INTRODUCTION

Energetic materials are unique for having a strong exothermic reactivity, which has made them desirable for both military and commercial applications. Energetic materials are commonly divided into high explosives, propellants, and pyrotechnics. We will focus on high explosive (HE) materials here, although a great deal of commonality exists between the classes of energetic materials. Although the history of HE materials is long, their condensed-phase properties are poorly understood.

Understanding the condensed-phase properties of HE materials is important for determining stability and performance. Information regarding HE material properties [such as the physical, chemical, and mechanical behaviors of the constituents in plastic-bonded explosive (PBX) formulations] is necessary for efficiently building the next generation of explosives as the quest for more powerful energetic materials (in terms of energy per volume) moves forward.1

There is a need to better understand the physical, chemical, and mechanical behaviors when modeling HE materials from fundamental theoretical principles. Among the quantities of interest in PBXs, for example, are thermodynamic stabilities, reaction kinetics, equilibrium transport coefficients, mechanical moduli, and interfacial properties between HE materials and the
polymeric binders. These properties are needed (as functions of stress state and temperature) for the development of improved micro-mechanical models,\textsuperscript{2} which represent the PBX at the level of high explosive grains and polymeric binder.\textsuperscript{3,4} Improved micro-mechanical models are needed to describe the responses of PBXs to dynamic stress or thermal loading, thus yielding information for use in developing continuum models.

Detailed descriptions of the chemical reaction mechanisms of condensed energetic materials at high densities and temperatures are essential for understanding events that occur at the reactive front under combustion or detonation conditions. Under shock conditions, for example, energetic materials undergo rapid heating to a few thousand degrees and are subjected to a compression of hundreds of kilobars,\textsuperscript{5} which results in almost 30\% volume reduction. Complex chemical reactions are thus initiated, in turn releasing large amounts of energy to sustain the detonation process. Clearly, understanding of the various chemical events at these extreme conditions is essential in order to build predictive material models. Scientific investigations into the reactive process have been undertaken over the past two decades. However, the sub-microsecond time scale of explosive reactions, in addition to the highly exothermic conditions of an explosion, make experimental investigation of the decomposition pathways difficult at best.

More recently, new computational approaches to investigate condensed-phase reactivity in energetic materials have been developed. Here we focus on two different approaches to condensed-phase reaction modeling: chemical equilibrium methods and atomistic modeling of condensed-phase reactions. These complementary approaches assist in understanding the chemical reactions of high explosives. Chemical equilibrium modeling uses a highly simplified thermodynamic picture of the reaction process, which leads to a convenient and predictive model of detonation and other decomposition processes. Chemical equilibrium codes are often used in the design of new materials, both at the level of synthesis chemistry and formulation.

Atomistic modeling is a rapidly emerging area. The doubling of computational power approximately every 18 months that is predicted by Moore’s law has made atomistic condensed-phase modeling more feasible. Atomistic calculations employ far fewer empirical parameters than chemical equilibrium calculations. Nevertheless, the atomistic modeling of chemical reactions requires an accurate global Born–Oppenheimer potential energy surface. Traditionally, such a surface is constructed by representing the potential energy surface with an analytical fit. This approach is only feasible for simple chemical reactions involving a small number of atoms. More recently, first principles molecular dynamics, where the electronic Schrödinger equation is solved numerically at each configuration in a molecular dynamics simulation, has become the method of choice for treating complicated chemical reactions.\textsuperscript{6}
CHEMICAL EQUILIBRIUM

The energy content of an HE material often determines its practical utility. Accurate estimates of the energy content are essential in the design of new materials\(^1\) and for understanding quantitative detonation tests.\(^7\) The useful energy content is determined by the anticipated release mechanism. Because detonation events occur on a microsecond time frame, chemical reactions significantly faster than this may be considered to be in an instantaneous chemical equilibrium. It is generally believed that reactions involving the production of small gaseous molecules (CO\(_2\), H\(_2\)O, etc.) are fast enough to be treated in chemical equilibrium for most energetic materials. This belief is based partly on success in modeling a wide range of materials with the assumption of chemical equilibrium.\(^8\)–\(^12\)

Unfortunately, direct measurements of chemical species involved in the detonation of a solid or liquid HE material are difficult to perform. Blais, Engelke, and Sheffield\(^13\) have measured some of the species produced in detonating nitromethane using a special mass spectroscopic apparatus. These measurements pointed to the importance of condensation reactions in detonation. The authors estimate that the hydrodynamic reaction zone of detonating base-sensitized liquid nitromethane is 50\(\mu\) in thickness, with a reaction time of 7 ns. The hydrodynamic reaction zone dictates the point at which the material ceases to release enough energy to drive the detonation wave forward. Reactions may continue to proceed behind the reaction zone, but the time scales for such reactions are harder to estimate. Typical explosive experiments are performed on parts with dimensions on the order of 1–10 cm. In this case, hydrodynamic confinement is expected to last for roughly 1\(\mu\)s, based on a high-pressure sound speed of several centimeters/microsecond. Thus, chemical equilibrium is expected to be a valid assumption for nitromethane, based on the time scale separation between the 7-ns reaction zone and the microsecond time scale of confinement. The formation of solids, such as carbon, or the combustion of metallic fuels, such as Al, is believed to yield significantly longer time scales of reaction.\(^14\) In this case, chemical equilibrium is a rough, although useful, approximation to the state of matter of a detonating material.

Thermodynamic cycles are a useful way to understand energy release mechanisms. Detonation can be thought of as a cycle that transforms the unreacted explosive into stable product molecules at the Chapman–Jouguet (C-J) state,\(^15\) which is simply described as the slowest steady-state shock state that conserves mass, momentum, and energy (see Figure 1). Similarly, the deflagration of a propellant converts the unreacted material into product molecules at constant enthalpy and pressure. The nature of the C–J state and other special thermodynamic states important to energetic materials is determined by the equation of state of the stable detonation products.
A purely thermodynamic treatment of detonation ignores the important question of reaction time scales. The finite time scale of reaction leads to strong deviations in detonation velocities from values based on the Chapman–Jouguet theory. The kinetics of even simple molecules under high-pressure conditions is not well understood. High-pressure experiments promise to provide insight into chemical reactivity under extreme conditions. For instance, chemical equilibrium analysis of shocked hydrocarbons predicts the formation of condensed carbon and molecular hydrogen. Similar mechanisms are at play when detonating energetic materials form condensed carbon. Diamond anvil cell experiments have been used to determine the equation of state of methanol under high pressures. We can then use a thermodynamic model to estimate the amount of methanol formed under detonation conditions.

Despite the importance of chemical kinetic rates, chemical equilibrium is often nearly achieved when energetic materials react. As discussed, this is a useful working approximation, although it has not been established through direct measurement. Chemical equilibrium can be reached rapidly under high-temperature (up to 6000 K) conditions produced by detonating energetic materials. We begin our discussion by examining thermodynamic cycle theory as applied to high explosive detonation. This is a current research topic because high explosives produce detonation products at extreme pressures and temperatures: up to 40 GPa and 6000 K. These conditions make it extremely difficult to probe chemical speciation. Relatively little is known about the equations of state under these conditions. Nonetheless, shock experiments on a wide range of materials have generated sufficient information to allow reliable thermodynamic modeling to proceed.
One of the attractive features of thermodynamic modeling is that it requires very little information regarding the unreacted energetic material; elemental composition, density, and heat of formation of the material are the only information needed. As elemental composition is known once the material is specified, only density and heat of formation need to be predicted.

The C–J detonation theory\textsuperscript{15} implies that the performance of an explosive is determined by thermodynamic states, the C–J state, and the connected expansion region, as illustrated in Figure 1. As detonation processes are so rapid, there is insufficient time for thermal conduction during expansion, which implies that the expansion from the C–J state lies on an adiabat: 
\[
dE = -p dV.
\]
The adiabatic expansion of the detonation products releases energy in the form of PV work and heat. Subsequent turbulent mixing of the detonation products in air surrounding the energetic material leads to combustion processes that release more energy.

Thermochemical codes use thermodynamics to calculate states illustrated in Figures 1 and 2 and, thus, predict explosive performance. The allowed thermodynamic states behind a shock are intersections of the Rayleigh line (expressing conservation of mass and momentum) and the shock Hugoniot (expressing conservation of energy). The C–J theory assumes that a stable detonation occurs when the Rayleigh line is tangent to the shock Hugoniot, as shown in Figure 2.

This point of tangency can be determined, assuming that the equation of state \( P = P(V, E) \) of the products is known. The chemical composition of the products changes with the thermodynamic state, so thermochemical codes must solve for state variables and chemical concentrations simultaneously. This problem is relatively straightforward, given that the equation of state (EOS) of the fluid and solid products are known.

\[\text{Figure 2} \text{ Allowed thermodynamic states in detonation are constrained to the shock Hugoniot. Steady-state shock waves follow the Rayleigh line.}\]
One of the most difficult parts of this problem is describing the EOS of the fluid components accurately. Because of its simplicity, the Becker–Kistiakowski–Wilson (BKW)\(^2\) EOS is used in many practical applications involving energetic materials. Numerous parameter sets have been proposed for the BKW EOS.\(^{22–25}\) Kury and Souers\(^7\) have critically reviewed these sets by comparing their predictions to a database of detonation tests. They concluded that the BKW EOS does not model the detonation of a copper-lined cylindrical charge adequately. The BKWC parameter set\(^2\) overcomes this deficiency partially through multivariate parameterization techniques. However, the BKWC parameter set is not reliable when applied to explosives that are very high in hydrogen content.

It has long been recognized that the validity of the BKW EOS is questionable.\(^1\) This is particularly important when designing new materials that may have unusual elemental compositions. Efforts to develop better EOSs have been based largely on the concept of model potentials. With model potentials, molecules interact via idealized spherical pair potentials. Statistical mechanics is then employed to calculate the EOS of the interacting mixture of effective spherical particles. Most often, the exponential-6 (exp-6) potential is used for the pair interactions:

\[
V(r) = \frac{\epsilon}{\alpha - \frac{6}{r}} \left[ 6 \exp \left( \frac{\alpha r}{r_m} \right) - \alpha \left( \frac{r_m}{r} \right)^6 \right] \tag{1}
\]

Here, \(r\) is the distance between particles, \(r_m\) is the minimum of the potential well, \(\epsilon\) is the well depth, and \(\alpha\) is the softness of the potential well.

The Jacobs–Cowperthwaite–Zwissler (JCZ3) EOS was the first successful model based on a pair potential that was applied to detonation.\(^2\) This EOS was based on fitting Monte Carlo simulation data to an analytic functional form. Ross, Ree, and others successfully applied a soft-sphere EOS based on perturbation theory to detonation and shock problems.\(^10,28–30\) Computational cost is a significant difficulty with an EOS based on fluid perturbation theory. Byers Brown\(^3\) developed an analytic representation of the Kang et al. EOSs using Chebyshev polynomials. The accuracy of the Byers Brown EOS has been evaluated by Charlet et al.;\(^1\) these authors concluded that Ross’s approach is the most reliable. Fried and Howard\(^3\) have used a combination of integral equation theory and Monte Carlo simulations to generate a highly accurate EOS for the exp-6 fluid.

The exp-6 model is not well suited to molecules with large dipole moments. To account for this, Ree\(^9\) used a temperature-dependent well depth \(\epsilon(T)\) in the exp-6 potential to model polar fluids and fluid phase separations. Fried and Howard have developed an effective cluster model for HF.\(^3\) The effective cluster model is valid for temperatures lower than the variable well-depth model, but it employs two more adjustable parameters than does the latter. Jones et al.\(^3\) have applied thermodynamic perturbation theory to
polar detonation-product molecules. Despite these successes, more progress needs to be made in the treatment of polar detonation-product molecules.

Efforts have been made to develop EOS for detonation products based on direct Monte Carlo simulations instead of on analytical approaches.\textsuperscript{35–37} This approach is promising given recent increases in computational capabilities. One of the greatest advantages of direct simulation is the ability to go beyond van der Waals 1-fluid theory, which approximately maps the equation of state of a mixture onto that of a single component fluid.\textsuperscript{38}

In most cases, interactions between unlike molecules (treated as single spherical sites) are treated with Lorentz–Berthelot combination rules.\textsuperscript{39} The rules are used to determine the interactions between unlike molecules and those of like molecules. The rules specify the interactions between unlike molecules to be the arithmetic or geometric averages of single-molecule pairwise interactions. It seems that these rules work well in practice, although they have not been extensively tested through experiment. Highly non-additive pair interactions have been proposed for N\textsubscript{2} and O\textsubscript{2}.\textsuperscript{30} The resulting N\textsubscript{2} model accurately matches double-shock data, but it is not accurate at lower temperatures and densities.\textsuperscript{32} A combination of experiments on mixtures along with advancements in theory is needed to develop reliable unlike-pair interaction potentials.

The exp-6 potential has also proved successful in modeling chemical equilibrium at the high pressures and temperatures characteristic of detonation. However, to calibrate the parameters for such models, it is necessary to have experimental data for product molecules and mixtures of molecular species at high temperature and pressure. Static compression and sound-speed measurements provide important data for these models.

Exp-6 potential models can be validated through several independent means. Fried and Howard\textsuperscript{33} have considered the shock Hugoniot of liquids and solids in the “decomposition regime” where thermochemical equilibrium is established. As an example of a typical thermochemical implementation, consider the Cheetah thermochemical code.\textsuperscript{32} Cheetah is used to predict detonation performance for solid and liquid explosives. Cheetah solves thermodynamic equations between product species to find chemical equilibrium for a given pressure and temperature. From these properties and elementary detonation theory, the detonation velocity and other performance indicators are computed.

Thermodynamic equilibrium is found by balancing chemical potentials, where the chemical potentials of condensed species are functions of only pressure and temperature, whereas the potentials of gaseous species also depend on concentrations. To solve for the chemical potentials, it is necessary to know the pressure-volume relations for species that are important products in detonation. It is also necessary to know these relations at the high pressures and temperatures that typically characterize the C–J state. Thus, there is a need for improved high-pressure equations of state for fluids, particularly for molecular fluid mixtures.
In addition to the intermolecular potential, there is an intramolecular portion of the Helmholtz free energy. Cheetah uses a polyatomic model to account for this portion including electronic, vibrational, and rotational states. Such a model can be expressed conveniently in terms of the heat of formation, standard entropy, and constant-pressure heat capacity of each species.

We now consider how the EOS described above predicts the detonation behavior of condensed explosives. The overdriven shock Hugoniot of an explosive is an appropriate EOS test, because it accesses a wide range of high pressures. Overdriven states lie on the shock Hugoniot at pressures above the C–J point (see Figure 2). The Hugoniot of penta-erythritol tetranitrate (PETN) is shown in Figure 3. Fried, Howard and Souers40 have calculated the Hugoniot with the exp-6 model and with the JCZS41 product library. Figure 3 shows that the exp-6 model lies within 1% of the measured data for pressures up to 120 GPa (1.2 Mbar). The JCZS model is accurate to within 1% up to a pressure of 90 GPa, but it shows a disagreement with experiment at 120 GPa. As the exp-6 model is not calibrated to condensed explosives, such agreement is a strong indication of the validity of the chemical equilibrium approximation to detonation.

Despite the many successes in the thermochemical modeling of energetic materials, several significant limitations exist. One such limitation is that real systems do not always obtain chemical equilibrium during the relatively short (nanoseconds-microseconds) time scales of detonation. When this occurs, quantities such as the energy of detonation and the detonation velocity are commonly predicted to be 10–20% higher than experiment by a thermochemical calculation.
Chemical kinetic modeling is another way to treat detonation. Several well-developed chemical kinetic mechanisms exist for highly studied materials such as hexahydro-1,3,5-trinitro-1,3,5-s-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). Unfortunately, detailed chemical kinetic mechanisms are not available for high-pressure conditions. Some workers have applied simplified chemical kinetics to detonation processes. The primary difficulty in high-pressure chemical kinetic models is a lack of experimental data on speciation. First principles simulations, discussed below, have the potential to provide chemical kinetic information for fast processes. This information could then conceivably be applied to longer time scales and lower temperatures using high-pressure chemical kinetics.

Finally, there are several issues to be addressed in determining the EOS of detonation products. Although the exp-6 model is convenient, it does not treat electrostatic interactions adequately. In a condensed phase, effects such as dielectric screening and charge-induced dipoles need to be considered. Also, non-molecular phases are possible under high-pressure and temperature conditions. Molecular shape is also neglected in exp-6 models. Although the small size of most detonation product molecules limits the importance of molecular shape, lower temperature conditions could yield long-chain molecules, where molecular shape becomes more important.

The possible occurrence of ionized species as detonation products is a further complication that cannot be modeled using the exp-6 representation alone. Recent results on the superionic behavior of water at high pressures (see discussion below) provide compelling evidence for a high-pressure ionization scenario. These results suggest, for example, that polar and ionic species interactions may account for approximately 10% of the (C–J) pressure of PETN. In addition, we note that thermochemical calculations of high explosive formulations rich in highly electronegative elements—such as F and Cl—typically have substantially higher errors than calculations performed on formulations containing only the elements H, C, N, and O. The difficulty in modeling the C–J states of these formulations successfully may be from the neglect of ionic species.

Bastea, Glaesemann, and Fried have extended the exp-6 free energy approach to include the explicit thermodynamic contributions arising from dipolar and ionic interactions. The main task of their theory involves calculating the Helmholtz free energy (per particle) of the detonation products—\( f \). The theory starts with a mixture of molecular species whose short-range interactions are well described by isotropic, exp-6 potentials. This mixture includes, for example, all molecules commonly encountered as detonation products, such as \( \text{N}_2, \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{NH}_3 \) and \( \text{CH}_4 \). As documented previously, a one-fluid representation of this system, where one replaces the different exp-6 interactions between species by a single interaction depending on both individual interactions and mixture composition, is a very good approximation. Bastea, Glaesemann, and Fried therefore, chose this nonpolar and neutral one-component exp-6 fluid to be the reference fluid. If the mixture
components possess no charge or permanent dipole moments, the calculation of the corresponding free energy per particle, designated as \( f_{\text{exp-6}} \), suffices to yield the mixture thermodynamics and all desired detonation properties. This physical model has been used in many thermochemical codes for the calculation of high explosives behavior.

It is worth noting that at high detonation pressures and temperatures the behavior of the exp-6 fluid so introduced is dominated by short-range repulsions and is similar to that of a hard repulsive sphere fluid. In fact, the variational theory treatment\(^{45}\) of the exp-6 thermodynamics employs a reference hard sphere system with an effective, optimal diameter \( \sigma_{\text{eff}} \) that depends on density and temperature. Bastea, Glaesemann, and Fried pursued this connection to the hard sphere fluid by considering first a fluid of equisized hard spheres of diameter \( \sigma \) with dipole moments \( \mu \). For this simple model of a polar liquid, Stell et al.\(^{46,47}\) had previously suggested a Padé approximation approach for calculating the free energy \( f_d \),

\[
f_d = f_0 + \Delta f_d
\]

\[
\Delta f_d = \frac{f_2}{1 - f_3/f_2}
\]

where \( f_0 \) corresponds to the simple hard sphere fluid and \( f_2 \) and \( f_3 \) are terms (second and third order, respectively) of the perturbation expansion in the dipole–dipole interaction (\( \sim \mu^2 \)) such that

\[
f_d = f_0 + f_2 + f_3 + \ldots
\]

The first order term \( f_1 \) can be shown to be identically zero, whereas \( f_2 \) and \( f_3 \) have been calculated explicitly.\(^{46}\) The resulting thermodynamics can be written in scaled variables as

\[
\Delta f_d = \Delta f_d(\rho^*, \beta_d^*)
\]

\[
\rho^* = \rho\sigma^3
\]

\[
\beta_d^* = \frac{\mu^2}{k_B T\sigma^3}
\]

where \( \rho \) is the (number) density and \( T \) is the temperature. The same Padé approximation also holds for a mixture of identical hard spheres with different dipole moments \( \mu_i \).\(^{48,49}\) We note that within this approximation, it is easy to show that the mixture thermodynamics is equivalent with that of a simple hard spheres polar fluid with an effective dipole moment \( \mu \) given by

\[
\mu^2 = \sum_i x_i \mu_i^2
\]

where \( x_i = \rho_i/\rho \) is the concentration of particles with dipole moment \( \mu_i \).
We also adopt the above combination rule (Eq. [6]) for the general case of exp-6 mixtures that include polar species. Moreover, in this case, we calculate the polar free energy contribution $\Delta f_d$ using the effective hard sphere diameter $\sigma_{\text{eff}}$ of the variational theory.

We show a comparison of this procedure with MD simulation results for an exp-6 model of polar water in Figures 4 and 5. Also shown are the results of

**Figure 4** Comparison of pressure results for a model of polar water at $T = 2000$ K: MD simulations (symbols), newly developed theory for polar fluids (lower line) and exp-6 calculations alone (upper line).

**Figure 5** Same as Figure 4 for energy per particle.
The reactivity of energetic materials at extreme conditions

exp-6 thermodynamics alone. For both the pressure and the energy, the agreement is very good and the dipole moment contribution is sizeable.

The thermodynamic theory for exp-6 mixtures of polar materials is now implemented in the thermochemical code Cheetah. We considered first the major polar detonation products \( \text{H}_2\text{O}, \text{NH}_3, \text{CO}, \) and \( \text{HF} \). The optimal exp-6 parameters and dipole moment values for these species were determined by fitting to a variety of available experimental data. We find, for example, that a dipole moment of 2.2 Debye for water reproduces very well all available experiments. Incidentally, this value is in very good agreement with values typically used to model supercritical water.

A comparison of our Cheetah polar water model predictions with both high-pressure Hugoniot data, and low-density (steam at 800 K) experimental data is presented in Figure 6. The agreement is very good for both cases.

The newly developed equation of state was applied to the calculation of detonation properties. In this context, one stringent test of any equation of state is the prediction of detonation velocities as a function of initial densities, and we chose for this purpose PETN. The Cheetah results are shown in Figure 7 along with the experimental data. The agreement is again very good.

Advances continue in the treatment of detonation mixtures that include explicit polar and ionic contributions. The new formalism places on a solid footing the modeling of polar species, opens the possibility of realistic multiple fluid phase chemical equilibrium calculations (polar—nonpolar phase segregation), extends the validity domain of the EXP6 library, and opens the possibility of applications in a wider regime of pressures and temperatures.

![Figure 6](image_url) Comparison of theory for polar water: experimental data (Hugoniot—circles and steam at \( T = 800 \text{ K} \)—diamonds) and theory (lines).
Predictions of high explosive detonation based on the new approach yield excellent results. A similar theory for ionic species model\textsuperscript{43} compares very well with MD simulations. Nevertheless, high explosive chemical equilibrium calculations that include ionization are beyond the current abilities of the Cheetah code, because of the presence of multiple minima in the free energy surface. Such calculations will require additional algorithmic developments. In addition, the possibility of partial ionization, suggested by first principles simulations of water discussed below, also needs to be added to the Cheetah code framework.

**ATOMISTIC MODELING OF CONDENSED-PHASE REACTIONS**

Chemical equilibrium methods provide useful predictions of the EOS of detonation processes and the product molecules formed, but no details of the atomistic mechanisms in the detonation are revealed. We now discuss condensed-phase detonation simulations using atomistic modeling techniques to evaluate reaction mechanisms on the microscopic level.

Numerous experimental studies have investigated the atomistic details of HE decomposition by examining the net products after thermal (low-pressure) decomposition (see, for example, Ref. 54). For RDX and HMX, the rate limiting reaction is most likely NO\textsubscript{2} dissociation and a plethora of final products in the decomposition process have been isolated. Several theoretical studies have also
been reported on the energetics of gas-phase decomposition pathways for HE materials using a variety of methods. For example, we point to work on RDX and HMX where both quantum chemistry\textsuperscript{42,58–57} and classic simulations of unimolecular dissociation\textsuperscript{58,59} were used.

Gas-phase results provide insight into the reaction pathways for isolated HE molecules; however, the absence of the condensed-phase environment is believed to affect reaction pathways strongly. Some key questions related to condensed-phase decomposition are as follows: (1) How do the temperature and pressure affect the reaction pathways? (2) Are there temperature or pressure-induced phase-transitions that play a role in the reaction pathways that may occur? (3) What happens to the reaction profiles in a shock-induced detonation? These questions can be answered with condensed-phase simulations, but such simulations would require large-scale reactive chemical systems consisting of thousands of atoms. Here we present results of condensed-phase atomistic simulations, which are pushing the envelope toward reaching the required simulation goal.

In our group, we are considering whether non-molecular phases of such species could be formed at conditions approaching those of detonation. Condensed phase explosives typically have C–J pressures in the neighborhood of 20–40 GPa and temperatures between 2500 K and 4000 K. Early in the reaction zone, energetic materials are thought to be cooler but more compressed. The Zeldovich–von Neumann–Döring\textsuperscript{60–62} (ZND) state is defined by the Hugoniot of the unreacted material, which can be probed by shock experiments carefully designed to avoid HE initiation. Estimates of the temperature at the ZND state are in the neighborhood of 1500 K, whereas pressures as high as 60 GPa are possible.

One possible non-molecular phase that may exist is a superionic solid. Superionic solids are compounds that exhibit exceptionally high ionic conductivity, where one ion type diffuses through a crystalline lattice of the remaining types. In this unique phase of matter, chemical bonds are breaking and reforming rapidly. Since their discovery in 1836, a fundamental understanding of superionic conductors has been one of the major challenges in condensed matter physics.\textsuperscript{63} In general, it has been difficult to create a simple set of rules governing superionic phases. Studies have been limited mostly to metal-based compounds, such as AgI and PbF\textsubscript{2}.\textsuperscript{63} However, the existence of superionic solid phases of hydrogen-bonded compounds had been theorized previously.\textsuperscript{64,65}

Recent experimental and computational results indicate the presence of a high-pressure triple point in the H\textsubscript{2}O phase diagram,\textsuperscript{66–68} including a so-called superionic solid phase with fast hydrogen diffusion.\textsuperscript{68,69} Goldman et al. have described the emergence of symmetric hydrogen bonding in superionic water at 2000 K and 95 GPa.\textsuperscript{69} In symmetric hydrogen bonding, the intramolecular X–H bond becomes identical to the intermolecular X–H bond, where X is an electronegative element. It has been suggested that for superionic solids a mixed ionic/covalent bonding character stabilizes the mobile ion during the
diffusion process. Symmetric hydrogen bonding provides mixed ionic/covalent bonding and thus could be a key factor in superionic diffusion in hydrogen-bonded systems. Because of current limitations in diamond anvil cell techniques, the temperatures and pressures that can be investigated experimentally are too low to probe the role of hydrogen bonding in previously studied hydrides (i.e., H₂O and NH₃). On the other hand, current shock compression experiments have difficulty resolving transient chemical species.

The density profiles of large planets, such as Uranus and Neptune, suggest that a thick layer of “hot ice”, exists which is thought to be 56% H₂O, 36% CH₄, and 8% NH₃. This hot ice layer has lead to theoretical investigations of the water phase diagram, in which Car-Parrinello Molecular Dynamics (CPMD) simulations were conducted at temperatures and pressures ranging from 300 K to 7000 K and 30–300 GPa. In these molecular dynamics simulations, the electronic degrees of freedom are treated explicitly at each time step, effectively solving the electronic Schrödinger equation at each step. At temperatures above 2000 K and pressures above 30 GPa, a superionic phase was observed in which the oxygen atoms had formed a bcc lattice, and the hydrogen atoms were diffused extremely rapidly (ca. 10⁻⁴ cm²/s) via a hopping mechanism between oxygen lattice sites. Experimental results for the ionic conductivity of water at similar state conditions agree well with the results from Ref. 3, confirming the idea of a superionic phase and indicating a complete atomic ionization of water molecules under extreme conditions (P > 75 GPa, T > 4000 K).

More recent quantum-based MD simulations were performed at temperatures up to 2000 K and pressures up to 30 GPa. Under these conditions, it was found that the molecular ions H₃O⁺ and OH⁻ are the major charge carriers in a fluid phase, in contrast to the bcc crystal predicted for the superionic phase. The fluid high-pressure phase has been confirmed by X-ray diffraction results of water melting at ca. 1000 K and up to 40 GPa of pressure. In addition, extrapolations of the proton diffusion constant of ice into the superionic region were found to be far lower than a commonly used criterion for superionic phases of 10⁻⁴ cm²/s. A great need exists for additional work to resolve the apparently conflicting data.

The superionic phase has been explored with more extensive CPMD simulations. Calculated power spectra (i.e., the vibrational density of states or VDOS) have been compared with measured experimental Raman spectra at pressures up to 55 GPa and temperatures of 1500 K. The agreement between theory and experiment was very good. In particular, weakening and broadening of the OH stretch mode at 55 GPa was found both theoretically and experimentally.

A summary of our results on the phase diagram of water is shown in Figure 8. We find that the molecular to non-molecular transition in water occurs in the neighborhood of the estimated ZND state of HMX. This transition shows that the detonation of typical energetic materials occurs in the neighborhood of the molecular to non-molecular transition.
For our simulations, we used CPMD v.3.91, with the BLYP exchange-correlation functional,78,79 and Troullier–Martins pseudo-potentials80 for both oxygen and hydrogen. A plane wave cut-off of 120 Ry was employed to ensure convergence of the pressure, although all other properties were observed to converge with a much lower cut-off (85 Ry). The system size was 54 H2O molecules. The temperature was controlled by using Nose–Hoover thermostats81 for all nuclear degrees of freedom. We chose a conservative value of 200 au for the fictitious electron mass and a time step of 0.048 fs.

Initial conditions were generated in two ways: (1) A liquid configuration at 2000 K was compressed from 1.0 g/cc to the desired density in sequential steps of 0.2 g/cc from an equilibrated sample. (2) An ice VII configuration was relaxed at the density of interest and then heated to 2000 K in steps of 300 degrees each, for a duration of 0.5–1 ps. While heating, the temperature was controlled via velocity scaling. We will refer to the first set of simulations as the “L” set and the second as the “S” set. Unless stated otherwise, the results (including the pressures) from the “S” initial configurations are those reported. Once the desired density and/or temperature was achieved, all simulations were equilibrated for a minimum of 2 ps. Data collection from the simulations was obtained for 5–10 ps after equilibration.

The calculated diffusion constants of hydrogen and oxygen atoms are shown in Figure 9. The inset plot shows the equation of state for this isotherm for both “L” and “S” simulations. The two results are virtually identical up until 2.6 g/cc. At 34 GPa (2.0 g/cc), the hydrogen atom diffusion constant has achieved values associated with superionic conductivity (greater than

Figure 8 The phase diagram of H2O as measured experimentally68 (black solid) and through first principles simulations of the superionic phase (gray dash).68,69 The estimated ZND state of HMX is shown as a square for reference.
10^{-4} \text{ cm}^2/\text{s}). The diffusion constant remains relatively constant with increasing density, in qualitative agreement with the experimental results of Chau et al.\textsuperscript{72} for the ionic conductivity.

In contrast, the O diffusion constant drops to zero at 75 GPa (2.6 g/cc) for both “L” and “S” initial configurations. The surprisingly small hysteresis in the fluid to superionic transition allows us to place the transition point between 70 GPa (2.5 g/cc) and 77 GPa (2.6 g/cc). The small hysteresis is most likely caused by the weak O–H bonds at the conditions studied, which have free energy barriers to dissociation comparable with $k_B T$ (see below). Simulations that start from the “L” initial configurations are found to quench to an amorphous solid upon compression to 2.6 g/cc.

The transition pressure of 75 GPa is much higher than the 30 GPa predicted earlier.\textsuperscript{65} This difference is likely caused by the use of a much smaller basis set (70 Ry) by Cavazzoni et al. Our results are also in disagreement with simple extrapolations of the proton diffusion constant to high temperatures.\textsuperscript{77}

Radial distribution functions (RDFs) for the “S” simulations are shown in Figure 10. Analysis of the oxygen–oxygen RDF (not shown) for all pressures yields a coordination number of just over 14 for the first peak, which is consistent with a high-density bcc lattice in which the first two peaks are broadened because of thermal fluctuations. The RDF can be further analyzed by calculating an “average position” RDF in which the position of each oxygen is averaged over the course of the trajectory. The results for
75–115 GPa indicate the presence of a bcc lattice undergoing large amplitude vibrations, even though each RDF in Figure 10 has width similar to that of a liquid or a glass. The RDFs for the amorphous phase (not shown) are similar to those of the solid phase obtained in the “S” simulations.

The O–O and H–H RDFs (not shown) indicate that no O–O or H–H covalent bonds are formed during the simulations at all densities. The \( g(ROH) \) shows a lattice-like structure at 115 GPa, which is consistent with proton diffusion via a hopping mechanism between lattice sites.\(^{65}\) At 34 GPa, the coordination number for the first peak in \( g(ROH) \) is 2, which indicates molecular \( H_2O \). Between 95 GPa and 115 GPa, however, the coordination number for the first peak in \( g(ROH) \) becomes four, which indicates that water has formed symmetric hydrogen bonds where each oxygen has four nearest-neighbor hydrogens.

Concomitant with the change in the oxygen coordination number is a shift of the first minimum of the O–H RDF from 1.30 Å at 34 GPa to 1.70 Å at 115 GPa. We observe a similar structural change in the H–H RDF in which the first peak lengthens from 1.63 Å (close to the result for ambient conditions) to 1.85 Å. These observations bear a strong resemblance to the ice VII to ice X transition in which the covalent O–H bond distance of ice becomes equivalent to the hydrogen bond distance as pressure is increased.\(^{82}\) However, the superionic phase differs from ice X, in that the position of the first peak in \( g(ROH) \) is not half the distance of the first O–O peak.\(^{82}\) We analyze the effect

![Figure 10 O–H radial distribution function as a function of density at 2000 K. At 34 GPa, we find a fluid state. At 75 GPa, we show a “covalent” solid phase. At 115 GPa, we find a “network” phase with symmetric hydrogen bonding. Graphs are offset by 0.5 for clarity.](image-url)
of the change in $g(\text{ROH})$ below in terms of the molecular speciation in the simulations.

We determined the free energy barrier for dissociation by defining a free energy surface for the oxygen–hydrogen distances, viz. $W(r) = -k_B T \ln [g(\text{ROH})]$, where $W(r)$ is the free energy surface (potential of mean force). The results are shown in Figure 11.

The free energy barrier can then be defined as the difference in height between the first minimum and the second maximum in the free energy surface. The free energy barrier is 11 kcal/mol at 34 GPa and 8 kcal/mol at 115 GPa. The remainder of the results discussed below are for the “S” simulations.

We now analyze the chemical species prevalent in water at these extreme conditions by defining instantaneous species based on the O–H bond distance. If that distance is less than a cut-off value $r_c$, we count the atom pair as being bonded. Determining all bonds in the system gives the chemical species at each point in time. Species with lifetimes less than an O–H bond vibrational period (10 fs) are “transient” and do not represent bound molecules. The optimal cut-off $r_c$ between bonded and nonbonded species is given by the location of the maximum in the free energy surface.\textsuperscript{83}

Using the free energy maximum to define a bond cut-off provides a clear picture of qualitative trends. As expected from the $g(\text{ROH})$, at 34 GPa, the free energy peak is found at 1.30 Å, which is approximately the same value obtained from simulations of ambient water. At 75 GPa, the free energy peak maintains almost the same position but broadens considerably. At 115 GPa, the peak has sharpened once again, and the maximum is now at 1.70 Å.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ROH_free_energy_surface.png}
\caption{ROH free energy surface at 2000 K. The lines are spaced by a factor of 4 kcal/mol for clarity.}
\end{figure}
Given the above definition of a bond distance, we can analyze species lifetimes. The lifetime of all species is less than 12 fs above 2.6 g/cc, which is roughly the period of an O–H bond vibration (ca. 10 fs). Hence, water does not contain any molecular states above 75 GPa and at 2000 K but instead forms a collection of short-lived “transient” states. The “L” simulations at 2.6 g/cc (77 GPa) and 2000 K yield lifetimes nearly identical to that found in the “S” simulations (within 0.5 fs), which indicates that the amorphous states formed from the “L” simulations are closely related to the superionic bcc crystal states found in the “S” simulations.

Species concentrations are shown in Figure 12. At 34 GPa (2.0 g/cc), H₂O is the predominant species, with H₃O⁺ and OH⁻ having mole fractions of ca. 5%. In addition, some aggregation has occurred in which neutral and ionic clusters containing up to six oxygens have formed. The concentrations of OH⁻ and H₃O⁺ are low for all densities investigated and nonexistent at 95 and 115 GPa (2.8 and 3.0 g/cc, respectively). The calculated lifetimes for these species are well below 10 fs for the same thermodynamic conditions (less than 8 fs at 34 GPa). At pressures of 95 and 115 GPa, the increase in the O–H bond distance leads to the formation of extensive bond networks (Figure 13). These networks consist entirely of O–H bonds, whereas O–O and H–H bonds were not found to be present at any point.

A maximally localized Wannier function analysis was performed to better analyze the bonding in our simulations. The maximally localized Wannier functions express the quantum wave function in terms of functions localized at centers, rather than as delocalized plane waves. The positions of these centers give us insight into the localization of charge during the

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**Figure 12** Mole fraction of species found at 34–115 GPa and 2000 K. The filled circles correspond to H₃O⁺, whereas the open circles correspond to OH⁻.
simulation. We computed the percentage of O–H bonds with a Wannier center along the bond axis. Surprisingly, the results for pressures of 34–75 GPa consistently showed that 85–95% of the O–H bonds are covalent. For 95 GPa and 115 GPa, we find about 50–55% of the bonds are covalent. This result is consistent with symmetric hydrogen bonding, for which the split between ionic and covalent bonds would be 50/50. The above simulations show that the molecular to non-molecular transition in H₂O lies just above the operating range of most typical condensed explosives—about 50 GPa. This range presents a considerable challenge for thermochemical calculations, because a simple statistical mechanical treatment of non-molecular phases such as superionic water does not yet exist.

**FIRST PRINCIPLES SIMULATIONS OF HIGH EXPLOSIVES**

Quantum mechanical methods can now be applied to systems with up to 1000 atoms; this capacity is not only from advances in computer technology but also from improvements in algorithms. Recent developments in reactive classical force fields promise to allow the study of significantly larger systems. Many approximations can also be made to yield a variety of methods, each of which can address a range of questions based on the inherent accuracy of the method chosen. We now discuss a range of quantum mechanical-based methods that one can use to answer specific questions regarding shock-induced detonation conditions.

Atomistic simulations have been performed on condensed-phase HMX, which is a material that is widely used as an ingredient in various explosives and propellants. A molecular solid at standard state, it has four known...
polymorphs, of which δ-HMX is believed to be the most highly reactive. In fact, β-HMX often transforms into δ-HMX before reacting violently. Manaa et al. have conducted quantum-based molecular dynamics simulations of the chemistry of HMX and nitromethane under extreme conditions, which are similar to those encountered at the C–J detonation state. They studied the reactivity of dense (1.9 g/cm³) fluid HMX at 3500 K for reaction times up to 55 ps, using the “Self-Consistent Charge Density-Functional Tight-Binding” (SCC-DFTB) method. Stable product molecules are formed rapidly (in a less than 1 ps) in these simulations. Plots of chemical speciation, however, indicate a time greater than 100 ps is needed to reach chemical equilibrium. Reactions occur rapidly in these simulations because the system is “preheated” to 3500 K. In a detonation, on the other hand, a temperature close to 3500 K would only be found after stable product molecules had been formed. The initial temperature of unreacted nitromethane, after being shocked, has been estimated to be 1800 K. HMX likely has a similar initial temperature to that of nitromethane. Nonetheless, the simulations of Manaa et al. provide useful insight into the chemistry of dense, hot energetic materials, which demonstrate that they are a useful complement to more traditional gas phase calculations.

Numerous experimental characterizations of the decomposition products of condensed-phase HMX exist at low temperatures (i.e., < 1000 K, well below detonation temperature). These studies tend to identify final gas products (such as H₂O, N₂, H₂, CO, and CO₂) from the surface burn, and the authors aspire to establish a global decomposition mechanism. Similar experimental observations at detonation conditions (temperatures 2000–5000 K and pressures 10–30 GPa) have not been realized to date, however. Computer simulations provide the best access to the short time scale processes occurring in these regions of extreme conditions of pressure and temperature. In particular, simulations employing many-body potentials or tight-binding models have emerged as viable computational tools, the latter of which has been demonstrated successfully in the studies of shocked hydrocarbons.

Lewis et al. calculated four possible decomposition pathways of the α-HMX polymorph: N–NO₂ bond dissociation, HONO elimination, C–N bond scission, and concerted ring fission. Based on energetics, it was determined that N–NO₂ dissociation was the initial mechanism of decomposition in the gas phase, whereas they proposed HONO elimination and C–N bond scission to be favorable in the condensed phase. The more recent study of Chakraborty et al. using density functional theory (DFT), reported detailed decomposition pathways of β-HMX, which is the stable polymorph at room temperature. It was concluded that consecutive HONO elimination (4 HONO) and subsequent decomposition into HCN, OH, and NO are the most energetically favorable pathways in the gas phase. The results also showed that the formation of CH₂O and N₂O could occur preferably from secondary decomposition of methylenenitramine.
The computational approach to simulate the condensed-phase chemical reactivity of HMX employed by Manaa et al.\textsuperscript{20} is based on implementing the SCC-DFTB scheme.\textsuperscript{91} This approach is an extension of the standard tight-binding approach in the context of DFT that describes total energies, atomic forces, and charge transfer in a self-consistent manner. The initial conditions of the simulation included six HMX molecules, which correspond to a single unit cell of the $\delta$-phase, with a total of 168 atoms. The density was 1.9 g/cm$^3$ and the temperature 3500 K in the simulations. These thermodynamic quantities place the simulation in the neighborhood of the C--J state of $\delta$-HMX (3800 K, 2.0 g/cm$^3$) as predicted through thermochemical calculations. The closest experimental condition corresponding to this simulation would be a sample of HMX that is suddenly heated under constant volume conditions, such as in a diamond anvil cell. A molecular dynamics simulation of the 168-atom system was conducted at constant volume and constant temperature. Periodic boundary conditions, whereby a particle exiting the supercell on one side is reintroduced on the opposite side with the same velocity, were imposed.

Under the simulation conditions, the HMX was found to exist in a highly reactive dense fluid. Important differences exist between the dense fluid (supercritical) phase and the solid phase, which is stable at standard conditions. One difference is that the dense fluid phase cannot accommodate long-lived voids, bubbles, or other static defects, whereas voids, bubbles, and defects are known to be important in initiating the chemistry of solid explosives.\textsuperscript{107} On the contrary, numerous fluctuations in the local environment occur within a time scale of tens of femtoseconds (fs) in the dense fluid phase. The fast reactivity of the dense fluid phase and the short spatial coherence length make it well suited for molecular dynamics study with a finite system for a limited period of time; chemical reactions occurred within 50 fs under the simulation conditions. Stable molecular species such as H$_2$O, N$_2$, CO$_2$, and CO were formed in less than 1 ps.

Figure 14 displays the product formation of H$_2$O, N$_2$, CO$_2$, and CO. The concentration $C(t)$ is represented by the actual number of product molecules formed at time $t$. Each point on the graphs (open circles) represents an average over a 250-fs interval. The number molecules in the simulation were sufficient to capture clear trends in the chemical composition of the species involved. It is not surprising to find that the rate of H$_2$O formation is much faster than that of N$_2$. Fewer reaction steps are required to produce a triatomic species like water, whereas the formation of N$_2$ involves a much more complicated mechanism.\textsuperscript{108} Furthermore, the formation of water starts around 0.5 ps and seems to have reached a steady state at 10 ps, with oscillatory behavior of decomposition and formation clearly visible. The formation of N$_2$, on the other hand, starts around 1.5 ps and is still progressing (as the slope of the graph is slightly positive) after 55 ps of simulation time, albeit slowly.
Because of the lack of high-pressure experimental reaction rate data for HMX and other explosives with which to compare, we produce in Figure 15 a comparison of dominant species formation for decomposing HMX that have been obtained from entirely different theoretical approaches. The concentration of species at chemical equilibrium can be estimated through thermodynamic calculations with the Cheetah thermochemical code.\textsuperscript{32,109} The results of the MD simulation compare well with the formation of H$_2$O, N$_2$, and HNCO predicted by Cheetah. The relative concentrations of CO and CO$_2$, however, are reversed, possibly because of the limited time duration of the simulation. Another discrepancy is that Cheetah predicts carbon in the diamond phase is in equilibrium with the other species at a concentration of 4.9-mol/kg HMX. No condensed carbon was observed in the simulation. Several other products and intermediates with lower concentrations, common to the two methods, have also been identified, including HCN, NH$_3$, N$_2$O, CH$_3$OH, and CH$_2$O. A comparison between

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14}
\caption{Product particle-number formations for H$_2$O, N$_2$, CO$_2$, and CO as a function of time.}
\end{figure}
the two vastly different approaches needs to be established when using much longer simulation times. Also, the product-molecule set of the thermochemical code needs to be expanded with important species determined from quantum-based simulations. It should also be noted that the accuracy of DFT calculations for chemistry under extreme conditions needs further experimental validation.

One expects the Cheetah results where more CO₂ than CO is formed as final products, because disproportionation of CO to condensed C + CO₂ is energetically favorable. The results displayed in Figure 14 show that at a simulation time of 40 ps the system is still in the second stage of reaction chemistry. At this stage, the CO concentration is rising but has not yet undergone the water gas shift reaction \((\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2)\) conversion. Interestingly, this shift occurs around 50 ps in the simulation, when CO₂ molecules are being formed while the CO concentration is correspondingly diminished.

Although the simulation sheds light on the chemistry of HMX under extreme conditions, some methodological shortcomings need to be overcome in the future. The demanding computational requirements of the quantum-based MD method limit its applicability to short times and high-temperature conditions. For example, the simulations discussed on HMX took over a year of wall clock time. Moreover, the SCC-DFTB method is not as accurate as high-level quantum-based methods. Nonetheless, the SCC-DFTB approach could still be considered as a promising direction for future research on the chemistry of energetic materials.
CONCLUSIONS

The ability to model chemical reaction processes in condensed-phase energetic materials at the extreme conditions typified by a detonation is progressing. Chemical equilibrium modeling is a mature technique with some limitations. Progress in this area continues, but it is hampered by a lack of knowledge of condensed-phase reaction mechanisms and rates. A useful theory of the equation of state for ionic and highly polar molecular species needs to be more fully developed. The role of unconventional molecular species in detonation needs to be investigated, and high-pressure chemical kinetics needs to be developed further as a field of study.

Atomistic molecular dynamics modeling is computationally intensive and is currently limited in the realm of detonations to picosecond time scales. Nonetheless, this methodology promises to yield the first reliable insights into the condensed-phase processes responsible for high explosive detonation. First principles simulations reveal that the transition to non-molecular phases lies close to the operating range of common explosives such as HMX. Additional work is necessary to extend the time scales involved in atomistic simulations. Alternatively, advanced force fields may offer the ability to model the reactions of energetic materials for periods of many picoseconds. Recent work in implementing thermostat methods appropriate to shocks may promise to overcome time scale limitations in the non-equilibrium molecular dynamics method itself and allow the reactions of energetic materials to be determined for up to several nanoseconds.

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