

# Modeling Gas Phase RDX Combustion with Intrinsic Low Dimensional Manifolds.

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## Summary

The combustion of a well-stirred system of gases which result from the decomposition of cyclotrimethylenetrinitramine (RDX), a common solid explosive, is studied using the technique of intrinsic low-dimensional manifolds (ILDM). The method provides a systematic way to overcome the severe stiffness which is associated with full models of gas phase RDX combustion, and thus significantly improves computational efficiency. Here, results are shown which demonstrate the existence of an ILDM in a limited region of composition space for 1) isochoric, isothermal ( $T = 3000\text{ K}$ ), and 2) adiabatic, isobaric ( $P = 32\text{ MPa}$ ) combustion of RDX using a standard detailed kinetics model which accounts for 45 species and 232 elementary reaction steps. While the ILDM method has been used to simulate many problems in hydrocarbon combustion, this is thought to be the first application to systems which derive from solid explosives. The full model predicts the ratio of the time scale of the slowest reaction mode to that of the fastest reaction mode to reach values near  $10^{10}$ , which indicates severe stiffness is present. The ILDM method systematically eliminates most of this stiffness by equilibrating fast time scale events and describing parametrically a low dimensional manifold upon which slow time scale events evolve.

## Background

It is well known that in order to accurately simulate a wide variety of thermochemical phenomena, the effects of detailed finite rate chemistry must be incorporated into models. The development of these detailed models over the past decades has provided a strong link between traditional collision-based gas phase chemistry and fundamental fluid mechanics. However, implementation of fully detailed chemistry models with the obligatory numerical resolution has proved to require a prohibitive amount of computational resources for all but the simplest of flows. While the addition of species and reaction mechanisms induces an increase in computational time required to simulate a given event, a more serious problem is often the severe stiffness associated with the differential equations which model the chemistry. In general, the time scales of reaction, found by eigensystem analysis of locally linearized systems, are often widely disparate; in the RDX system studied here, their ratio is as high as  $10^{10}$ . This leads to computations which routinely take hundreds of hours on supercomputers; such efforts are often impractical.

Consequently, it becomes necessary to implement some strategy to reduce the stiffness introduced by the chemistry. The simplest, full equilibrium, is effectively an ILDM of dimension zero; however, this approach will necessarily miss the coupling of events which occur at time scales of chemical reaction. Simple and often useful strategies which capture some of the kinetic time scales employ explicit one- and two-step models, *e.g.* Ward, *et al.*, 1998, or Westbrook and Dryer, 1981. Also useful are the commonly employed partial equilibrium and steady state modeling assumptions. As shown by Maas and Pope, 1992, such assumptions are often not robust. While they may be useful in the range in which they have been calibrated, it is often easy to find scenarios where such models cannot accurately reproduce the results of full kinetic models. As a consequence, Maas and Pope and simultaneously Goussis and Lam, 1992, have advocated methods which systematically reduce chemical kinetic models in such a way that consistency with full model equations is maintained to a user-specified precision. A number of studies have appeared in recent years advancing the technique and some variants, Blansenbrey, *et al.*, 1998; Eggels, *et al.*, 1997; Hamiroune, *et al.*, 1998; Lam, 1993; Schmidt, *et al.*, 1996; Norris, 1998; and Yang and Pope, 1998ab.

Here, the method of Maas and Pope, 1992, as we apply it in the first part of this study to find one-dimensional manifolds, is summarized. The isothermal, isochoric combustion of a well-stirred system of  $n$  species with  $l$  elements leads to  $n - l$  non-linear ordinary differential equations, which evolve in an  $n - l$  dimensional composition space. The ILDM method identifies  $m$  dimensional subspaces ( $m < n - l$ ) on which slower time scale events evolve. For example, for a one-dimensional manifold, we take  $m = 1$ . Fast time scale events rapidly move onto the manifold, and can be projected onto it, avoiding costly explicit time integration. The manifold is determined prior to actual calculations which may use the method. One first determines the equilibrium point of the system and the local real Schur decomposition, which gives local eigenvalues and associated orthonormal Schur vectors for a system linearized about the equilibrium point. One then perturbs  $m$  of the species away from equilibrium to a prescribed values to form  $m$  algebraic equations; these are solved simultaneously with  $n - l - m$  algebraic equations which arise from considering the combination of the forcing term of length  $n - l$  projected onto the basis defined by the  $n - l - m$  orthonormal Schur vectors associated with the  $n - l - m$  fastest time scales. These equations are solved with a predictor-corrector technique coupled with a Newton's method iteration to solve for the concentrations at a new point on the manifold. The new manifold point is used as a seed for calculation of further points. An arc-length parameterization of the manifold is employed to overcome difficulties associated with turning points of the manifold in composition space. This method is also extended for computing manifolds for an adiabatic, isobaric system.

## Results

The method is applied to gas phase RDX combustion. Modeling RDX combustion, such as done by Liao, 1997, or Beckstead and Davidson, 1998, is complex, and must consider solid phase decomposition, zones of bubbly liquids, and zones of gas phase reactions. In a given one dimensional calculation, Liao reports that computation of the gas phase combustion process requires the bulk of the computational resources. The model of gas phase combustion was that of Prasad, *et al.*, 1995, which considered 45 species and 232 reaction steps.

Figure 1 gives results for a full simulation of an isochoric, isothermal RDX gas phase combustion. Figure 1a shows a plot of the evolution of each of the eigenvalues with time. The largest eigenvalue has a value of  $1 \times 10^{16} s^{-1}$ , giving rise to a fastest time scale of  $10^{-16} s$ ; such a result seems unphysically fast for a collision-based model and indicates the underlying model should be examined. The slowest time scale is around  $10^{-5} s$  near equilibrium. The local condition number, the ratio of the largest eigenvalue to the smallest, has its evolution shown in Fig. 1b. It is seen to approach  $10^{11}$  near equilibrium. Plots of the evolution of the molar concentrations of two species,  $[N_2]$  and  $[CO_2]$ , are shown in Fig. 1c,d. In all plots there is evidence of change on fine and coarse time scales, with the entire event concluding near  $t = 0.01 ms$  ( $10^{-5} s$ ). Not shown on the plot are events which evolve on the finest time scales. For instance, the initial values of both  $[N_2]$  and  $[CO_2]$  are actually zero.

The  $[N_2] - [CO_2]$  phase portraits for the same system are shown in Fig. 2a. Here calculations for a variety of initial conditions have been shown, where  $\alpha$  is a parameter which is varied in such a way that the initial number of elements remains constant in each calculation, while the initial concentrations of RDX gas and  $H_2$ ,  $N_2$  and  $CO_2$  are allowed to vary. It is seen that each phase trajectory approaches the same equilibrium point. Moreover, each trajectory approaches a common one-dimensional manifold in this phase plane. Superposed onto the plot are the results of an independent calculation of the ILDM, done with the technique outlined in the previous section. It is clear that the trajectories obtained from full solution to the equations are approaching the ILDM. Figure. 2b shows the existence of a one-dimensional ILDM for the adiabatic, isobaric combustion of RDX. For the long term, it will be necessary to develop manifolds of variable dimension which will likely be necessary to account for variation at a threshold time scale. Moreover, it will ultimately be necessary to demonstrate the efficacy of the method in the solution of systems with time and space variation.

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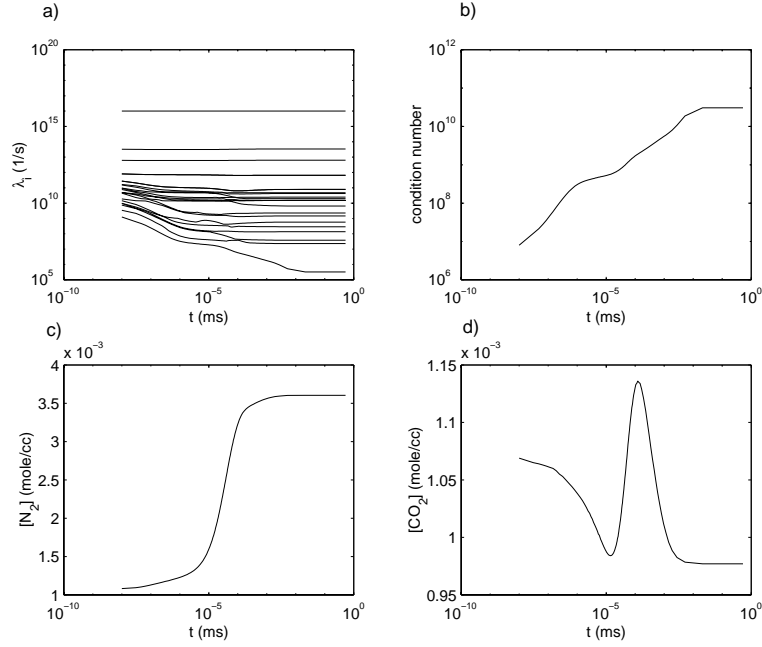


Figure 1: Results from full simulation of 45 species, 232 step decomposition of well-stirred, isochoric, isothermal gas phase RDX,  $T = 3000\text{ K}$ , a) eigenvalue variation with time, b) condition number variation with time, c)  $N_2$  concentration variation with time, d)  $CO_2$  concentration variation with time.

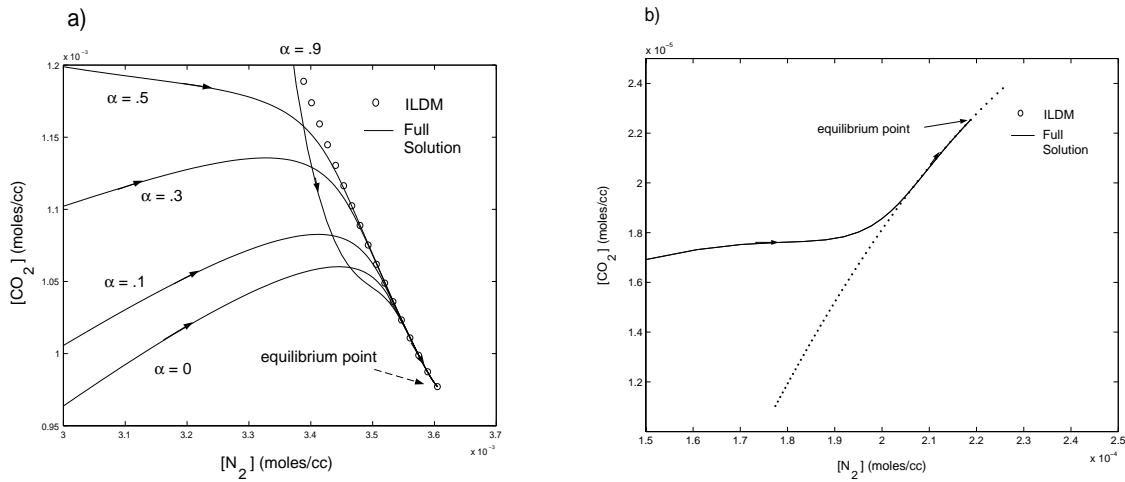


Figure 2:  $[N_2] - [CO_2]$  phase portraits for various initial conditions and projection of intrinsic low dimensional manifold for RDX combustion, a) isochoric, isothermal combustion, b) adiabatic, isobaric combustion.