



Atomistic Studies of Fundamental Properties and Processes in Energetic Materials: Relevance to Mesoscale Initiation Phenomena^{*)}

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Abstract: Genuine, physics-based understanding of initiation phenomena in plastic-bonded explosives (PBXs) requires knowledge of the physics and chemistry at mesoscopic scales that are far larger than can be simulated directly using atomistic detail, yet far smaller than is directly resolvable in practical engineering scale continuum simulations. Initiation is determined by localization phenomena that arise due to the heterogeneous character of most explosive formulations. Indeed, the “average” temperature behind a weak shock is not a useful measure for understanding initiation phenomena; rather, it is the tails of the distributions in temperature, stress, and strain rates, localized to small, spatially distributed volumes in the material (hot spots), that dictate the outcome of a given loading event. Important factors for predicting hot spot formation and subsequent extinction or growth/coalescence include particle size, concentration, morphology, and void content; physical and chemical interactions between grains and binder; thermophysical and mechanical properties of the constituents and interfaces between them; and, of course, the inherent chemical stability of the explosive component(s) in the formulation. We are in the process of computing many of the thermophysical and mechanical properties required for a complete specification of constituent models for use in mesoscale simulations, wherein grains and binder in representative volumes of a PBX are spatially resolved and then studied within a continuum hydrodynamic framework. In addition to calculating specific properties of interest, we have recently undertaken a series of large-scale molecular dynamics simulations of energetic crystals to understand dissipation phenomena in dynamically loaded single- or poly-crystalline samples; for instance, plastic deformation and stress/energy localization mechanisms, phase transitions, and so on. Recent and ongoing work in these areas will be discussed, along with their specific relevance to emerging mesoscale simulation capabilities.

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Introduction

In order to understand and predict initiation in plastic-bonded explosives (PBXs), for example behind a weak shock, there are at least three key classes of knowledge that we must have in order to claim a credible predictive capability:

- the mechanisms and resulting spatio-temporal distributions of energy localization, typically measured in a reference frame that moves with the shock front [1];
- the thermal and mechanical parameters required for specification of the equation of state, which enable predictions of local temperature and stress [2]; and
- the correct chemical reactions rates, which should ideally be expressed as functions of temperature and pressure, rather than pressure.

While the need for the second and third points above is presumably obvious, the need to characterize the distributions of temperature and stress state behind the shock, and the underlying unit mechanisms by which these non-uniform conditions arise [3, 4], may be somewhat less well recognized. For a weak shock, the bulk temperature due to simple hydrodynamic heating is not high enough to lead to prompt chemical reaction [5]. Rather, it is only in regions of space corresponding to the extreme tails of the temperature and pressure distributions – the hot spots – that fast chemistry will occur and then either spread or quench depending on the spatial density and size of the hot spots. Given the complexity of a real PBX, it necessary to capture this information within a statistical framework. (It is important to emphasize the focus in this paper on ignition phenomena as opposed to strong shock initiation, for which the role of “hot spots” may be substantially less than has generally been assumed in the past [6].)

Experimental determination of many of the processes and properties mentioned above is difficult for high explosives, due in part to the complicated molecular/crystal structures involved and also to the extremely fast reaction rates that arise for many thermodynamic conditions of interest. Indeed, for many common explosives, even the “simplest” parameters are known only at a few temperatures and pressures, and often with relatively large uncertainties. Moreover, the error bars typically increase the further one departs from ambient conditions [7]. As a concrete example that applies to weak shock ignition, absence of knowledge of the temperature (and pressure?)

dependence of the specific heat can lead to errors of hundreds of degrees in predicted temperature such that, if “real” rather than calibrated chemical rates are to be used, induction times for reaction can be off by orders of magnitude [8]. The most common way around this problem is to take as fixed a few key parameters in the equation of state, and then adjust others to match, for example, the principal shock Hugoniot locus. These “knobs” become problematic for more complicated scenarios, however; as, for example, in the case of multi-shock stimuli that take one far from the principal Hugoniot. However, assessment of experiments even for such simple quantities as the bulk modulus and its initial pressure derivative can be problematic [9].

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 equation of state and dissipation models for plastic-bonded explosives (PBXs). The main materials we have studied by these methods include TATB [10]; RDX [11, 12]; β -, α -, δ -, and liquid HMX [13-18]; Estane™, a poly(ester urethane) copolymer [19]; and bis(2,2-dinitropropyl)formal/acetal (BDNPF/A) [20]. The three-dimensionally periodic simulation cells in our more recent work typically contain $\sim 10^2$ molecules, with simulation times of 2-10 nanoseconds (ns). While much of this work has focused on verification and validation (V&V [21]), 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 PBX 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 [8, 22], predominantly at the Los Alamos and Sandia National Laboratories. With the recent completion of a force field for BDNPF/A [20], we should, in principle, be able to study all relevant intermolecular interactions in PBX-9501 [23].

In addition to classical molecular dynamics and Monte Carlo simulations, we have employed condensed phase electronic-structure methods to study the zero Kelvin structures and properties of crystalline HMX [24] and PETN [25]. Highly parallel, $O(N)$ algorithms implemented in the MondoSCF quantum chemistry code [26] used in Ref. [25] 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. [25] is the first published application of MondoSCF to high explosives.

The importance of atomistic computations in explosive science

Useful roles for atomistic studies

A large number of atomistic studies of condensed phase high explosives have been published, with a rate that has increased noticeably in recent years [27]. 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 [12]. Another useful role is to provide information about properties in thermodynamic regimes that are difficult, if not impossible, to probe experimentally for some high explosives (*e.g.*, liquid HMX [16, 17]). Although unavailable experimentally, some of these quantities are key to the parameterization of improved mesoscale models [2, 8]. In situations for which independent experimental determinations of some property are at odds with one another, molecular simulation approaches are potentially 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 [9, 15, 25, 28, 29] and coefficients of thermal expansion [14, 30-33], let alone more complicated objects such as the elastic tensor [12, 15, 34]. Finally, molecular-scale calculations can provide insights into fundamental processes and mechanisms at a level unlikely to ever be matched experimentally.

Factors to consider when assessing atomistic simulation results

In spite of the fact that we are gaining increased confidence in atomistic simulations as a viable tool for use in explosive science, it is vitally important to maintain a healthy skepticism when assessing the results of a molecular dynamics simulation. From a philosophical point of view, *Caveat Emptor* (Let the Buyer [End User] Beware.) Among the questions that should be asked by anyone contemplating the use of atomistic simulation results as input to their own research are:

- Is the force field used validated against a variety of experimental data?
- Are the computational methods employed sound for the problem addressed?
- Are the time and length scales accessible in the simulations compatible with the phenomena of interest?

- Are the results likely to be highly corrupted by pesky quantum effects not accounted for in a classical simulation?
- Was care taken to ensure convergence of the results, and are statistical measures of precision provided?

With a little imagination, one can draw meaningful analogies between each of the items above and corresponding ones relevant to larger spatial scales such as continuum hydrodynamic simulations (constitutive models, mesh refinement, *etc.*).

Representative results from older work

Table 1 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 [12]. (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 [35].) The two sets of experimental results are based on resonant ultrasound spectroscopy (RUS) [36, 37]. In the present comparison we make no attempt to account for the difference between isothermal and isentropic elastic tensors, 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 for individual elements of the elastic tensor is surprisingly good, and derived values for the isotropic moduli are in even better agreement. (The level of agreement seen here for the experimental and calculated elastic tensor is somewhat unusual, since the elastic tensor for polyatomic molecules is highly sensitive to the curvature of the force field near the potential energy minimum [34]; in those instances for which experimental data are available, the elastic tensor is among the most incisive measures of the accuracy of the force field near equilibrium.)

Table 1. Calculated and measured atmospheric pressure elastic tensors for RDX

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, Dick, and Hooks ^c (2005)	21.3	25.6	19	4.27	5.38	7.27	8.67	6.4	5.72

a. Ref. [12], isothermal-isobaric, rigid molecule Monte Carlo, T=304 K.

b. Ref. [36], resonant ultrasound spectroscopy.

c. Ref. [37], resonant ultrasound spectroscopy.

A much more sophisticated, flexible-molecule force field has been used in a series of studies of liquid and crystalline HMX [13]. Among the liquid state properties of HMX for which predictions have been reported are atmospheric pressure self-diffusion and shear viscosity coefficients [16] and thermal conductivity [17], 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 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 [38].

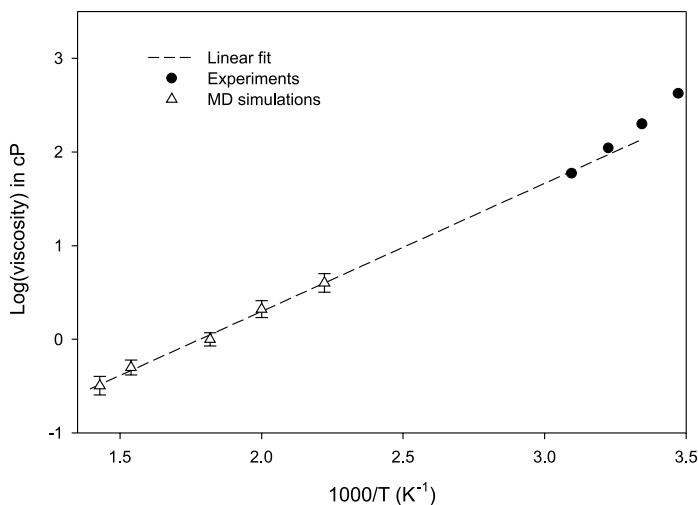


Figure 1. Calculated and measured shear viscosity of BDNPF/A, plotted as $\log(\text{viscosity})$ -vs- $1/T$. Line is a fit through calculated results.

Very recently [20], we completed the development of a force field for bis(2,2-dinitropropyl)formal/acetal, which is the plasticizer in the binder for PBX-9501. a comparison of the measured and calculated shear viscosities for that eutectic mixture is depicted in Figure 1. It was necessary to use temperature extrapolation to compare to experiment, since the simulation times required to obtain converged values of the shear viscosity near room temperature would have been prohibitively long. However, the measured and calculated results appear to

be consistent. Additional force field validation calculations for BDNPF/A and other model compounds can be found in Ref. [20].

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 ns 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 [15], 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 $550 \text{ K} \leq T \leq 850 \text{ K}$, and were designed to bracket the existence interval for the liquid at atmospheric pressure. (Obviously, the melting and boiling points will increase with increasing pressure.) In Figure 2 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.

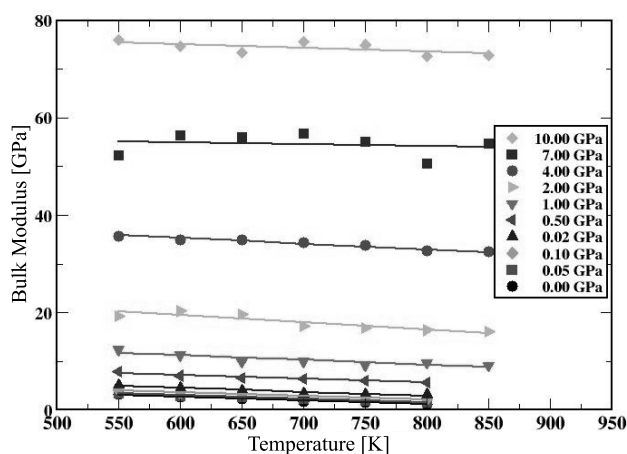


Figure 2. Calculated bulk modulus of liquid and glassy HMX as a function of temperature and pressure.

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 Figure 3. 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 [5]. It is important to understand that Figure 3 does not reflect a rigorous prediction based on free energy calculations to obtain the coexistence curves by matching chemical potentials, or even from two-phase simulations such as have been performed recently for nitromethane by Thompson and co-workers [39], in which crystalline and liquid volumes contained within a single periodic simulation cell were gradually heated until melting of the crystalline phase into the liquid was observed.

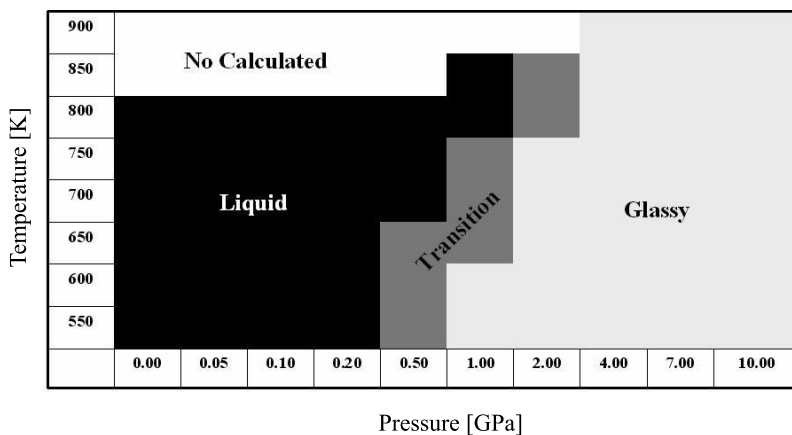


Figure 3. Predicted “phase diagram” for the onset of glass-like behavior of HMX at elevated pressures and temperatures, based on a variety of structural and dynamical measures.

Electronic structure studies of hydrostatic compression of β -HMX

As a follow-on to our preceding electronic-structure studies of the PETN zero Kelvin isotherm (cold curve) [25], 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 [28, 29, 40] and computational [11, 15, 35, 41] studies (including one each at non-ambient temperatures [40, 41]) is that, while all of the published computed isotherms are in better agreement with the 1978 isotherm of Olinger *et al.* [28], Menikoff and Sewell [8] concluded that the 1999 Yoo and Cynn isotherm [29] 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 U_s - U_p planes, respectively) compared to shock hugoniot data, which is an aphysical result.

As in our PETN study [25], 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.*, $(a_1, b_1, c_1) = (\epsilon a_0, \epsilon b_0, \epsilon c_0)$, where ϵ is slightly less than unity]; in subsequent steps, we simply enforce $x_{k+1}/x_{k,r} = x_{k,r}/x_{k-1,r}$ (where $x = a, c, \beta$ are varied independently; b provides closure at the desired volume $V = abc \sin \beta$; subscript r denotes a fully relaxed structure from a preceding sequence of line searches; and no reference to experiment 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 , using a 5th-degree polynomial fit to Olinger’s data [28]; and enforce volume closure *via* the monoclinic angle β instead of the lattice length b .

In Figure 4 we show the PBE/6-31G** energy difference ΔE versus hydrostatic volumetric compression ratio V/V_0 (left panel) and the associated P - V/V_0 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 crystal purity and differences between the shock Hugoniot of single crystals and the initial porosity in pressed powders.

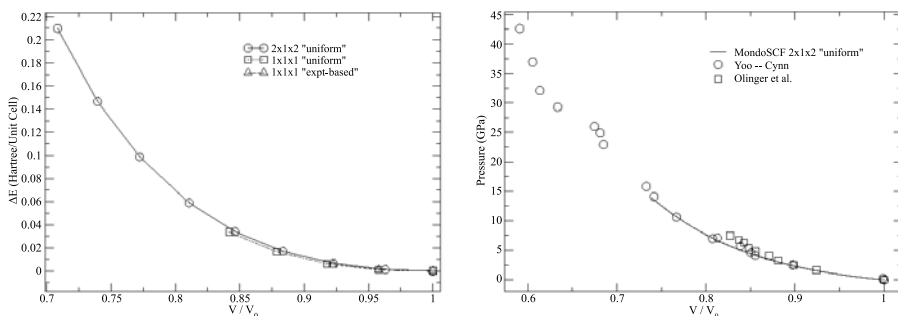


Figure 4. Calculated relative energies (left panel) and pressures (right panel) versus compression ratio V/V_0 for β -HMX, at the PBE/6-31G** level. The full curves in both panels are based on a primary cell containing eight molecules, with full optimization of cell contents at each volume.

In Figure 5 we compare the results for calculated linear compressions of the monoclinic lattice parameters to the results of Olinger *et al.* [28, 42] based on the “uniform” and “experimentally-guided” protocols described above. Note that the MondoSCF PBE/6-31G** predictions for variation in lattice length a and monoclinic angle β are predicted fairly accurately using either protocol. By contrast, calculations 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 Figure 5), whereas experiment indicates significant anisotropy.

Our motivation for designing the “experimentally-guided” protocol was concern that there might exist geometrically nearby “energy valleys,” due for instance to subtle conformational changes in molecular geometry, that would depend sensitively on our initial guess for the crystal structure away from zero pressure. In such an instance, an initially shallow barrier between valleys would likely become steeper and deeper with increasing compression, effectively “steering” our predictions away from the experimental result (in much the same way that a hiker might veer far off course by choosing the wrong drainage at the foot of a mountain range). However, the results in Figure 5 indicate that, with repeated iterations of the “line search algorithm,” cycling over the monoclinic

lattice parameters, the PBE/6-31G** prediction using the experimental protocol tends towards, and appears to be converging to, the “uniform” result. (The arrows in Figure 5 point from the result of the first iteration towards that of the final one.) This suggests that the chosen model chemistry and/or basis set is insufficient for β -HMX crystal. It also underscores the need to perform repeated optimization cycles in this kind of calculation since, at least for the specified lattice optimization protocol, a single iteration can lead to incorrect conclusions.

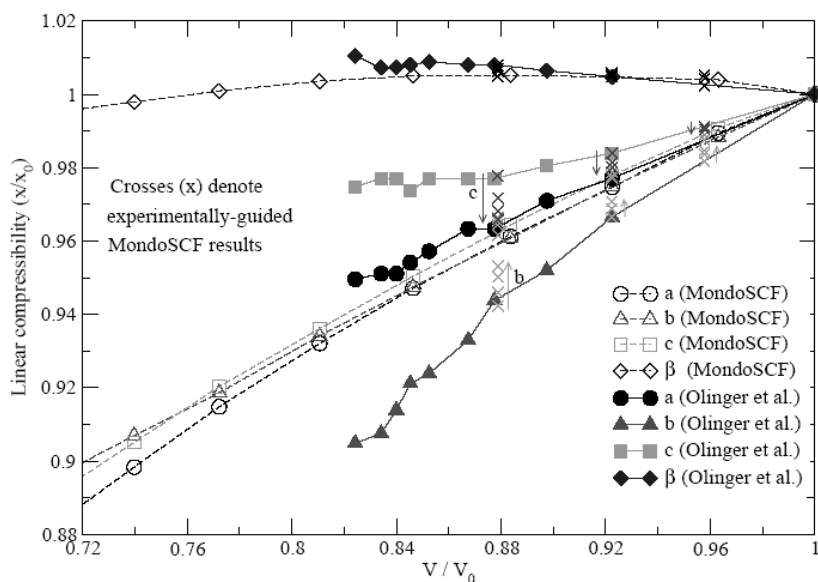


Figure 5. Comparisons of the linear compressions in β -HMX predicted using PBE/6-31G**, based on the “uniform” and “experimentally-guided” protocols. The results suggest that PBE/6-31G** is an insufficient model chemistry/basis set combination for β -HMX crystal.

Very recently, the ability to automatically perform optimization of lattice degrees of freedom in conjunction with optimization of molecular geometry has been incorporated into MondoSCF, along with the ability to employ hybrid density functionals such as PBE0 that generally do a better job at predicting molecular crystal structures for materials in which dispersion interactions are significant. While still at the validation stage, we expect that these two advances in code capability will improve our ability to calculate cold curves for energetic materials.

Preliminary medium- and large-scale molecular dynamics simulations of shocked HMX

We have begun to consider the feasibility of million or even multi-million molecule simulations of plasticity (and dissipation more generally) 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 that have evolved for metals since the first suggestion of dislocations in the 1930s. With specific connection to energetic materials, we view this work as a logical extension to some of the studies performed by Armstrong and co-workers [3, 4].

Figure 6 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 determining the origins and time scales for plastic relaxation in these kinds of materials.

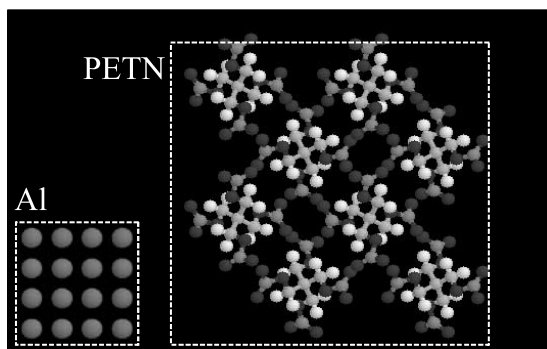


Figure 6. Comparison of Aluminum and PETN crystal structures.

In Figure 7 we show initial and final snapshots from a simulation of shocked α -HMX, calculated using the LAMMPS computer code developed at Sandia National Laboratory [43]. Our choice to consider α -HMX is based on its orthorhombic structure, which is a present limitation with the LAMMPS code. 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 “medium-scale” simulation was 4096 α -HMX molecules (512 unit cells, 114,688 atoms; initial

physical dimensions: 12 nm x 41.4 nm x 2.4 nm), 256 of which formed a rigid, immobile slab (left edge; see Figure 7). The remaining molecules were assigned an initial particle velocity of 3 km s⁻¹ 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 bottom snapshot corresponds to a time of approximately 4.4 ps, for which roughly six molecular layers are unshocked (right-hand edge). Close inspection reveals an initial zone of relatively ordered uniaxial compression (starting about seven layers in from the right-hand edge), behind which significant disordering occurs. The preliminary results shown here do not indicate obvious plastic deformation of the compressed solid along slip planes, but may hint at melting within the material.

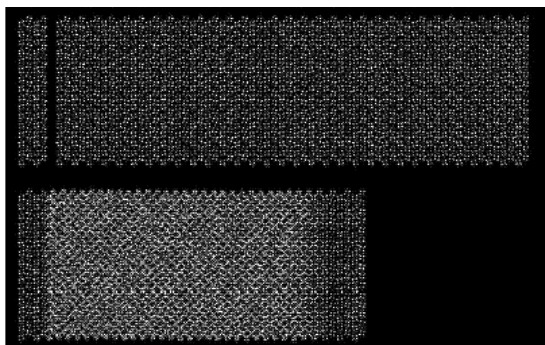


Figure 7. Snapshots from a simulation of shocked α -HMX containing 4096 fully flexible molecules. The shock is directed along the *b* crystallographic axis, with a particle velocity of 3.0 km s⁻¹.

Results for a shock analogous to the one just described, but directed along the *c* crystallographic axis are shown in Figures 8 and 9. Figure 8 contains the initial and final snapshots from the simulation, and is intended for comparison with Figure 7 to underscore the anisotropic nature of the molecular crystal. Figure 9 contains plots of the density (left panel) and “components” of temperature parallel and transverse to the direction of shock propagation (right panel).

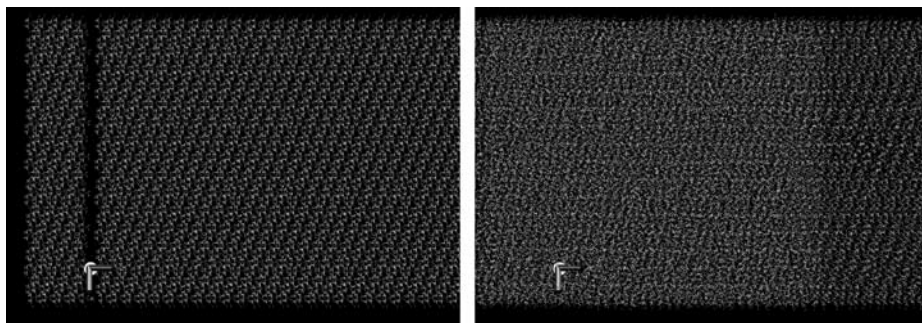


Figure 8. As in Figure 7, but for a shock directed along the c crystal axis.

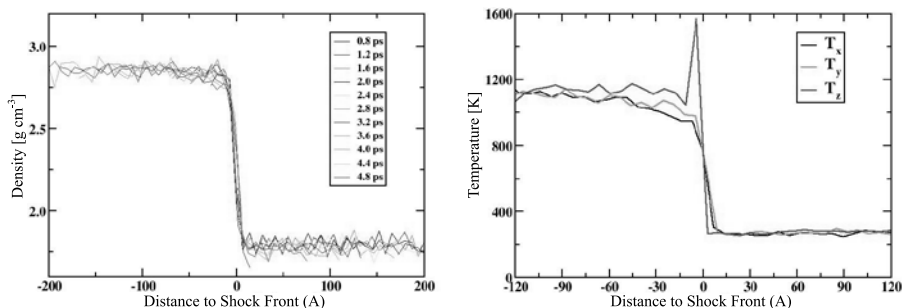


Figure 9. Density (left panel) and temperature (right panel) for the shock shown in Figure 8. Densities at several different instants are superimposed, referenced to the shock front; temperatures were obtained by averaging over several instants, yielding three traces.

We have also performed much larger simulations, containing 65,536 fully flexible HMX molecules colliding with a fixed slab of 1,024 molecules. We think that these much larger simulations (physical dimensions 3.0 nm x 156.4 nm x 38.7 nm) are required in order to eliminate (or at least mitigate) boundary condition effects in the directions transverse to shock propagation. An example is shown in Figure 10, for the case of a shock directed along the b -crystallographic axis with a particle velocity of 2.0 km s^{-1} . In this case, complex structure behind the shock front is evident, and signs of plastic relaxation are present (notice for example the “rough” upper and lower edges of the simulation cell). Even in this case, we are still considering “thin slab geometries” in which the constraint of a system whose dimension into the plane of the page is only 3.0 nm possibly affects the observed result. Nevertheless, these calculations are useful as a “scoping tool” prior to performing much larger simulations corresponding to a simulation cell that is nearly square in the directions normal to shock propagation.

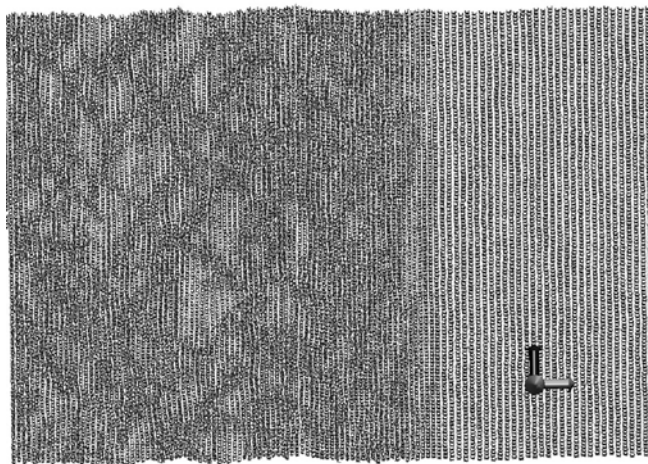


Figure 10. Cutout from a shock in system containing 65,536 flexible α -HMX molecules. The shock is propagating from left to right along the b crystallographic axis with a particle velocity of 2.0 km s^{-1} .

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 on classical molecular dynamics or Monte Carlo and focused on predictions of equilibrium properties of HMX requested by mesoscale modelers. Among the high-priority properties yet to be calculated are the temperature and pressure dependent specific heats of the various phases [44], the melting curve $T_m = T_m(P)$ [45], and the (rate dependent) shear modulus of the liquid/glassy states as functions of thermodynamic state. In addition to calculations of the properties just listed for individual materials, the recent completion of the force field for BDNPF/A [20] should enable detailed study of 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. Even with the very

recent incorporation of “automated” lattice optimization into MondoSCF, it may be necessary to incorporate at least some level of finite-temperature annealing to achieve high confidence in the calculated zero Kelvin properties. It is anticipated that practical calculations of vibrational spectra and chemical energetics (and dynamics, for carefully chosen situations) will soon be feasible, for primary cells approaching 1000 atoms. These calculations should become even more reliable, and interesting, once spin-unrestricted states are incorporated into MondoSCF.

With reasonable allocations of time on 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 ongoing validation and application of reactive force fields to high explosives (*e.g.*, ReaxFF [46], 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 force field 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 accuracy of the force field in the regions of configuration space of most 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 already to yield fairly credible results [47].)

Thus, it is our opinion that, with careful thought and planning, combined with a healthy dose of self-criticism and skepticism, atomistic simulation methods constitute a practically useful means of obtaining equilibrium properties of molecular systems in regimes that might not otherwise be obtainable. They will begin to play even larger roles than at present [47, 48] in understanding non-equilibrium processes and mechanisms in energetic materials, for both non-reactive and reactive systems. In summary, we think that, in the not-too-distant future, atomistic simulation methods should be capable of providing *significant*

insights into each of the three distinct classes of knowledge required to understand initiation, as outlined in the opening paragraph of this contribution.

Acknowledgment

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