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RECENT ADVANCES IN MODELING HUGONIOTS WITH CHEETAH

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Abstract. We describe improvements to the Cheetah thermochemical-kinetics code's equilibrium solver to enable it to find a wider range of thermodynamic states. Cheetah supports a wide range of elements, condensed detonation products, and gas phase reactions. Therefore, Cheetah can be applied to a wide range of shock problems involving both energetic and non-energetic materials. An improve equation of state is also introduced. New experimental validations of Cheetah's equation of state methodology have been performed, including both reacted and unreacted Hugoniots

Keywords: Cheetah, thermochemistry, equation of state, Hugoniot.
PACS: 82.20.-w, 82.33.Vx, 47.40.-x, 95.30.Tg.

INTRODUCTION

Cheetah [1] is a thermochemical-kinetics code based upon solving chemical equilibrium or kinetic equations. Cheetah is used for the development, characterization, and assessment of explosives, pyrotechnics, gun and rocket propellants, materials, and planet interiors [2]. The gas equation of state (EOS) is an exponential-6 model of interacting fluids [3]. The condensed EOS is an enhanced Murnaghan EOS [4]. Any thermodynamic potential or thermodynamic second derivative can be conveniently calculated. The solution state can be constrained by physical properties: volume V (equivalently: density ρ), energy E, entropy S, temperature T, Helmholtz free energy A, pressure P, enthalpy H, Gibbs free energy G, the Hugoniot, or the Rayleigh line.

To maintain code quality, an extensive automatic test suite has been developed to verify code functionality. The suite consists of over 300 Cheetah runs, with many including multiple calculations within them. Results are automatically compared to archived results. Scripts regularly scan the source code and verify that all commands are in the test suite.

The aforementioned test suite verifies that Cheetah gives the expected result, but does not verify that the expected result is physically accurate. Another test suite, called "fits", is used for this purpose. The fits system compares Cheetah to more than 3000 unique experimental data points. More specifically, the suite contains as of this report: 147 Hugoniots fits (both reacted and unreacted), 7 shock temperature fits, 9 re-shock Hugoniot fits, 12 isothermal compression fits, 13 sound speed fits, 126 heat capacity fits, and 24 phase diagram fits. The test suites (in particular the Hugoniot data), along with user needs, has driven significant improvements to both the methodologies in the code and the EOS library.

IMPROVEMENTS TO THE EOS

Cheetah 4.0 includes version 2 of the exponential 6 EOS. Version 2 completed the stoichiometric set for most elements used (solid, liquid and gas states). To improve accuracy, new chemical species, such as FeS_2, have been added. For species where multiple solid states exist, such as Fe_3O_4 and phosphorous, the EOS now includes multiple solid phases. Some materials had liquid phases added, such as Ti_2O_3. In addition to enlarging the EOS library, the fits test suite allowed careful optimization of the EOS. The details of these improvements will be the subject of a later work, while this work will focus more on computational improvements to the Cheetah code.

IMPROVED SOLUTIONS OF STATES

The equilibrium solver in Cheetah 3.0 could not easily handle all possible states. Unfortunately, the limitations were not obvious, because they were dependent upon the chemical system. In this work, we describe advances in Cheetah 4.0 which allow it to solve a wider range of problems than 3.0.

The interface to the existing equilibrium solver has been significantly enhanced. Cheetah 4.0 makes a substantially better initial guess at the target thermodynamic state. The first step in this process is to set the V, T, and/or P to the requested values. Since at most two of these can be specified, unspecified V, T and P are set to the last calculated state's value (for the first state with this composition, they are set to reasonable generic values). If two are specified, then the third is found iterately. If only V is specified then P is found. For all other states, V is found which is consistent with P and T.

Cheetah 4.0 has also significantly improved algorithms for "sneaking up" on hard to solve thermodynamic states. This provides Cheetah with better recovery from initial failure. Cheetah tries successively smaller steps from the current state to the target state.

These two subtle, but important, enhancements have resulted in many states converging that would not easily converge in Cheetah 3.0.

Cheetah requires a value of gaseous P, thus low gas states were problematic in Cheetah 3.0. This resulted in the inability to run thermites. Cheetah 4.0 adds infinitesimal quantities of generic gas, thus guaranteeing that P is defined. The amount is set small enough to avoid affecting properties. In Cheetah 3.0, the user could add Argon to achieve a similar effect, but it did change the results.

A new solver that minimizes free energy has been implemented. Although only the Donlp2 SQP solver [5] is implemented, a generic interface allows other solvers to easily be added. We have modified Donlp2 to verify solution validity. Only state types for with a corresponding thermodynamic potential exists can be solved (V and T; P and T; V and E; S and V; S and P; P and H). Although the Hugoniot is not directly solvable, the Donlp2 method is a user selectable option for solving the initial state point, which can be troublesome. For example, the following calculation does not solve directly without using Donlp2 [6]:

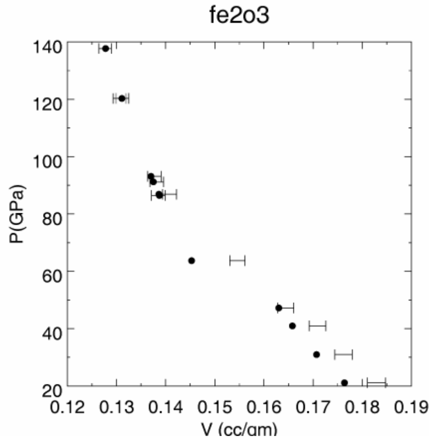
comp,ap,20,rdx,25,al,33,nto,10,htpb,10.5,n-100,1.5
point, p, 2, t, 400

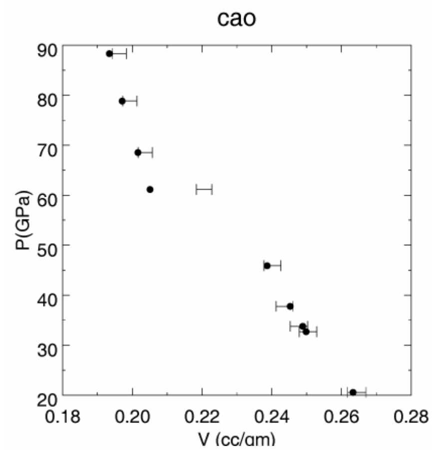
RESULTS AND DISCUSSION

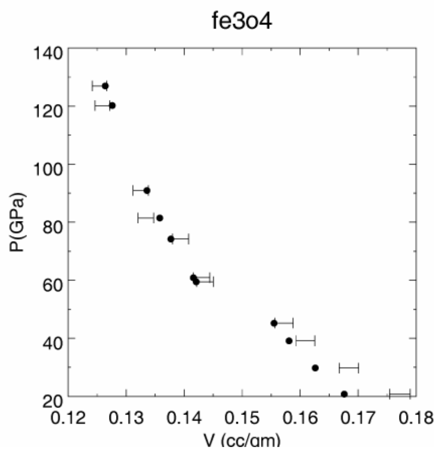
The advances in solver capabilities have made many Hugoniots easily attainable. All Hugoniots presented in this work required extensive manual manipulation to work in Cheetah 3.0, and/or the Hugoniots required the addition of a substantial amount of Argon to improve numerical stability. Both of these solutions under Cheetah 3.0 were unsatisfactory because either they required an expert user or chemical modification of the system. Experimental data is from LANL shock data [7] and the Russian shock database [8]. Results are presented in Fig. 1-2. Agreement with experiment is quite good (and better than in Cheetah 3.0), although the kink in the Fe_2O_3 is slightly too low of a pressure. The success in reproducing known Hugoniots provides confidence in its ability to calculate properties of system without experiments.

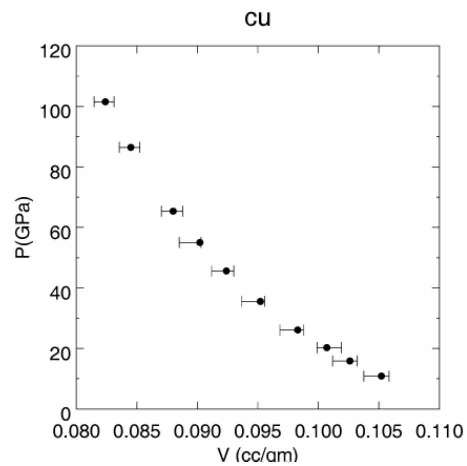
CONCLUSIONS

The Cheetah code has advanced substantially from version 3.0 to version 4.0. We improved the thermodynamic engine and solver system in Cheetah. The improved engine can find a wider range of states, including states with little or no gas. Version 2.0 of the exponential-6 EOS has improved accuracy of the computed results. Many Hugoniots are now easily and accurately calculated in Cheetah 4.0, that were not calculatable in Cheetah 3.0. The success in reproducing known Hugoniots provides us with confidence in Cheetah's ability to calculate properties of systems for which the experimental data is not known.









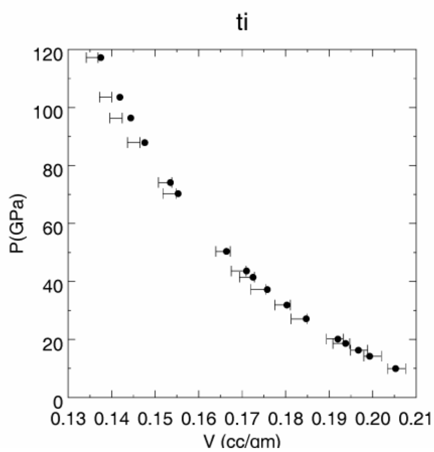
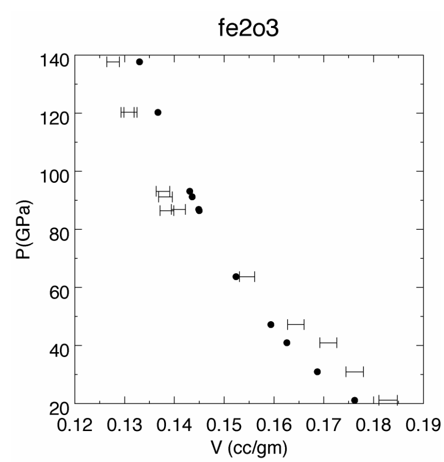
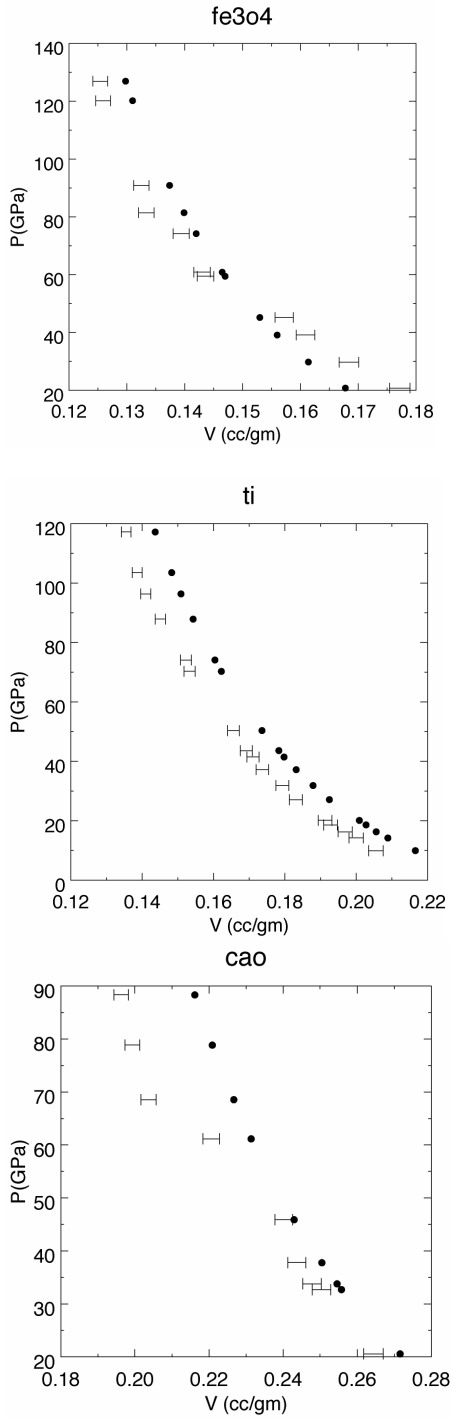


Figure 1. Metal and metal oxide Hugoniots compared to experimental data, calculated with Cheetah 4.0.





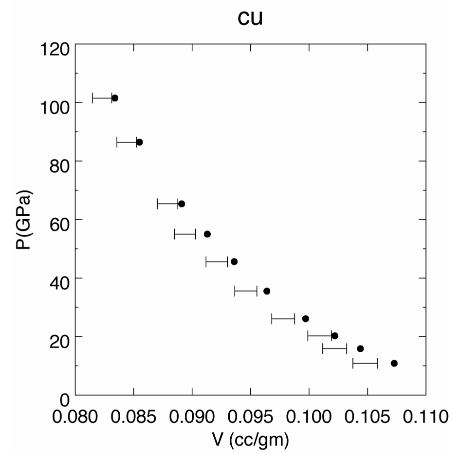


Figure 2. Metal and metal oxide Hugoniots compared to experimental data, calculated with Cheetah 3.0.

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