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HIGH-EXPLOSIVE PROPERTIES FROM CLASSICAL MOLECULAR DYNAMICS SIMULATIONS AND QUANTUM-CHEMICAL COMPUTATIONS

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ABSTRACT

We are using classical molecular dynamics and condensed phase electronic-structure methods to predict some of the thermophysical and mechanical properties that are needed as input to realistic mesoscale models for plastic-bonded explosives. The main materials studied to date are HMX, PETN, Estane copolymer, and bis(2,2-dinitropropyl) formal/acetal (BDNPF/A). Emphasis is placed on non-reactive properties and thermodynamic states relevant to cookoff and shock initiation phenomena. Both crystal and liquid-state properties are of interest. Typical simulation sizes and times are $\sim 10^2$ molecules and 2-10 ns, respectively. The overarching goal is to develop internally consistent model thermodynamic and elastic mechanical descriptions for the materials. Prioritization among the set of properties amenable to atomistic simulation is made based on ongoing interactions with mesoscale modelers at Los Alamos and elsewhere. Recent work will be summarized and our view of profitable directions for future research will be discussed, including preliminary results for large-scale molecular dynamics simulations of shock response of crystalline HMX.

I. Introduction

Over roughly the last decade we have employed classical molecular dynamics and Monte Carlo methods to predict some of the thermophysical and mechanical properties that are needed as input to realistic mesoscale models for plastic-bonded explosives (PBXs). The main materials we have studied by these methods include: TATB [1], RDX [2,3]; β -, α -, δ -, and liquid HMX [2,4,5,6,7,8,9]; and EstaneTM, a poly(ester urethane)

copolymer [10]. The three-dimensionally periodic simulation cells in our more recent work typically contain $\sim 10^2$ molecules, with simulation times of 2-10 nanoseconds. While much of this work has focused on verification and validation (V&V [11]), the overarching goal of these “medium scale” atomistic studies is to develop internally consistent model thermodynamic and elastic mechanical descriptions for the materials, suitable for use in, or as a guide to the formulation of, mesoscale simulations in which the grains and binder in a plastic-bonded explosive are resolved within a continuum hydrodynamic or material-point method (MPM) framework. Emphasis in our work is placed on non-reactive properties and thermodynamic states relevant to cookoff and shock-initiation phenomena. Prioritization among those properties amenable to atomistic simulation is made based on ongoing interactions with mesoscale modelers [12,13], predominantly at the Los Alamos and Sandia National Laboratories. Upon completion of a quantum chemistry-based force field for bis(2,2-dinitropropyl)formal/acetal (BDNPF/A) [14], we should, in principle, be able to study all relevant intermolecular interactions in PBX-9501 [15].

In addition to classical molecular dynamics and Monte Carlo simulations, we have employed condensed phase electronic-structure methods in our work to study the zero Kelvin structures and properties of crystalline HMX [16] and PETN [17]. Highly parallel, $O(N)$ algorithms implemented in the MondoSCF quantum chemistry code [18] used in Ref. [17] enable “routine” fully optimized, all-electron, density functional electronic-structure predictions of zero temperature molecular crystal structures as a function of material density – that is, the cold curve. In this work we are able to use high-level functionals and basis sets (e.g., PBE/6-31G**), and primary cells containing hundreds of atoms. The PETN study described in Ref. [17] is the first published application of MondoSCF to high explosives.

In Section II we briefly sketch our view on “good” roles for atomistic simulations in connection with high explosives (and most other materials, for that matter). We also include a few results from our older work, which hopefully serve as reference points for what can realistically be extracted from atomistic simulation. Vignettes of work presently underway are given in Section III; *as such, the results shown there should be regarded as “snapshots in time” rather than “final product.”* We conclude in Section

IV with some thoughts about probable future roles for classical and electronic structure-based atomistic simulations of energetic materials.

II. Why even bother with atomistic computations in explosive science?

A large number of atomistic studies of condensed phase high explosives have been published, with a rate that has increased noticeably in recent years [19]. Based on our own experience, we have come to view *judicious* application of atomistic simulation approaches as a credible tool for prediction of high explosive thermophysical and elastic mechanical properties. In particular, we think that, given a validated potential-energy surface, molecular simulations can serve as a complement to experimental data by extending regions in thermodynamic space for which information is available [3]. Another useful role is to provide information about properties in thermodynamic regimes that are difficult, if not impossible, to probe experimentally with existing technology for some high explosives (e.g., liquid HMX [7,8]). Although unavailable experimentally, some of these quantities are key to the parameterization of improved models for use in mesoscopic simulations [12,20]. Finally, in situations for which independent experimental determinations of some property are at odds with one another, molecular simulation tools can potentially be useful as a tool for interpreting the differences based on, for example, differing methods of data collection and/or analysis. Such situations are more common than one might think, even for “simple” properties such as the isotherm and bulk modulus [6,17,21,22,23] and coefficients of thermal expansion [5,24,25,26,27], let alone more complicated objects such as the elastic tensor [6,28].

Representative results from previously published work

Table I contains calculated and measured elastic tensors for RDX at “room temperature” and atmospheric pressure. The calculated results are based on “early” isothermal-isobaric Monte Carlo realizations that used small primary cells and rigid molecules [3]. (The rigid-molecule approach has been used extensively by others in studies of high explosives, most notably in a series of papers by Thompson and co-workers [29].) The two sets of experimental results are based on resonant ultrasound spectroscopy (RUS) [30,31]. In the present comparison we make no attempt to account for the difference between isothermal and isentropic elastic tensors, C_{ij}^T and C_{ij}^S , respectively, as they are expected to differ by only a few percent. In spite of the relatively severe approximations

made in this early study, the agreement between the simulated results and experiment is surprisingly good.

Table I. Calculated and measured elastic tensors for RDX at atmospheric pressure.

Source	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
Simulation ^a (2000)	27.5	24.6	18.0	8.4	5.3	8.0	6.5	5.9	6.4
Hausühl ^b (2001)	19.58	24.98	17.89	4.06	5.15	6.90	8.19	5.90	5.80
Schwarz & Hooks ^c (2004)	21.3	25.6	19	4.27	5.38	7.27	8.67	6.4	5.72

a. Ref. [3], isothermal-isobaric, rigid molecule Monte Carlo, T=304 K.

b. Ref. [30], resonant ultrasound spectroscopy.

c. Ref. [31], resonant ultrasound spectroscopy.

A much more sophisticated, flexible-molecule force field has been used in a series of studies of liquid and crystalline HMX [4]. Among the liquid state properties of HMX for which predictions have been reported are atmospheric pressure self-diffusion and shear viscosity coefficients [7] and thermal conductivity [8], each extending from 550 K to 800 K. These temperatures bracket the nominal HMX melting and boiling points, respectively, at atmospheric pressure. Although there are no experimental data for direct validation, the predictions of the liquid thermal conductivity are generally consistent with experimental data for the solid at elevated temperature (and which most likely consists of a mixture of β - and δ -HMX, with some amount of degradation products), and correspond fairly closely to the (constant) liquid state value for thermal conductivity used in some of the combustion simulations of Beckstead and co-workers [32].

III. Selected highlights from ongoing research

Further studies of the HMX liquid equation of state

Continued studies of the HMX liquid equation of state are underway by Jaramillo and Sewell, to yield liquid-state properties as functions of pressure and temperature, and to map out where in thermodynamic space the onset of glassy behavior occurs (based on the ~ 10 nanosecond time scale of our simulations). The force field and computational protocol are essentially identical to those used in our recent study of the elastic properties of crystalline HMX [6], except that in the liquid studies we constrain the primary simulation cell to cubic geometries. The calculations span the intervals $0 \text{ GPa} \leq p \leq 10 \text{ GPa}$ and $550 \text{ K} \leq T \leq 850 \text{ K}$. These represent the nominal melting and boiling

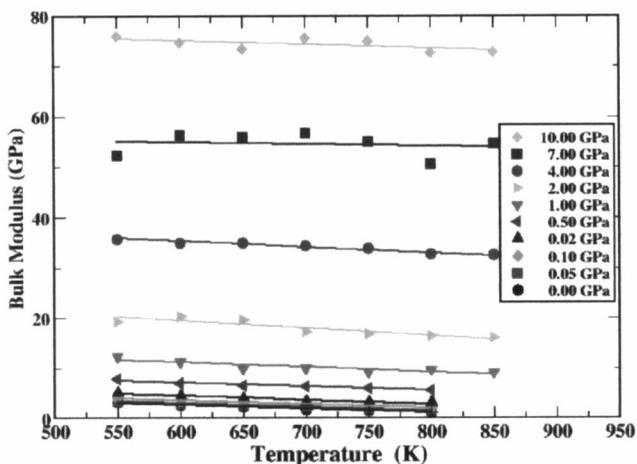


Figure 1. Calculated temperature-dependent bulk modulus of “liquid” HMX, for hydrostatic pressures between 0 and 10 GPa and 550 K ≤ T ≤ 850 K.

temperatures, respectively, at atmospheric pressure. In Fig. 1 we show the calculated bulk modulus as a function of temperature, with separate curves for several pressures between zero and ten GPa. The bulk modulus at a given thermodynamic state was obtained from an analysis of the volume fluctuations

sampled in our isothermal-isobaric simulations via the relation $B = \langle V \rangle \kappa T / \sigma_V^2$, where $\langle V \rangle$ and σ_V^2 are the average volume and its variance, determined from the simulation.

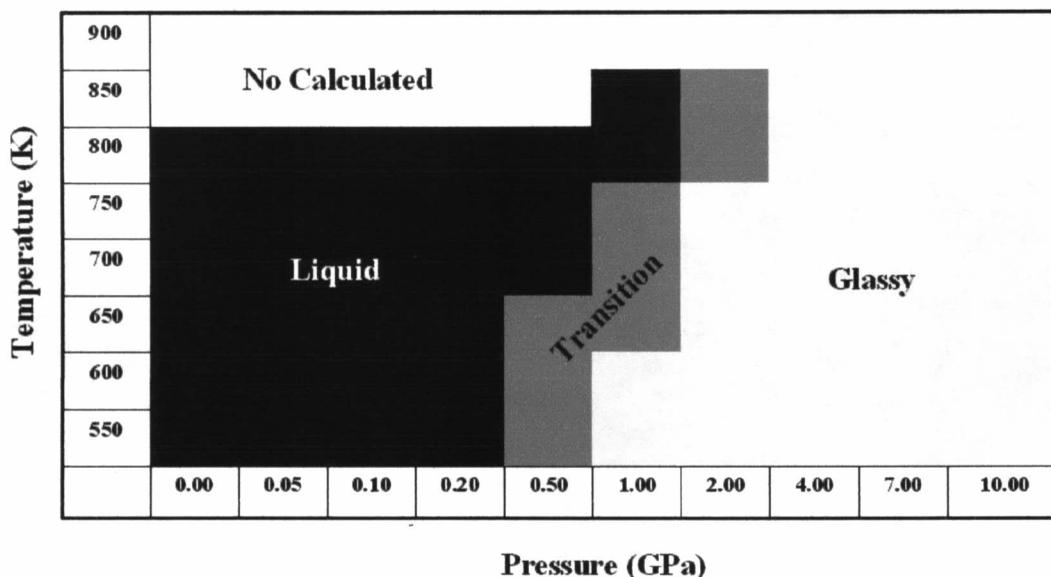


Figure 2. Predicted “phase diagram” for the onset of glass-like behavior of HMX at elevated pressures and temperatures, based on the structural and dynamical measures listed in the text.

Based on calculations of molecular self-diffusion coefficients, time scales for molecular rotation, and radial distribution functions (none of which are shown), we conclude that, for the relatively short (but nevertheless relevant for mesoscale simulation)

time scale of ~ 10 ns, the onset of glassy-like behavior in liquid HMX occurs at fairly low temperatures, even for modest pressures. The bottom-line results obtained to date are shown in Fig. 2. The figure is something of an “amalgam” of the results for the various measures listed above, but suggests that, for most pressures above about one GPa, HMX behaves more like an amorphous, glassy material than as a liquid, for temperatures below about 900 K. This may be of practical importance in discriminating among candidate dissipative mechanisms in HMX at the moderately high pressures and temperatures relevant to weak-shock initiation [33].

High-level electronic structure studies of the hydrostatic compression of β -HMX

As a follow-on to our preceding electronic-structure studies of the PETN zero Kelvin isotherm (cold curve) [17], we have undertaken analogous calculations for β -HMX. The interest in re-visiting β -HMX isotherm, in spite of the existence of at least three each experimental [21,22,34] and computational [2,6,29,35] studies (including one each at non-ambient temperatures [34,35]) is that, while all of the simulated isotherms are in better agreement with the 1978 isotherm of Olinger et al. [21], Menikoff and Sewell [12] concluded that the 1999 Yoo and Cynn isotherm [22] is more consistent with the preponderance of data for shocked β -HMX. In particular, the extrapolated Olinger isotherm appears to be too stiff/steep (in the P-V and Us-Up planes, respectively) compared to shock hughoniot data, which is an aphysical result.

As in our PETN study [17], we use a three-dimensionally periodic, all-electron density functional treatment, at the PBE/6-31G** level; and fully optimize the cell contents *and* the symmetry class-restricted lattice parameters (in this case lattice lengths a , b , and c ; and monoclinic angle β) at a given volume compression V/V_0 . Most of the calculations were performed using 32 or 64 processors. Two different computational protocols were used, both of which yield hydrostatic conditions through a series of sequential “line searches” along the monoclinic lattice parameters, with geometry optimization of the cell contents at each step. There are two differences between the protocols. In one case, which we refer to as “uniform” optimization, we initially assume uniform relative compression along a , b , and c to obtain a starting guess for the first geometry optimization [i.e., $(a_1, b_1, c_1) = \alpha(a_0, b_0, c_0)$]; in subsequent steps, we simply enforce $x_{k+1}/x_k = x_k/x_{k-1}$ (where $x = a, c, \beta$ are varied independently; b provides closure at

the desired volume $V=abc\sin\beta$, and no reference to experimental compression is required). The second approach, which we refer to as “experimentally-based,” differs in that we initially follow the experimental linear compressions along a , b , c , and β , via a 5th-degree polynomial fit to Olinger’s data [36]; and enforce volume closure *via* the monoclinic angle β instead of the lattice length b . As of this writing, we only have a few data points obtained using the experimentally-based protocol.

In Fig. 3 we show the PBE/6-31G** energy difference versus hydrostatic compression volume ratio V/V_0 (left panel) and associated pressure-volume (P-V) relationship (right panel). We also include both published experimental P-V data sets for comparison. From the relative energies, we conclude that the results are not highly sensitive to primary cell size. (This is only true for large values of V/V_0 , however; thus, all subsequent calculations will only be shown for the 2x1x2 case.) The right panel is perhaps more interesting in that, for the 2x1x2 “uniform” case shown, PBE/6-31G** predicts better agreement with Yoo and Cynn than with Olinger et al., in contrast to all preceding computational studies of which we are aware. In the absence of the present results, one might credibly argue that “reconciliation” among the various experimental and theoretical results could be rationalized in terms of effects due to crystal purity and differences between the shock hugoniot of single crystals the inevitable initial porosity in pressed powders.

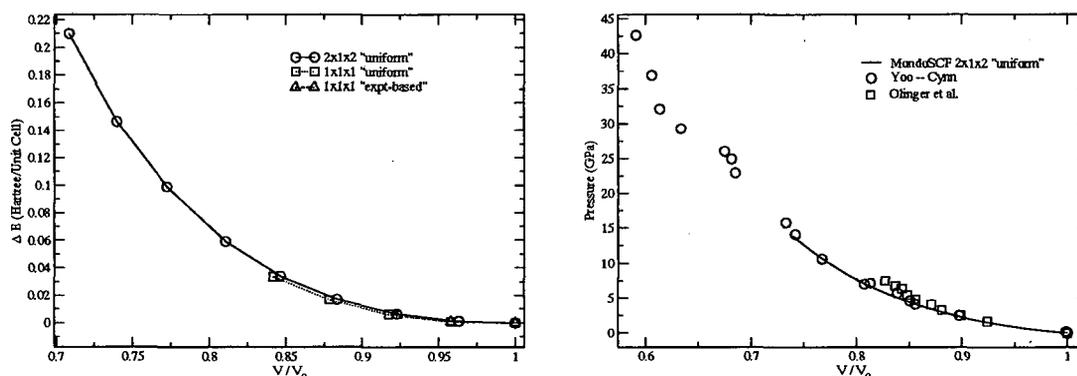


Figure 3. Calculated relative energies (left panel) and pressures (right panel) versus compression ratio for β -HMX, at the PBE/6-31G level. The full curves in both panels are based on a primary cell containing eight molecules, with full optimization of cell contents at each volume. See text for details.**

In Fig. 4 we compare the results for linear compressions of the monoclinic lattice parameters to the results of Olinger et al. [21] based on the “uniform” protocol described above (left panel) and preliminary results for the “experimentally-based” approach (right panel) – only three compressions were available at the time of this writing. Note that the MondoSCF PBE/6-31G** predictions for variation in lattice length a and monoclinic angle β are fairly accurately predicted using either protocol. By contrast, calculations

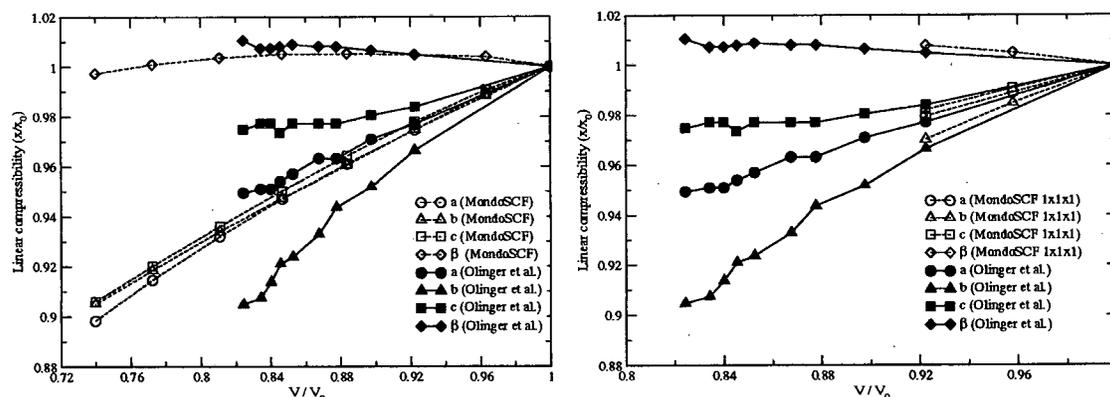


Figure 4. Comparisons of the linear compressions in β -HMX predicted using PBE/6-31G, based on the “uniform” protocol (left panel) and “experimentally-based” protocol (right panel). See text for details.**

based on the “uniform” approach underestimate the compressibility along the b axis while overestimating it along the c axis. The calculated linear compressibilities based on the “uniform” approach are essentially isotropic (in the scaled sense depicted in Fig. 4), whereas experiment indicates significant anisotropy. By contrast, the preliminary results in the right-hand panel of Fig. 4 indicate that using experiment as a “guide” leads to predictions for the optimized lattice parameters that are in much better agreement with measured data.

In Sewell’s opinion, this sensitivity should raise a red flag (or at least a pink one!) since it appears that, even for a crystal as “simple” as β -HMX at low levels of compression, one may, at low temperatures (zero Kelvin in the present case), be faced with an energy landscape that requires either a robust optimizer or some practically useful molecular dynamics or Monte Carlo scheme to anneal the systems at a given density. This sensitivity also suggests that calculations in which not all symmetry-unrestricted variables are explicitly optimized should be treated as suspect. It is also

prudent to examine lower symmetry configurations in the neighborhood of the symmetry-based minimum, to ensure that the quantum calculation does not find nearby, lower-energy, lower-symmetry states. This was addressed in our PETN work [17] where we examined orthorhombic states near the tetragonal minimum, but remains to be tested for β -HMX. One might argue, based on the present results, that failure to investigate these details of protocol amounts to intellectual negligence.

Preliminary “almost large scale” molecular dynamics simulations of shocked HMX

Very recently, we have begun to consider the feasibility of million or even multi-million molecule simulations of plasticity in polyatomic molecular and polymeric systems, under a variety of dynamic loading scenarios. We strongly suspect that the dominant dissipative mechanisms culminating in plastic deformation in complicated polyatomic molecular materials will differ significantly from the relatively tidy models

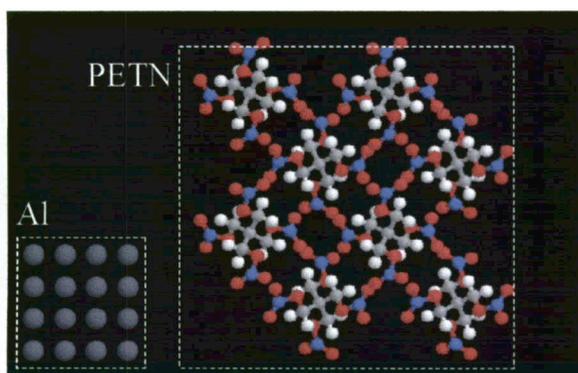


Figure 5. Comparison of crystal structures of aluminum and PETN.

that have evolved for metals since the first suggestion of dislocations in the 1930s. Fig. 5 depicts 2x2x1 projections of the crystal structures of aluminum and PETN, shown on the same scale.

Beyond the obvious fact that the molecular materials of interest to us contain many intramolecular degrees of freedom (as opposed to none for simple metals), we expect that specific topological features (rings, floppy arms,

pendent nitro groups, etc.) will play important roles in understanding the origins and time scales for plastic relaxation in these kinds of materials.

In Fig. 6 we show initial and final snapshots from a *preliminary* simulation of shocked α -HMX, calculated using the LAMMPS computer code developed at Sandia National Laboratory [37]. Our choice to consider α -HMX is based on its orthorhombic structure and evidence of potential slip planes at 45 degrees relative to the shock direction for two principal crystal orientations. Microcanonical (NVE) conditions were used, with periodic boundary conditions applied in the transverse directions. A large region of

vacuum was included at the right-hand end of the simulation cell. The total system size in this “almost large-scale” simulation was 4096 α -HMX molecules (512 unit cells, 114,688 atoms; initial physical dimensions: 12 nm x 41 nm x 0.24 nm), 256 of which formed a rigid, immobile slab (left edge; see Fig. 6). The remaining molecules were given an initial particle velocity of 3 km/sec directed towards the immobile slab. The orientation is such that vertical and horizontal axes in the figure correspond to the a and b crystallographic directions, respectively; hence, the shock is directed along b , and propagates from left to right. The snapshot corresponds to a time approximately 4.4 ps into the simulation. Close inspection, which may be difficult given the published resolution, reveals an initial zone of relatively ordered uniaxial compression (right-hand edge of the compressed material), behind which significant disordering occurs. The preliminary results shown here do not, however, indicate obvious plastic deformation of the compressed solid along slip planes, but may hint at melting within the material. We re-emphasize that this is a preliminary result; and that we intend to consider additional shock directions, particle velocities and larger simulation sizes, for both α - and β -HMX.

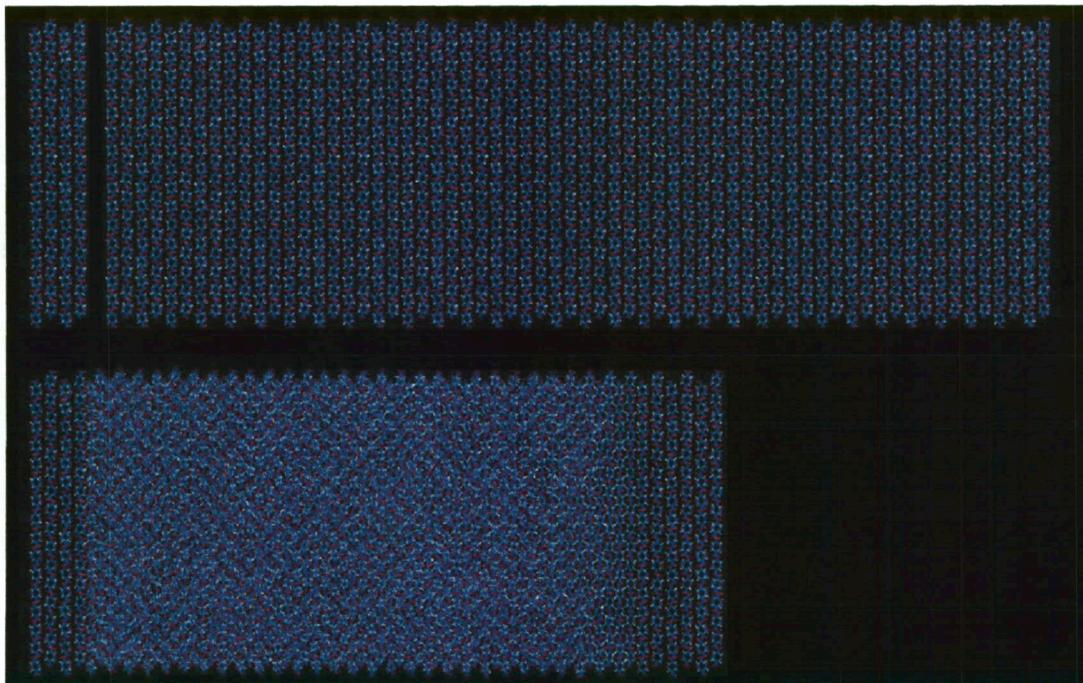


Figure 6. Snapshots from a preliminary simulation of shocked α -HMX. The time required for this ~ 4.4 ps simulation was 324 CPU-hours (27 cpus x 12 hours).

IV. Concluding remarks

Atomistic simulation methods are increasingly useful for the prediction of constituent properties of high explosives that are difficult to obtain experimentally. Up until the present time, most of our studies of “real” condensed-phase explosives have been based classical molecular dynamics or Monte Carlo and focused on calculation of equilibrium properties of HMX requested by mesoscale modelers. Among the high-priority properties yet to be completed are the temperature and pressure dependent specific heats of the various phases [38], the melting curve $T_m=T_m(P)$ [39], and the (rate dependent) shear modulus of the liquid/glassy states as functions of thermodynamic state. Also, in the near future it should be possible to study essentially all non-reactive intermolecular interactions among the constituents of PBX-9501.

As the new results shown here indicate, emerging condensed phase electronic-structure methods enable cold-curve calculations using sophisticated model chemistries and basis sets, for periodic systems containing hundreds of atoms. However, these results also demonstrate the importance of careful thought and a skeptical eye in designing the computational protocol, and the probable need to incorporate at least some level of finite-temperature annealing in cases where high-accuracy linear hydrostatic compressibilities are unavailable to “get started” up the isotherm. It is anticipated that practical calculations of vibrational spectra and chemical energetics (and dynamics, for carefully chosen situations) will soon be feasible. These calculations should become even more reliable, and interesting, once Hartree-Fock exact exchange and spin-unrestricted spin states are incorporated into MondoSCF.

With reasonable (or is it insatiable?) access to large Linux clusters, million-molecule simulations of shocks and other dynamic loading scenarios in “inert” high explosives are essentially within reach, using realistic particle velocities, to study dissipation and plastic deformation in these large polyatomic systems. This line of research should be of use in the development of improved formulations of plasticity in organics. One of the major hurdles that must be overcome, however, is the question of how to identify, characterize, and quantify plasticity and plastic deformation mechanisms for this class of materials. While it is unclear exactly what these mechanisms will be, it is

almost certain that they will be significantly different from those in metals. Moreover, with the formulation and ongoing validation and application of reactive force fields to high explosives (e.g., ReaxFF [40], developed at CalTech), it should be possible in the not-too-distant future to consider similar calculations for reactive shocks or cookoff in systems containing tens of thousands of molecules.

Finally, given the difficulty in obtaining reliable experimental data for force field validation for states far from equilibrium, it may be profitable to merge the capabilities of cutting-edge tools like MondoSCF and ReaxFF (and related formulations under development by others), by using high-level, benchmark electronic-structure calculations of energies and forces for condensed-phase geometries sampled in ReaxFF dynamics simulations, in order to improve the robustness of the force field in the real regimes of interest. (This is essentially an extension to the condensed phase of the philosophy used in the gas phase to parameterize the present version of ReaxFF, which appears to already yield fairly credible results [⁴¹].)

Thus, it is our opinion that, with careful thought and planning, combined with a healthy dose of self-criticism and skepticism, atomistic studies will continue to provide useful information about equilibrium properties. We anticipate that they will soon begin to play increasingly important roles in understanding non-equilibrium processes and mechanisms, for both non-reactive and reactive systems.

¹ T.D. Sewell, "Monte Carlo simulations of crystalline TATB," in *Decomposition, Combustion, and Detonation Chemistry of Energetic Materials, Materials Research Society Symposium Proceedings*, T.B. Brill, T.P. Russell, W.C. Tao, and R.B. Wardle Eds., (MRS, Pittsburgh, 1996) Volume 418, p. 67.

² T.D. Sewell, "Monte Carlo calculations of the hydrostatic compression of hexahydro-1,3,5-trinitro-1,3,5-triazine and b-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine," *Journal of Applied Physics* **83**, 4142 (1998).

³ T.D. Sewell and C.M. Bennett, "Monte Carlo calculations of the elastic moduli and pressure-volume-temperature equation of state for hexahydro-1-3-5-trinitro-1,3,5-triazine," *Journal of Applied Physics* **88**, 88 (2000).

⁴ The body of HMX simulations resulting from the collaboration between T.D. Sewell at Los Alamos and the G.D. Smith group at the University of Utah are based on a flexible molecule, quantum chemistry-based force field: G.D. Smith and R.K. Bharadwaj, "Quantum chemistry based force field for simulations of HMX," *Journal of Physical Chemistry B* **103**, 3570 (1999).

⁵ D. Bedrov, C. Ayyagari, G.D. Smith, T.D. Sewell, R. Menikoff, and J.M. Zaug, "Molecular dynamics simulations of HMX crystal polymorphs using a flexible molecule force field," *J. Computer-Aided Materials Design* **8**, 77 (2002).

⁶ T.D. Sewell, R. Menikoff, D. Bedrov, and G.D. Smith, "A molecular dynamics simulation study of elastic properties of HMX," *Journal of Chemical Physics*. **119**, 7417 (2003).

-
- ⁷ D. Bedrov, G.D. Smith, and T.D. Sewell, "Temperature-dependent shear viscosity coefficient of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX): A molecular dynamics simulation study," *Journal of Chemical Physics* **112**, 7203 (2000).
- ⁸ D. Bedrov, G.D. Smith, and T.D. Sewell, "Thermal conductivity of liquid octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from molecular dynamics simulations," *Chemical Physics Letters* **324**, 64 (2000).
- ⁹ D. Bedrov, G.D. Smith, and T.D. Sewell, "Thermodynamics and Mechanical Properties of HMX from Atomistic Simulations," in *Energetic Materials Part 1. Decomposition, Crystal, and Molecular Properties*, P. Politzer and J.S. Murray Eds. (Elsevier, Boston, 2003), Ch. 10, p. 279.
- ¹⁰ G.D. Smith, D. Bedrov, O. Byutner, O. Borodin, C. Ayyagari, and T.D. Sewell, "A quantum-chemistry-based potential for a poly(ester urethane)," *Journal of Physical Chemistry A*, **107**, 7552 (2003).
- ¹¹ Verification: are we solving the equations right? Validation: are we solving the right equations?
- ¹² R. Menikoff and T.D. Sewell, "Constituent properties of HMX needed for mesoscale simulations," *Combustion Theory and Modeling* **6**, 103 (2002).
- ¹³ M.R. Baer and T.D. Sewell, "Linking molecular dynamics to mesoscale simulation," in *Molecular Dynamics Simulations of Detonation Phenomena*, B.L. Holian, Ed. (WTEC, ____, 2004) Ch. 5, p. 79.
- ¹⁴ H. Davande, O. Borodin, G.D. Smith, and T.D. Sewell (in progress).
- ¹⁵ PBX-9501 is 95% by weight HMX, 2.5% Estane™, and 2.5% BDNPF/A. A small amount of Irganox™ stabilizer is also present in the formulation, but we have no plans to develop a force field for this trace component.
- ¹⁶ J.P. Lewis, T.D. Sewell, R.B. Evans, and G.A. Voth, "Electronic structure calculation of the structures and energies of the three pure polymorphic forms of crystalline HMX," *Journal of Physical Chemistry B* **104**, 1009 (2000).
- ¹⁷ C.K. Gan, T.D. Sewell, and M. Challacombe, "All electron density-functional studies of hydrostatic compression of pentaerythritol tetranitrate (PETN)," *Physical Review B* **69**, 035116 (2004).
- ¹⁸ M. Challacombe, E. Schwegler, C.J. Tymczak, C.K. Gan, K. Nemeth, A.M.N. Niklasson, H. Nymeyer, and G. Henkleman, MONDOSCF v1.0α7. A program suite for massively parallel, linear scaling SCF theory and ab initio molecular dynamics, 2001, <http://www.t12.lanl.gov/home/mchalla> [Los Alamos National Laboratory (LA-CC 01-2), copyright University of California.
- ¹⁹ The 2003 study *Molecular Dynamics Simulations of Detonation Phenomena*, chaired by B.L. Holian and funded by the International Technology Research Institute, contains what is probably the most complete and (then) up-to-date compendium of theoretical studies of energetic materials that has been compiled. Contributing authors include B.L. Holian, M.R. Baer, D. Brenner, D.D. Dlott, A. Redondo, B.M. Rice, T.D. Sewell, and C.A. Wight.
- ²⁰ T.D. Sewell and R. Menikoff, "Complete equation of state for beta-HMX and implications for initiation," to appear in *Proceedings of the 2003 APS Topical Conference on Shock Compression of Condensed Matter*, held 20-25 July 2003, Portland, OR; currently available at <http://t14web.lanl.gov/Staff/rsm/preprints.html#betaHMX>
- ²¹ B. Olinger, B. Roof, and H. Cady, "The linear and volume compression of beta-HMX and RDX," in *Symposium International Sur le Comportement Des Milieux Denses Sous Hautes Pressions* (CEA, Paris, 1978) p. 3.
- ²² C.-S. Yoo and H. Cynn, "Equation of state, phase transition, decomposition of beta -HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) at high pressures," *Journal of Chemical Physics* **111**, 10229 (1999).
- ²³ R. Menikoff and T.D. Sewell, "Fitting forms for isothermal data," *High Pressure Research* **21**, 121 (2001).

-
- ²⁴ M. Herrmann, W. Engel, and N. Eisenreich, “,” *Propellants, Explosives, and Pyrotechnics* **17**, 190 (1992).
- ²⁵ M. Herrmann, W. Engel, and N. Eisenreich, “Thermal analysis of the phases of HMX using x-ray diffraction,” *Zeitschrift für Kristallographie* **204**, 121 (1993).
- ²⁶ C.K. Saw, “Kinetics of HMX and phase transitions: effects of grain size at elevated temperature,” to appear in 12th International Detonation Symposium; held August 11-16, 2002, San Diego, CA. Currently available at <http://www.sainc.com/onr/detsymp/technicalProgram.htm>.
- ²⁷ See Ref. [9], Fig. 9 (p. 305).
- ²⁸ G.M. Day, S.L. Price, and M. Leslie, “Elastic constant calculations for molecular crystals,” *Crystal Growth and Design* **1**, 13 (2001). Note especially entries in the tables where multiple experimental data are presented for the same substance.
- ²⁹ D.C. Sorescu, B.M. Rice, and D.L. Thompson, “Theoretical studies of the hydrostatic compression of RDX, HMX, HNIW, and PETN crystals,” *Journal of Physical Chemistry B* **103**, 6783 (1999); and numerous references therein.
- ³⁰ S. Haussühl, “Elastic and thermoelastic properties of organic crystals...” *Zeitschrift für Kristallographie* **216**, 339 (2001).
- ³¹ Ricardo Schwarz and Dan Hooks (LANL), private communication of preliminary data (April 2004).
- ³² Merrill Beckstead, private communications to Tommy Sewell.
- ³³ RALPH, DISSIPATION PAPER
- ³⁴ J.C. Gump and S.M. Peiris, “High pressure and temperature x-ray diffraction study of β -HMX” (in preparation).
- ³⁵ T.D. Sewell (in preparation).
- ³⁶ For the present purpose, the differences between the linear compressions of Olinger et al. and Yoo & Cynn are probably negligible.
- ³⁷ S.J. Plimpton, “Fast Parallel Algorithms for Short-Range Molecular Dynamics,” *Journal of Computational Physics* **117**, 1 (1995); S.J. Plimpton, R. Pollock, M. Stevens, “Particle-Mesh Ewald and rRESPA for Parallel Molecular Dynamics Simulations,” in *Proceedings of the Eighth SIAM Conference on Parallel Processing for Scientific Computing*, Minneapolis, MN, March 1997.
- ³⁸ Goddard and co-workers have done some preliminary calculations of the specific heat C_v of β -HMX for temperatures up to 3000 K. These can presently be found in annual reports of the CalTech ASC/ASAP Level One Alliance: <http://csdrm.caltech.edu/publications/annualreps.html>; see also Ref. [12], p. 108.
- ³⁹ P.M. Agrawal, B.M. Rice, and D.L. Thompson, “Molecular dynamics study of the melting of nitromethane,” *Journal of Chemical Physics* **119**, 9617 (2003). See also Fig. 1 of Ref. [12], and associated discussion.
- ⁴⁰ A. Strachan, A.C.T. van Duin, D. Chakraborty, S. Dasgupta, and W.A. Goddard III, “Shock waves in high-energy materials: the initial chemical events in nitramine RDX,” *Physical Review Letters* **91**, 098301 (2003).
- ⁴¹ On the basis of many calculations performed recently by Alejandro Strachan (LANL) and Adri van Duin (CalTech).