Special Feature 2001

Equation of State Data and Fitting Forms

Ralph Menikoff (T-14) and Thomas D. Sewell (T-14)

Numerical simulations of explosive systems require constitutive properties of the materials. The Los Alamos National Laboratory uses HMX (cyclo-tetramethylene-tetranitramine) as its main high-performance explosive. The HMX equation of state was determined in 1978 by Olinger, Roof, and Cady [1]. They used X-ray diffraction measurements to determine the room temperature isotherm (pressure as a function of density at constant temperature) up to a pressure of 8 GPa (~ 80,000 times atmospheric pressure). In analogy with shock Hugoniot data, they transformed the *P–V* data to the pseudo-velocity plane (shock velocity vs. particle velocity) and observed that the data are well fit by a straight line. This led to a Mie-Grüneisen form of equation state based on a linear U_s–U_p relation that is currently being used for HMX.

In 1999, Yoo, and Cynn [2] repeated the isothermal HMX experiment using recently developed techniques. By using a diamond anvil instead of a Bridgman anvil, they extended the domain of the measurements up to a pressure of 43 GPa. Their data can be well fit by a Birch-Murnaghan equation of state. Both the Hugoniot form of equation of state used by Olinger, Roof, and Cady and the Birch-Murnaghan form used by Yoo and Cynn have two adjustable fitting parameters. Moreover, both sets of parameters can be related to the bulk modulus and its pressure derivative at zero pressure. In the pressure domain common to both experiments, both forms of equation of state give reasonable least square fits.

What is of importance for studies of initiation of detonation waves is the equation of state in the neighborhood of the Chapman-Jouget point, which corresponds to a detonation velocity $U_s \approx 9$ mm/µs and a pressure $P \approx 40$ GPa. The extrapolation of fits to the data sets of Olinger, Roof, and Cady and of Yoo and Cynn are shown in Figure 1. We observe that the fits to the data at the CJ-point are significantly different.

Formulation of the best model equations of state compatible with multiple data sets necessitates accounting for different experimental techniques and associated uncertainties. The functional forms of the bulk modulus ($K(V) = -V\,dP/dV$) of the Hugoniot and Birch-Murnaghan fitting forms are different. Because of the curvature of the $U_s(U_p)$ locus for $U_p \approx 0$, this has a significant effect on the value of the bulk modulus at zero pressure and more importantly the slope of the isotherm in the *(Us, Up)*-plane. The curvature effect is common in molecular crystals such as HMX, polymers or plastics, or foams and liquids. This is in contrast to the conventional wisdom for solids, which really applies only to atomic crystals such as metals.

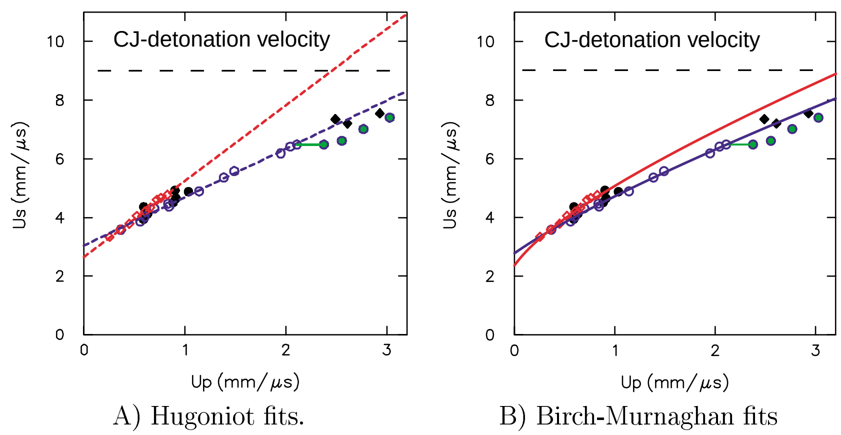

Figure 1: Fits to HMX data in (U_p, U_s)-plane. Red diamonds and blue circles are isothermal data of Olinger, Roof, and Cady [1] and Yoo and Cynn [2], respectively. Black circles are Hugoniot data for solvent pressed HMX (0.5% porosity) [3, p. 596], and black diamonds are Hugoniot data for single crystal HMX (unspecified orientation) [4] around the CJ-detonation pressure, 34–42 GPa. Green line indicates phase transition at 27 GPa in the isothermal data [2]. In addition: Dashed red and blue lines are linear fits to isothermal data. Solid red and blue lines are Birch-Murnaghan fits to Olinger, Roof, and Cady data and Yoo and Cynn data below phase transition at 27 GPa, respectively.

A measure of the goodness of fit is the reduced chi-squared parameter

$$\chi^2_\nu = \frac{1}{N-2}\sum_i \left[\frac{P_{\text{fit}}(V_i) - P_i}{\Delta P_i}\right]^2$$

where N is the number of data points (V_i, P_i) and ΔP_i is the experimental error bar. Based on the values of χ^2_ν both fits to both data sets are reasonably good. The sensitivity of the fitting parameters to the uncertainty in the data points is displayed in the contour plots of χ^2_ν shown in Figure 2. The maximum contour corresponds to one standard deviation. The fact that the "error ellipses" do not overlap implies there is a significant systematic difference between the experiments.

One of the important differences in the experiments is the choice of pressure mediums used to obtain a hydrostatic compression; methanol-ethanol mixture in the Bridgman anvil used by Olinger, Roof, and Cady vs. argon in the diamond anvil used by Yoo and Cynn. At high pressures, the pressure medium is not totally hydrostatic. Consequently, shear stress and stress gradients in the HMX sample can lead to errors in the determination of the pressure.

The discrepancy between the data sets leads us to consider the available Hugoniot data for HMX. Shock data for solvent pressed HMX and single crystal HMX are also shown in Figure 1. Overall, the Birch-Murnaghan fit is the most compatible with all the isothermal data and Hugoniot data. We are also studying other data. These include sound speed measurements at ambient conditions, shock Hugoniot measurements in HMX based plastic-bonded explosives (PBX-9501), and determinations of the von Neumann spike pressure of a CJ-detonation wave in PBX-9501.

In addition, there is an ongoing effort to determine material parameters for HMX from molecular dynamics calculations, see for example [5]. Further information is given in our recent paper [6] which is available from the web at

http://t14web.lanl.gov/Staff/rsm/preprints.html#IsothermFit.

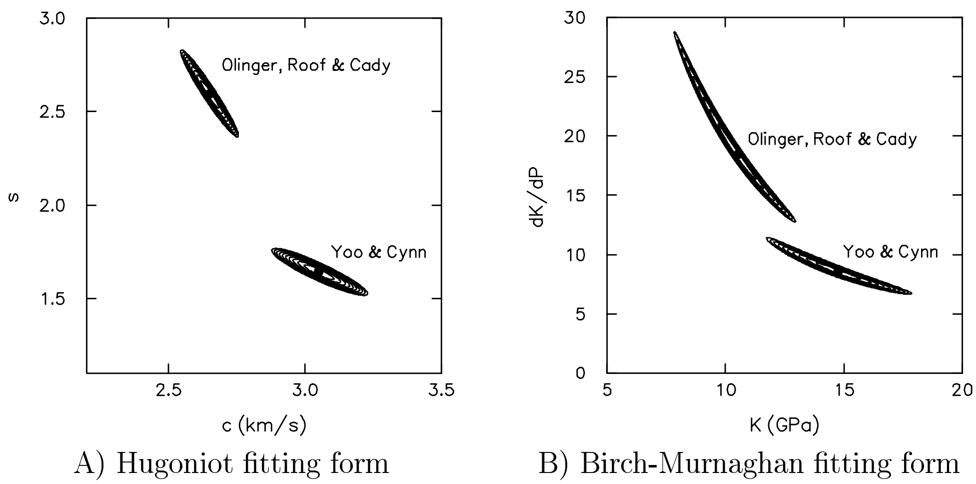

Figure 2: Contour plot of χ^2_ν ***for fits to the HMX data of Olinger, Roof, and Cady [1] and Yoo and Cynn [2] (restricted to*** $P < 27$ ***GPa). Ten contours for each fit are equally spaced between the minimum value and twice the minimum of*** χ^2_ν ***.***

[1] B. Olinger, B. Roof, and H. Cady. The linear and volume compression of β-HMX and RDX. In *Proc. Symposium (Intern.) on High Dynamic Pressures*, pages 3–8. C.E.A., Paris, France, 1978.

[2] C.-S.Yoo and H. Cynn. Equation of state, phase transition, decomposition of β-HMX. *J. Chem. Phys.*, 111:10229—10235, 1999.

[3] S. Marsh, editor. *LASL Shock Hugoniot Data*. Univ. Calif. press, 1980. On line,
http://lib-www.lanl.gov/books/shd.pdf.

[4] B. G. Craig. Data from shock initiation experiments. Technical report M-3-QR-74-1, Los Alamos Scientific Lab., 1974.

[5] D. Bedrov, C. Ayyagari, G. Smith, T. Sewell, R. Menikoff, and J. Zaug. Molecular Dynamics Simulations of HMX Crystal Polymorphs using a Flexible Molecular Force Field. *LA-UR-00-2377*.

[6] R. Menikoff and T. Sewell. Fitting Forms for Isothermal Data. *High Pressure Research*, (to appear), LA-UR-00-3608-rev.

Formulation of the best model equations of state compatible with multiple data sets necessitates accounting for different experimental techniques and associated uncertainties.

rtm@lanl.gov
sewell@lanl.gov

This paper is a portion of LA-UR-01-1847, May 2001.