take kinetic effects into account. We therefore give a brief review here.

Kinetic detonation theory describes the behavior of a steady state plane wave shock propagating in an infinite sea of HE. There is only one relevant spatial direction, which is normal to the shock front. The basic equations to be solved are the hydrodynamic Euler equations describing inviscid flow, coupled to chemical kinetic equations. The purpose of kinetic detonation theory is to describe the long-time, steady-state solutions to the chemical Euler equations.

The addition of chemical kinetics can add tremendous variety to the possible types of detonation. Without kinetics, unsupported detonation is completely determined by the CJ state, while piston-driven detonation is determined by a strong state S on the shock Hugoniot. This situation is illustrated in Figure 3.

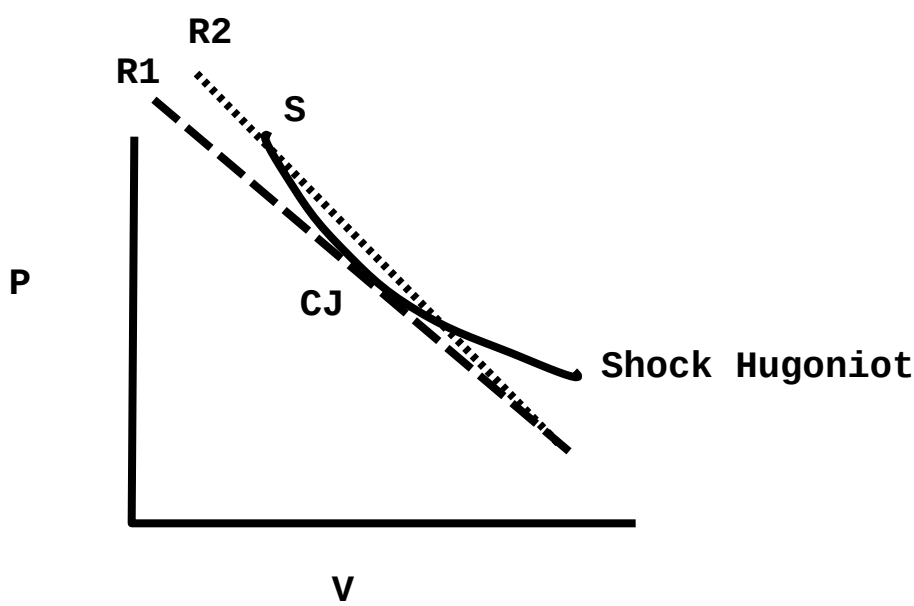

Figure 3. The shock Hugoniot, Rayleigh lines, and CJ point for overdriven and CJ detonation.

For CJ detonation, the Rayleigh line R1 (describing conservation of momentum) intersects the shock Hugoniot (describing conservation of energy). The slope of the Rayleigh line is proportional to the detonation velocity, so we see that the CJ state is the slowest propagating state that can intersect the shock Hugoniot (and thus conserve energy). Detonation waves faster than CJ can exist as piston-supported overdriven states. We show the Rayleigh line R2 intersecting the shock Hugoniot at the strong detonation point S.

With the introduction of chemical kinetics, the system proceeds along shock Hugoniots describing the partially reacted HE products. This situation is shown in Figure 4.

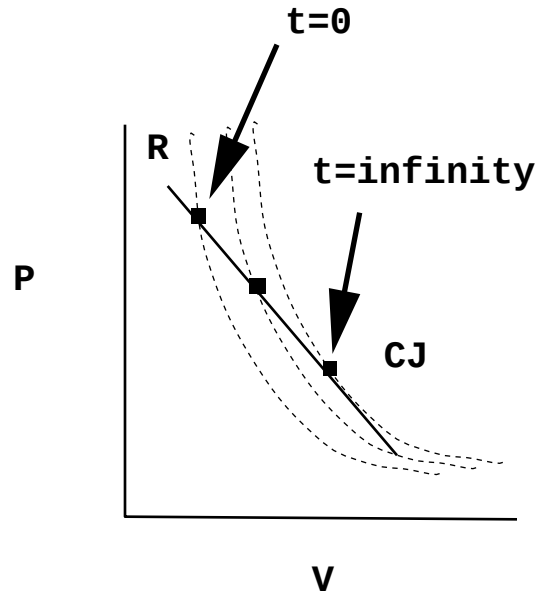

Figure 4. In ZND detonation, the shock pressure proceeds from the Von Neumann spike at t=0 to the CJ pressure in the long-time limit.

The pressure profile along the shock front changes from a square wave to a curve proceeding from the Von Neumann spike. The region in which the pressure is appreciably different from the CJ pressure is called the reaction zone. This situation is illustrated in Figure 5. The three points shown on the pressure profile correspond to the points drawn in Figure 4.

The situation we have described so far, where pressures fall monotonically from the Von Neumann to the CJ state, are typically called ZND detonation. There are several types of kinetic detonations, however, that do not fall into the ZND framework. The classic ZND framework assumes that each partially reacted shock Hugoniot has an intersection with the Rayleigh line going through the CJ state. It is possible, however, that the partial shock Hugoniot loses contact with the Rayleigh line. This situation is shown in Figure 6.

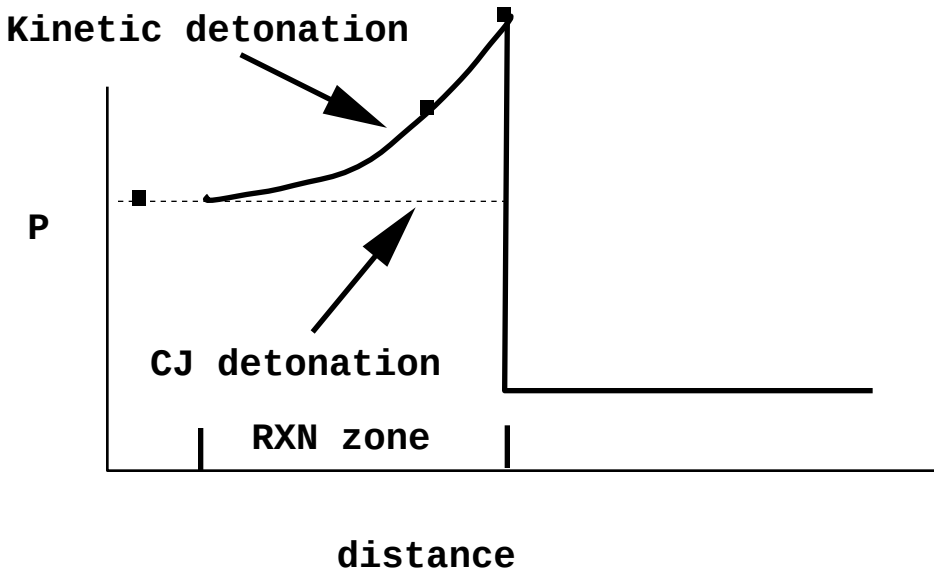

Figure 5. Shock pressures are shown for kinetic and CJ detonation theories.

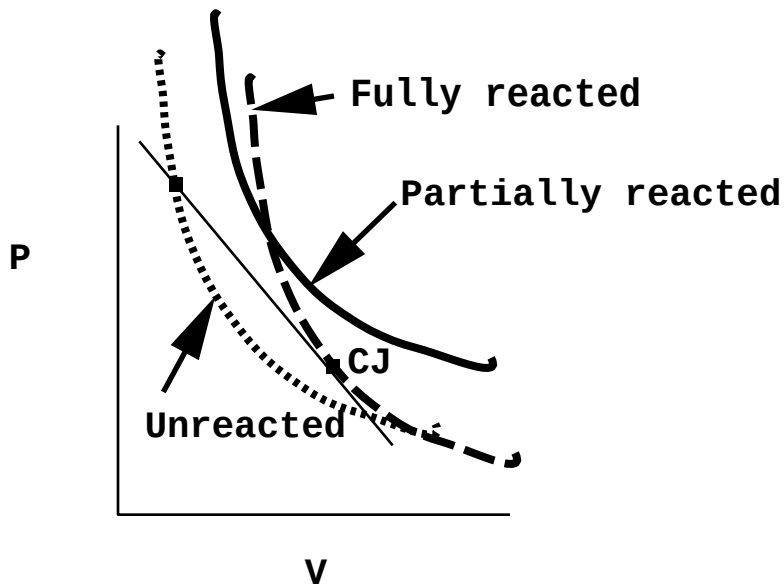

Figure 6. Partially reacted shock Hugoniots are shown for the pathological detonation case.

In the pathological detonation case there is *NO* possible way for the system to reach the CJ state. Physically pathological detonations are possible whenever reactions that reduce the pressure at constant volume and energy are present. The early pressure-producing reactions then "run ahead" of the late-time pressure-reducing reactions. The late-time reactions fall behind the sonic plane and therefore do not contribute to the steady state shock front.

We have found that many aluminized explosives can give rise to pathological detonations because aluminum combustion is a gas-robbing reaction. That is, heat may be

produced while pressure is reduced. Typically, aluminized explosives make up for this pressure loss by sustaining higher pressures upon adiabatic expansion from the CJ state, but this isn't relevant to the present discussion.

In the pathological case, only detonation velocities *faster* than CJ can propagate. Self-sustaining detonation occurs at an eigenvalue detonation velocity D^*. D^* is determined by the condition that there is no pressure produced by chemical reactions at the point of tangency between the partially reacted shock Hugoniot and the Rayleigh line. This situation is shown in Figure 7.

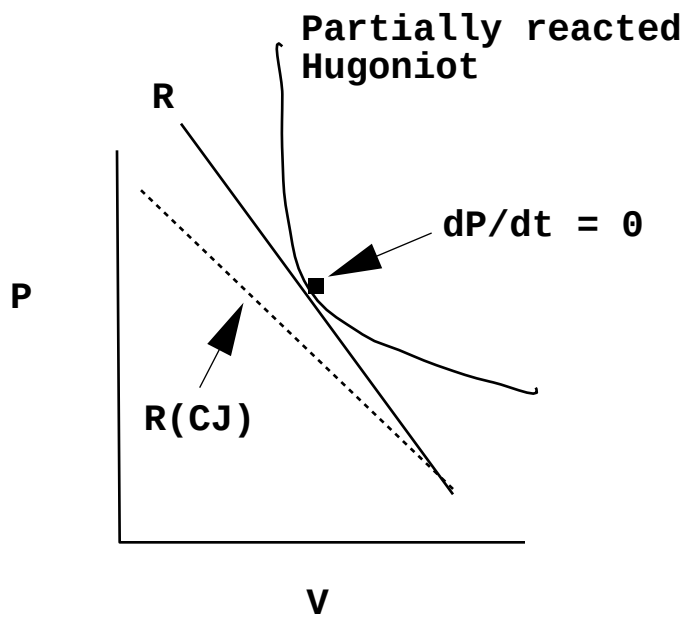

Figure 7. The eigenvalue Rayleigh line R is determined by the condition that dP/dt = 0 at the tangency point.

Wood-Kirkwood Detonation Theory

Wood-Kirkwood theory is more interesting than Zeldovich, Von Newman, and Doering theory because it is the interplay between the timescale of kinetics and the timescale of expansion that causes most observed nonideal effects in explosives. Zeldovich, Von Newman, and Doering theory predicts the existence of a Von Neumann spike and a finite-width reaction zone. Although these features are of scientific interest, the features of most practical interest are detonation velocity and the amount of energy delivered by the explosive. Zeldovich, Von Newman, and Doering theory always predicts the same detonation velocity as equilibrium CJ theory. The energy delivery upon expansion is not addressed at all in ZND theory. In WK theory the detonation velocity varies as a function of the relative rates of reaction and expansion. The theory automatically transitions from the shock front to an adiabatic expansion, so the energy delivery is a natural output of the theory.

Wood-Kirkwood theory starts with the hydrodynamic Euler equations coupled to chemical kinetics. The theory treats the detonation along the center of the cylinder. Radial

expansion is treated as a first-order perturbation to perfect one-dimensional detonation. Finally, the Euler equations are reduced to their steady state form. No other approximations are made in formulating the theory. The result is a set of ordinary differential equations that describe hydrodynamic variables and chemical concentrations along the center of the cylinder (Fig. 8).

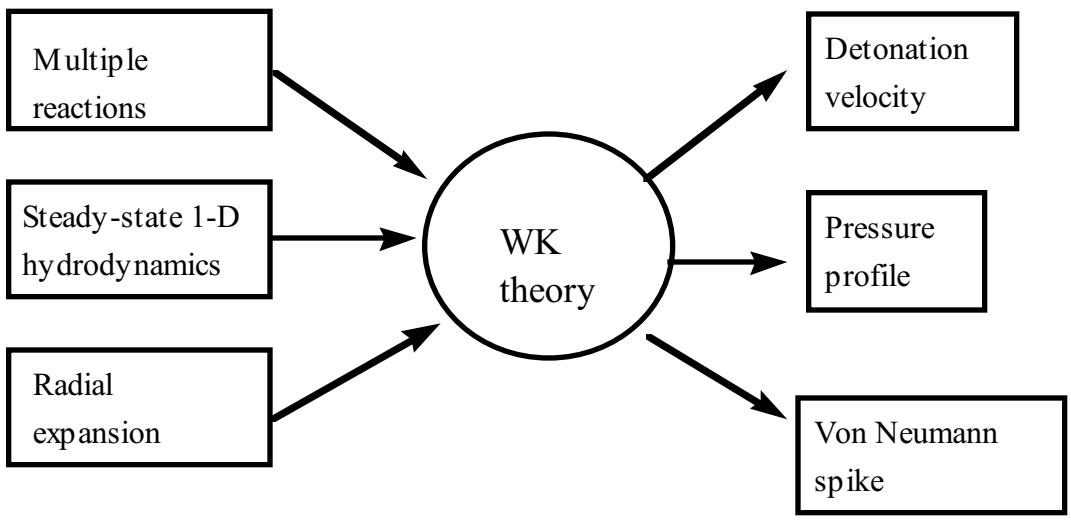

Figure 8. The inputs to and predictions of Wood-Kirkwood detonation theory.

The notation is as follows: we use cylindrical coordinates in a frame *moving with the shock velocity D*. *x* is the axial coordinate and r is the radial coordinate. *u* is the axial particle velocity in the moving frame (equal to D-U in the lab frame). The radial velocity is called ω. Subscripts denote a spatial derivative. Thus, ω_r is the derivative of the radial velocity with respect to radial coordinate; i.e., it is the divergence of the flow. The chemical concentrations are denoted by a vector *F*. The chemical kinetic rate laws are written as a vector *R*. η and ψ are reduced variables defined below.

The Wood-Kirkwood[2] equations are:

$$\begin{aligned} u_x &= \psi / \eta \\ \rho_x &= -(\rho / u)(u_x + 2\omega_r) \\ E_x + p v_x &= 0 \\ F_x &= R / u \end{aligned} \tag{8}$$

The initial conditions are the chemical concentrations (determining F, and the initial pressure and particle velocity. The initial state variables are found in CHEETAH by finding the intersection of the Rayleigh line with the unreacted shock Hugoniot. This can be done if the shock velocity is specified. From this point on, the system visits a series of (p,v) states of different with different chemical concentrations.

The nature of the WK solutions depends strongly on the reduced variables η and ψ. $\eta = 1 - u^2/c^2$ is called the *sonic parameter*.[5] When $\eta > 0$ the flow is subsonic, and

communication with the shock front is possible. The flow becomes supersonic and loses communication with the shock front when $\eta < 0$. The equation $\psi = (\partial P/\partial F)_{V,E} * R / \rho^2 - \omega_r$ is the *pressure production*.[5] When $\psi>0$, chemical reactions produce more pressure than is lost through radial expansion. When $\psi<0$, there is a net loss of pressure, either through pressure decreasing reactions or radial expansion. η is unitless, while ψ has units 1/time.

The result of solving the WK equations is the steady state shock profile in a radially expanding geometry along the center line of the flow. This yields the steady-state wave profile in the radially expanding geometry. The problem is then reduced to finding the particular steady-state solution that is self-propagating (i.e., not overdriven or underdriven).

The equations will be singular if η passes through zero unless ψ becomes zero at that point also. If ψ goes through zero when η is not zero, steady-state shock propagation at the specified shock velocity is not possible. It is also possible that η never goes through zero. These solutions are overdriven. Self-supported detonation occurs at the edge between over-driven and nonpropagating solutions. η must go through zero exactly when $\psi = 0$. It is possible to think of this as a kinetic CJ condition.

The WK equations have been extensively analyzed by Erpenbeck and coworkers.[4] It is found that the detonation velocity depends on the interplay between chemical kinetics and radial expansion. In the limit of no radial expansion, the ZND plane wave result is obtained. When radial expansion is allowed, however, the detonation velocity can vary from the CJ prediction. In the limit of strong radial expansion, the detonation wave fails: no velocity is found which satisfies the steady-state equations. Bdzil[6] has recently generalized WK theory to off-axis flow.

While WK theory is an important success in explaining qualitative features of detonation such as failure and the charge diameter effect, it has traditionally been applied only to the polytropic ideal gas equation of state (EOS):$E = pV / (\gamma - 1)$. Here the adiabatic exponent $\gamma = - (\partial \ln P / \partial \ln V)_S$.

In condensed explosives, it is known that the adiabatic exponent varies from roughly 3 at the CJ state to roughly 1 after adiabatic expansion. Therefore, the polytropic EOS is inadequate to quantitatively model condensed explosives. We have recently implemented WK detonation theory in the CHEETAH thermochemical code. This allows us to study kinetic effects on detonation in condensed explosives. We find that kinetic effects are probably significant in most energetic material detonations, even those usually considered “ideal.” We also find that highly nonideal explosives, such as AP, can be described with some success through the use of simple empirical reaction rate laws. More detailed chemical kinetic models will be pursued in the future.

Implementation of WK Theory

In order to implement the WK equations, several elements are needed: the specification of kinetic laws R, the expansion rate ω_r, and the equation of state of the mixture of detonation products and reactants. A difficulty encountered in implementing WK theory for

condensed materials is that most of the relevant detailed kinetic laws are unknown. As discussed above, we specify only a few kinetic laws describing reactions that are thought to strongly affect the detonation process—for instance, the overall rate of HE consumption.

Expansion Rate

Wood-Kirkwood theory requires the specification of the rate of radial expansion along the center streamline of the flow. One of the principal difficulties in using WK theory is the necessity of specifying the radial part of the flow in order to determine the steady state flow along the axis. Although it is impossible to know the exact nature of the radial flow without solving the fully coupled 2-D hydrodynamic problem, it is possible to roughly estimate its magnitude. In cases where the radial expansion produces a small perturbation to plane-wave propagation, a rough estimate is probably adequate.

We have implemented two radial flow models that have been used by researchers in the past. The first is simply taking the radial flow rate to be a constant: $\omega_r = C$. This is useful when there is relatively little information known about the problem. The constant C can be estimated from cylinder test data on a similar HE material: $C = V_r/R$, where V_r is the radial expansion velocity of the cylinder wall, and R is the cylinder radius.

The second radial flow model was suggested by Wood and Kirkwood: we take $\omega_r = (D-u) / R_c$. Here, D is the detonation velocity, and u is the particle velocity in the shock frame. R_c is the radius of curvature of the detonation front, evaluated at the center streamline. In order to use this model we must have an estimate of the radius of curvature of the detonation front. Radii of curvature of various explosives have been recently reviewed in a paper by Souers.[7]

Equation of State

The equation of state of the HE material is handled by Cheetah's equilibrium thermochemical capability. CHEETAH treats a single gas phase in thermodynamic equilibrium with several independent condensed phases: V = (gas) + V(solid products) + V(reactants). Here, V is the total volume of the system. We have broken the condensed phases into two categories for conceptual simplicity: the unreacted HE and solid products produced by the HE combustion.

We first consider the gas phase equation of state. The most commonly used nonideal EOS implemented in CHEETAH is the Becker-Kistiakowski-Wilson (BKW) equation of state (EOS).[8] BKW expresses the pressure in terms of effective molecular volumes (usually referred to as covolumes), and several fixed global EOS parameters:

$$\begin{aligned} pV/nRT &= 1+\beta x \exp(x/(\theta+T)^{\alpha}. \\ x &= \sum_i n_i k_i. \end{aligned} \tag{9}$$

Here, α, β, κ, and θ are global EOS parameters and x is the total molecular volume, which is based on the covolumes k_i and the mole numbers n_i. The BKW equation of state, while lacking a firm basis in statistical mechanics, has been shown to produce reliable predictions for detonation properties in over 30 years of use. Hobbs and Baer[9] have recently published an extensive library of reaction products based on the BKW equation of state containing more than 2000 gaseous species and 32 elements. More recently, Fried and Souers[10] have published a smaller, highly optimized BKW library. Fried and Souers have shown that their parametrization (BKWC) is capable of reproducing detonation velocities with an average error of less than 1.5% when evaluated for a wide range of compounds containing the elements H,C,N,O, and F.

The second nonideal gas equation of state is called JCZ3, after its developers, Jacobs, Cowperthwaite, and Zwissler.[11] JCZ3 is based on the Lennard-Jones 6-13.5 potential of interaction between molecular species: $V(r_{ij}) = (A/r_{ij})^{13.5} - (B./r_{ij})$.[6] The form of the gas EOS is based on fits to molecular dynamics simulation of the Buckingham potential. The JCZ3 EOS has been shown to be effective in reproducing detonation velocities for condensed explosives.

Finally, CHEETAH supports a two-term virial equation of state based on the Lennard-Jones 6-12 potential. The first virial coefficient is evaluated directly from the virial expansion of the 6-12 gas, while the expression for the hard-sphere second virial coefficient is used for the second term. The two-term virial EOS has been successfully used to predict the thermochemical properties of gun propellants in the BLAKE thermochemical code.[12] This EOS is most suited for the treatment of weakly nonideal gas mixtures.

We use a Murnaghan EOS[13] for the unreacted HE equation of state: $V(P) = V_0 / (1 + nP/B)^{1/n}$, where B is the bulk modulus and n is its pressure derivative. The Murnaghan EOS is calibrated to the unreacted shock Hugoniot of the explosive material. We find the Murnaghan EOS to be preferable to more sophisticated forms for the unreacted HE EOS because there is substantial extrapolation involved in applying the experimental unreacted shock Hugoniot (usually measured at pressures less than 20 kBar) to the Von Neumann spike (often 400 kBar).

The unreacted material's heat of formation, standard entropy, and heat capacity are also specified in kinetic CHEETAH. We use tabulated heats of formation for HE materials. Standard entropies are usually not known for high explosives. Since the transformation of the HE into its products is an irreversible reaction, however, the results are not sensitive to the choice of standard entropy. Finally, the heat of formation is determined by fitting measured heat capacity data to a single Einstein oscillator model.

For the equation of state of condensed products of detonation (e.g., C and Al_2O_3) we use either the Murnaghan EOS with thermal expansion or a simple polynomial EOS: $V(P,T) = \sum A_{ij} P^i T^j$. Many product species have been calibrated in the BKWS product library[9] with the polynomial EOS. The Murnaghan EOS with thermal expansion is $V(P,T) = V_0 \exp(-a_1 T + a_2 T^2) / (1 + nP/B)^{1/n}$. We use this form when implementing new condensed product equations of state.

Solution of the WK Equations

The initial conditions for the WK equations are the energy, density, and composition at the start of the shock front. We specify the initial composition to be the same as the unreacted material. The initial energy and density can be determined by specifying the detonation velocity. Finding the intersection of the unreacted shock Hugoniot with the Rayleigh line yields the pressure and density at the shock front. A thermodynamic equilibration at fixed composition then determines the energy at the shock front. Note that the detonation velocity is treated as a *specified* quantity here. In the next subsection we will discuss the determination of the detonation velocity.

As the equations are integrated, the shock wave structure is determined for positions behind the shock front. In practice, we use the "Lagrangian time" form of the WK equations, where the time variable is related to position by dx = u dt. This choice of variables is most natural for the integration of kinetic laws.

The WK equations support a variety of solutions that have been discussed in great detail by Erpenbeck.[4] Let us consider the behavior of the equations as a function of the specified detonation velocity D. There are three qualitatively different solutions possible. For special detonation velocities $D = D^*$, the solutions pass through the sonic plane, defined by $\eta = 0$. Points behind the sonic plane cannot communicate with the shock front. The WK equations are finite when $\eta = 0$ only if ψ also passes through zero. Therefore the sonic solutions are defined by the nonlinear equation $\psi(t,D) = \eta(t,D) = 0$.

The next possibility is that η never passes through zero. These solutions are *overdriven*; that is, the pressure increases with distance behind the shock front. These solutions correspond to a rear piston boundary condition that drives the shock front forward. Finally, if $\eta = 0$ when $\psi \neq 0$, the equations become infinite. This means that a steady state flow cannot occur at the specified detonation velocity D. Of all the solutions generated by the WK equations, only the sonic solutions $D = D^*$ have the pressure tend to zero as $x \Rightarrow \infty$. It is these solutions that correspond to steady-state self-propagating flow.

Determination of Self-propagating Solutions

We must find the detonation velocities satisfying

$$\psi(t,D) = \eta(t,D) = 0\,. \tag{10}$$

Since only a special few (usually just one) detonation velocity corresponds to self-propagating flow, the sonic solutions have been called "eigenvalue detonations" by previous researchers. This is somewhat of a misnomer, however, since the nonlinear equation of Eq. 10 cannot be mapped into an eigenvalue problem of linear algebra. Before embarking on the algorithms used to find sonic solutions, let us remark that Eq. 10 is equivalent to specifying the rear boundary condition $\lim x \Rightarrow \infty.\ p(x) = 0$.

The solution of Eq. 10 is complicated from a numerical point of view, because the WK equations will become singular for $D > D^*$. We have found it most robust to transform the root search problem into a minimization. We define a figure of merit function Y to be:

$$Y(D) = \min_{0<t<t_{\max}} \eta(t,D)^2 + t^2\psi(t,D)^2. \tag{11}$$

We have Y = 0 when Eq. 10 holds. ψ is multiplied by t in Y to yield a unitless function that works equally well for fast or slow reaction rates. The end of the trajectory t_{max} is set to be longer than chemical reaction timescales. If a singular solution is encountered (η goes to zero when ψ is nonzero), t_{max} is taken to be the time at which the singularity occurs.

We have implemented a specialized minimizer that is efficient at finding minima of Y. Although the implementation is somewhat cumbersome, the underlying principal is simple: we need to find minima of Y(D) that are very close to 0. These minima correspond to self-propagating detonation velocities D^*. In some cases no such minima exist; this indicates that the detonation wave has failed. In other cases more than one minimum exists; this necessitates an initial scan through values of D in order to bracket the minima. Once each minima is bracketed, a minimizer based on rational extrapolation is used to find the exact location of each minimum.

Application to HCNO explosives

An example of Cheetah's kinetic detonation capabilities might be helpful at this point. Nitromethane, which is a commonly studied explosive that is thought to be near the ideal limit, is a good test case. The reaction zone of NM has been estimated to be near 0.5 mm. The radius of curvature is used to specify expansion transverse to the detonation front by using the constant expansion model described in Section 3.1 Radii of curvatures and estimated reaction zones are listed in Table 1.

As a test case we have been studying HMX with two kinetically controlled reactions. The HMX is first converted to gases with a 10 ns timescale. This timescale is based on estimates of the reaction zone for ideal explosives like PETN. The gases are assumed to react rapidly, and are thus always kept in thermal equilibrium with respect to one another. The second reaction is the precipitation of gaseous species to make condensed carbon. A 1-microsecond timescale is used for this reaction, which is consistent with the reaction zone in high carbon explosives like TATB.

Table 1. Reaction zones and radii of curvature estimated for common explosives.

HE	Radius of curvature (mm)	RXN zone (mm)
PETN	1770	0.0
HMX	355	0.2
COMP-B	373	0.9
OCTOL	159	1.0
TATB	86	1.6
LX-17	171	2.5

To implement this in CHEETAH, we specified the following chemical reactions:

$$\begin{aligned} \mathrm{HMX} &\rightarrow 4\mathrm{CO} + 4\mathrm{H_2} + 4\mathrm{N_2} + 2\mathrm{O_2} \\ \mathrm{CO_2} &\rightarrow \mathrm{C} + \mathrm{O_2}. \end{aligned} \tag{12}$$

Only the concentrations of HMX and carbon are controlled by kinetics. The other concentrations are kept in constant thermal equilibrium. This is equivalent to specifying many fast gas reactions.

Recall that WK theory treats radial expansion as a perturbation on 1-D flow. We need to have some way of specifying to the 1-D flow how much radial expansion is occurring. This requires some sort of radial expansion model. The necessity for having such a model is one of the main difficulties we must address in developing a WK capability in CHEETAH. For the time being, we will model the divergence of the flow along the center line as a constant. This suffices to capture all of the important qualitative features. The expansion constant has units of 1/time. In Figure 9 we show the predicted variation of detonation velocity with expansion constant. The models are completely uncalibrated at this point, so detailed comparison with experiments is not yet appropriate. We estimate that the expansion constant should be roughly 0.025 m s^{-1} for a 25-mm cylinder. This number is taken by dividing the wall velocity by the cylinder radius. Note that there is a discernible (1%) size effect to the detonation velocity in this regime.

The detonation velocity for moderate or no expansion is higher than Cheetah's CJ prediction of 9.6 mm/us. This is due to the carbon kinetics. Kinetic detonations can "run ahead" of pressure-decreasing reactions. The precipitation of a solid like carbon from a gas is an example of a pressure-decreasing reaction. Effects like this may help thermochemical codes to achieve better predictions of the detonation velocity.

In Figure 10, we show the predicted variation of pressure with time for several expansion constants. The system proceeds from the Von Neumann spike through a sonic point. Past the sonic point the gases stop communicating with the shock front. The sonic points are visible as small "blips" on the graph. After the sonic point, the system transitions to an adiabatic expansion.

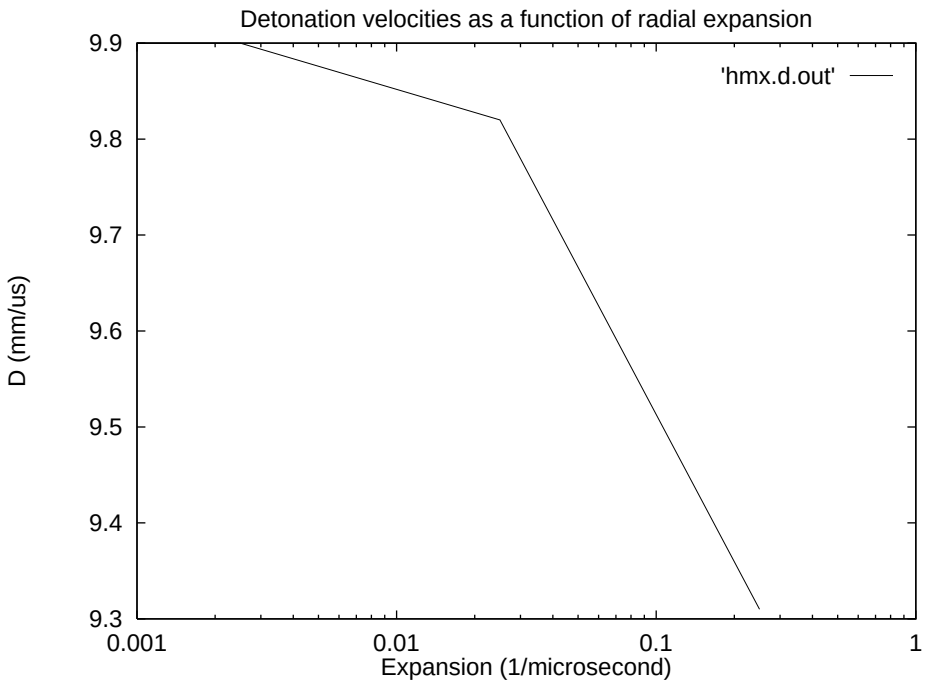

Figure 9. Predicted detonation velocities for HMX vs radial expansion.

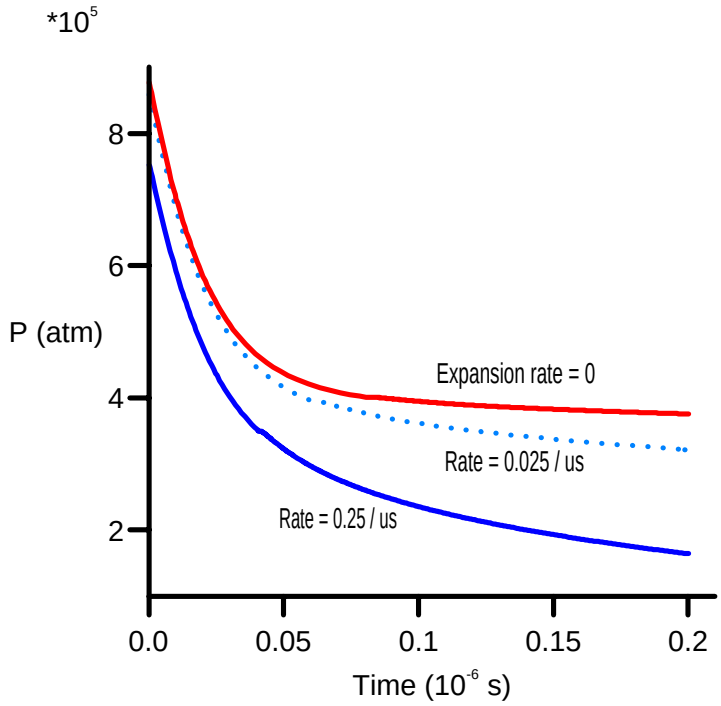

Figure 10. Predicted pressure profiles for HMX kinetic detonations at various expansion rates.

Note that the Von Neumann spike is higher in Figure 10 than is commonly supposed (C. Souers, private communication[14]). This is due to the unreacted HMX equation of state. We used the latest EOS put forth by Simpson.[15] Using an older HMX unreacted EOS gives much lower spike pressures. This in turn has the potential to affect the predicted detonation velocities.

We have performed an initial evaluation of detonation velocities predicted with CHEETAH's WK detonation capability. We selected a series of HEs where experimental radii of curvature were known. We then simply set the radial expansion ω_r to be equal to a constant $= U_P/R_c$, where U_P is the particle velocity in the lab frame, and R_c is the experimental radius of curvature. This relationship is known to hold at the shock front, and becomes more approximate as the reaction zone lengthens.

The kinetic scheme used was equally simple. We used a single constant reaction rate for the HE ignition, where the constant was determined by the estimated length of the reaction zone. Radii of curvature and reaction zones used are shown in Table 1.

The detonation velocities predicted in this way are shown in Figure 11. We find that the WK theory gives almost precisely the same result as CJ detonation for ideal explosives like PETN. As the reaction zone lengthens, the WK equations predict a growing departure from CJ theory. For the compounds with the largest reaction zone (e.g., LX-17) the WK equations overpredict the kinetic effect. The BKWC equation of state used by CHEETAH was calibrated to both nonideal and ideal explosives. Thus, there may be some "over-counting" of the kinetic effect because it was partially taken into account when BKWC was calibrated. Nonetheless, the WK treatment of the problem does reduce the error in the predicted detonation velocities. A gas equation of state that is calibrated only to ideal explosives is probably necessary in order to fully exploit the WK capability of CHEETAH.

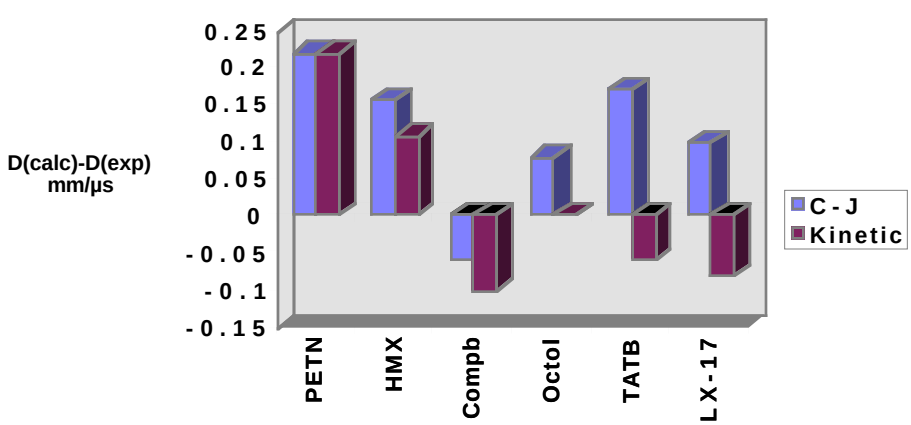

Figure 11. Detonation velocities predicted with CJ and kinetic modes of CHEETAH.

Linked Hydrocodes

There is a substantial need for improvements in the HE equation of state used in hydrodynamic codes. Current hydrodynamic codes typically use the JWL equation of state to represent the explosive. The main advantage of the JWL is its speed of evaluation. JWLs often have limited predictive ability. A manifestation of this is that the HE equation of state needs to be adjusted for differing device geometries. Using a thermochemical code, such as CHEETAH, for the HE equation of state should yield a much greater predictive capability. The HE chemical composition is then a direct input to the hydrodynamic code. The effect of varying the HE formulation on actual device performance can be determined—a task that is impossible with a simple JWL equation of state.

Linking a hydrodynamic code to a thermochemical code directly would be prohibitively slow if the thermochemical code was called on each evaluation of the HE equation of state. We have overcome this difficulty by using interpolation grids. When the hydrocode calls the HE equation of state P(V,E), a grid is dynamically filled with data points from CHEETAH calculations in the desired V,E neighborhood. The exact P(V,E) is then found from interpolation of the grid points. On subsequent calls to the same V,E neighborhood, interpolation can be used immediately.

We have linked CHEETAH to the KOWIN 1-D hydrocode. We have then used the linked code to compare with several plate push experiments. In the plate push experiment, a plane wave HE detonation is used to push a metal plate forward. The plate velocity is measured with a Fabry-Perot interferometer. In Figure 12, we show a comparison of CHEETAH's prediction for 26 mm of LX-14 pushing 20 mil of tantalum. In general, the CHEETAH results compare well with the experiment. The CHEETAH results appear to underpredict the push at low times, but the experimental uncertainty as reflected by the difference in the two records (corresponding to repeated experiments) also grows in this area.

We have also applied the code to a variety of other HEs. Although there is some variability in the quality of the results, we find that the errors with nonideal explosives such as TATB and LX-17 are systematically larger than those for ideal explosives. In Figure 13, we compare plate velocities for 20 mm of LX-17 pushing 20 mils of tantalum. The linked code prediction is systematically low in this case. We conjecture that this is due to the lack of a Von Neumann spike in the linked code. We plan to link kinetic CHEETAH with a hydrocode to see if the treatment of nonideal explosives can be improved by including the pressure transient of the spike.

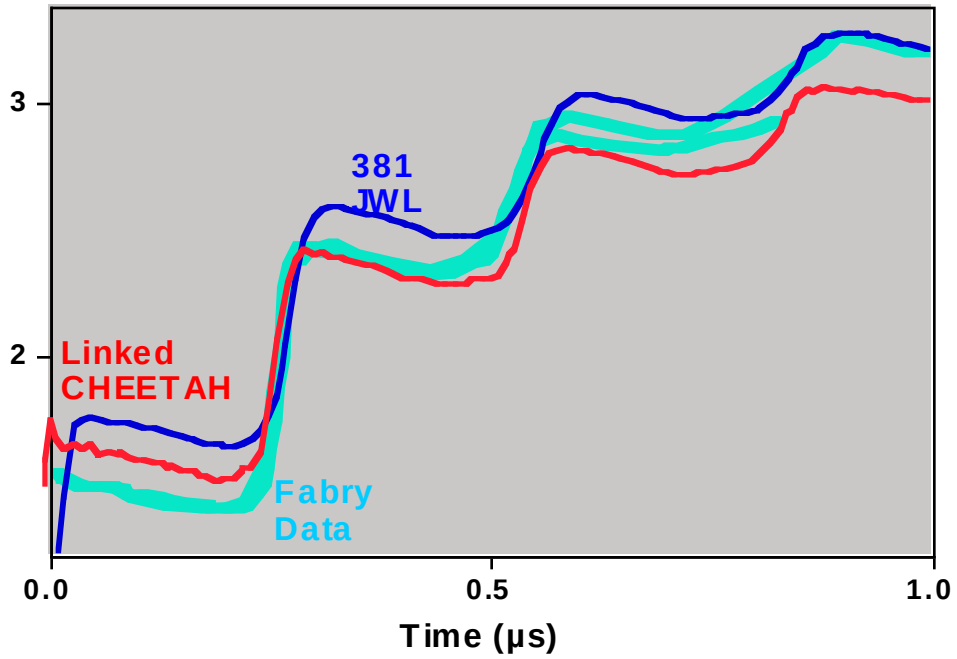

Figure 12. Predicted vs experimental plate velocities in mm/microsecond for 26 mm of LX-14 pushing a 20-mil tantalum plate.

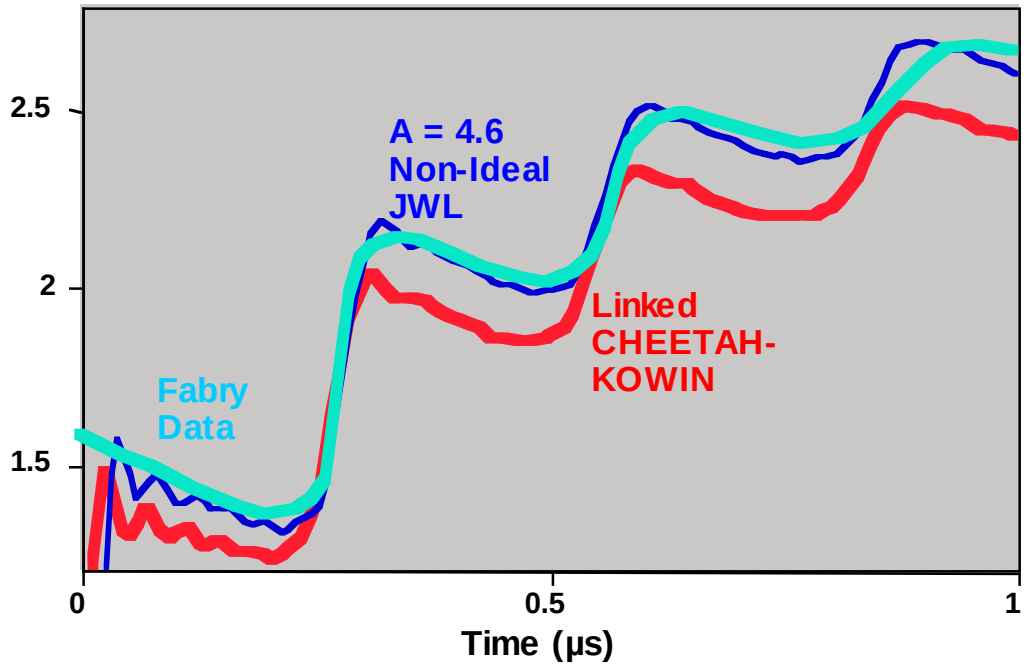

Figure 13. Predicted vs experimental plate velocities in mm/microsecond for 20 mm of LX-17 pushing a 20-mil tantalum plate.

Conclusions

There are many issues that must be addressed before kinetic CHEETAH becomes a practically useful tool. We have a skeletal algorithmic capability established in CHEETAH. This capability is in need of scientifically sound models, which in turn must be validated through experiment. Some particular problems are:

- There have been several models for the expansion rate tried in the past. We need to review these and compare them with hydrocode simulations of cylinder tests. The ultimate solution to this problem will be directly linking CHEETAH to a hydrocode.
- The unreacted EOS cannot be measured reliably in the high pressure shock regime. Molecular dynamics may be the best way to get good unreacted EOSs for CHEETAH. Comparisons with experimental spike pressures are only meaningful when integrated over the experimental response time.
- Kinetic detonation theory has the potential to change detonations predicted by CHEETAH significantly. The BKW parameter set used in CHEETAH may need to be recalibrated to work with kinetics. Or (preferably), we may need to move to more sophisticated gas equations of state. Even in this case, we may need separate calibrations for kinetic and nonkinetic detonation calculations.
- Very little is known about kinetics in the detonation regime. We are starting with a "back of the envelope" approach now. In the future more sophisticated models will probably be necessary. We must be careful not to let the level of model sophistication develop too far from the meager experimental data.

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