Sensitivity of pore collapse heating to the melting temperature and liquid-phase shear viscosity of HMX

Matthew P. Kroonblawd^{*,†} and Ryan A. Austin[‡]

*[†]Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory,
Livermore, CA 94550, United States*

*[‡]Engineering Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94550,
United States*

E-mail: kroonblawd1@llnl.gov

Abstract

A multiscale modeling strategy is used to quantify factors governing the temperature rise in hot spots formed by pore collapse from supported and unsupported shock waves in the high explosive HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). Two physical aspects are examined in detail, namely the melting temperature and liquid shear viscosity. All-atom molecular dynamics simulations of phase coexistence are used to predict the pressure-dependent melting temperature up to 5 GPa. Equilibrium simulations and the Green-Kubo formalism are used to obtain the temperature- and pressure-dependent liquid shear viscosity. Starting from a simplified continuum-based grain-scale model for HMX, we systematically increase the complexity of treatments for the solid-liquid phase transition and liquid shear viscosity in simulations of pore collapse. Using a realistic pressure-dependent melting temperature completely suppresses melting for supported shocks, which is otherwise predicted when treating it as a constant determined at atmospheric pressure. Alternatively, large melt pools form around pores during pressure release in unsupported shocks, even with a pressure-dependent melting temperature. Capturing the pressure dependence of the shear viscosity increases the peak temperature of melt pools by hundreds of Kelvin through viscous work. The complicated interplay of the solid-phase plastic work, solid-liquid phase transition, and liquid-phase viscous work identified here motivate taking a systematic approach to building increasingly complex grain-scale models and for guiding interpretation of predictions made using them.

1 Introduction

Initiation of high explosives is a prototypical multiscale problem wherein molecular-scale chemical reactions closely couple with crystal- and grain-scale mechanics, plasticity, phase transitions, and transport leading to complex material responses such as detonation. Energy localization in mechanically shocked explosives *via* the dynamic formation of hot spots at defect sites such as pores is a critical first step in the initiation of chemistry, leading to local

deflagration (burning) and the possible transition to detonation.¹⁻⁴ Multiphysics modeling in a continuum framework at sub-mm scales (colloquially, the *grain scale*) is widely recognized as a key route to parameterize and validate the kinds of engineering models used to inform design and gauge safety and performance.⁵⁻¹⁵ Grain scale models for studying hot spot formation and growth in explosives are highly specialized tools that incorporate judicious assessments of the primary physics and physical inter-dependencies at play for a given material and application space. Despite this, some physics terms in these models (e.g., phase boundaries and transport coefficients) have only reasonable “placeholder” parameters that are frequently treated as constants. This is true even in cases where these properties are expected to be strong functions of state variables, such as temperature and pressure, which vary significantly under conditions of interest. The lack of necessary data for calibrating separate physics terms stems from many properties being inseparable in integrated experiments and the complementary component-scale modeling philosophy that aims to match integrated responses, such as times of shock arrival or breakout. Making robust connections with atomistic modeling approaches has so far proven to be one of the most practical ways to obtain missing physics data.^{9,12,14,16} Placing grain scale models on firmer physical grounds is desirable both to improve predictive accuracy as well as to provide a means for systematic improvement.

The melting point of high explosives is expected to influence initiation properties for a number of reasons. Firstly, it largely determines the upper bound on heating due to plastic work, as static strength is lost upon melting. Significant increases in the melting point with pressure could defer loss of strength under shock conditions, thus enabling further heating of hot spots. The pressure dependence of the melting point may also suppress melting of bulk crystal in a shock, which would otherwise be predicted using simple assumptions.¹⁴ Once melting occurs, the liquid phase will develop shear stresses due to the viscous nature of the flow. The liquid-phase shear viscosity determines the deviatoric stresses that develop in response to a shearing rate, which then serves as a dissipative work contribution that

Figure 1: Snapshots of (a) an HMX molecule and (b) the unit cell¹⁹ for β -HMX in the $P2_1/n$ space group setting. Atoms are respectively colored cyan, blue, red, and white for carbon, nitrogen, oxygen, and hydrogen.

raises the temperature. Given the high shearing rates that can develop in bands of shear localization or turbulent flow, the viscous heating effect can be significant, perhaps serving to trigger chemical reactions in regions of intense heating.^{5,17,18} Predicting these heating effects *a priori* from even a limited set of physics terms is exceedingly difficult due to nonlinear coupling in a multiphysics treatment.

We focus here on accurately capturing the melting point and liquid-phase shear viscosity of the molecular organic high explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) for grain scale modeling of hot spot formation under shock loading. HMX crystallizes in the monoclinic β form at standard conditions¹⁹ (see Figure 1) and can transition through one or two high temperature crystal polymorphs before melting at pressures below ≈ 0.15 GPa.²⁰ Above this pressure, β is expected to directly melt to liquid, but neither the pressure-dependent melt line, nor other properties of the liquid, are known for the GPa-range pressures typical of shock initiation. Characteristics of shock-induced hot spot formation in β -HMX have been investigated for small <100 nm pores with all-atom molecular dynamics (MD) simulations^{21,22} and for larger micron-scale pores and cracks thought to be responsible for initiation using a variety of grain scale models.^{5,8,11,23} While aspects of these grain scale models can be quite sophisticated,^{5,7,10,11,13,24} incorporating for instance temperature/pressure dependent crystal elasticity and dislocation-based plasticity, their treatment of melting and the shear viscosity of the liquid is rather simplistic. Current HMX grain

scale models^{5,7,8,11,23} either omit melting or else treat the melt point and liquid viscosity as constants determined at atmospheric pressure^{25,26} or through empirical relationships such as the Lindemann law.^{27,28} The melt point in related explosives increases by a factor of two or more when the pressure is increased by only a few GPa.²⁹ Likewise, the shear viscosity of the liquid is expected to follow an Arrhenius temperature dependence and may also exhibit strong pressure dependence. Properly accounting for the temperature and pressure dependencies of these properties could play a significant role in determining the degree of local heating due to interactions between a shock and crystal defects.

We adopt a multiscale approach to study hot spots in HMX in which all-atom MD predictions are used to parameterize the melting and liquid viscosity terms in a grain scale model for direct simulation of pore collapse. Equilibrium MD simulations of solid-liquid phase co-existence are used to bracket the melting point up to 5 GPa and the Green-Kubo formalism is used to compute the shear viscosity of the liquid. While the elastic,^{30–33} plastic,^{34–38} and thermal transport^{39,40} properties of β -HMX are generally understood to be complicated and moderately anisotropic, we start from a simplified grain scale model and systematically increase its complexity in the treatment of the liquid phase. Taking a gradual rather than “all-in” approach to constructing grain scale models serves to better isolate effects due to inclusion of new physics. Consequences of grain scale model assumptions are simulated for long-pulse (supported) and short-pulse (unsupported) shocks, which captures limiting cases in experiments ranging from traditional gas guns to modern table-top laser-driven systems. While unsupported shocks have received little attention, we find that these conditions facilitate the formation of sizable melt pools that are hundreds of Kelvin hotter than the solid bulk due to viscous work.

2 Methods

2.1 Molecular Dynamics Simulations

2.1.1 General Simulation Details

Classical all-atom molecular dynamics (MD) simulations were performed using LAMMPS,⁴¹ 3D-periodic simulation cells, and a variant of the well-established non-reactive force field for HMX developed by Smith and Bharadwaj.⁴² The Smith-Bharadwaj HMX force field has been used extensively in simulation studies on HMX in both the crystal and liquid phases.^{22,26,30,32–40,43,44} Covalent force field interactions include harmonic functions for bonds, angles, and improper dihedrals and truncated cosine series for proper dihedrals. Non-bonded interactions are modeled using Buckingham (exp-6) repulsion and dispersion terms with Coulomb electrostatics between partial charges fixed on the nuclei. The only difference between the original HMX force field and the variant used here is the harmonic force constant for N–O bond stretching (taken from Ref. 44), which yields an improved vibrational spectrum compared to the original. All C–H bonds were constrained to their equilibrium values using RATTLE^{45,46} with the accuracy threshold set to 10^{-4} . Non-bonded terms were evaluated in real space up to a 15 Å cutoff and the electrostatic terms were evaluated beyond the cutoff using the particle-particle particle-mesh⁴⁷ (PPPM) k-space method with the accuracy threshold set to 10^{-7} .

The isochoric-isothermal (NVT) and isobaric-isothermal (NPT) ensembles were sampled using MD simulations at various points in this study. Trajectories were integrated with a 0.5 fs timestep. Isothermal simulations were performed using a Nosé-Hoover-style thermostat^{48,49} with the coupling parameter set to 100 fs. Isobaric simulations were performed using a Nosé-Hoover-style barostat⁵⁰ with the barostat coupling constant set to 1000 fs and the optional drag parameter set to 1.0 (unitless). All six stress components were independently coupled to their respective cell parameters in NPT simulations involving a crystal phase (LAMMPS setting *tri*) and pure liquid-phase NPT simulations used an isotropic barostat

Figure 2: Snapshots showing two projections of a two-phase simulation cell in which a β -HMX crystal slab with exposed (010) crystal faces is in contact with liquid. There are 240 molecules each in crystal and liquid regions. Atoms are respectively colored cyan, blue, red, and white for carbon, nitrogen, oxygen, and hydrogen.

(LAMMPS setting *iso*). All MD simulation snapshots were rendered using OVITO.⁵¹

2.1.2 Melt Line Calculation

The pressure-dependent melting point $T_m(P)$ of β -HMX was determined using NPT -MD simulations of solid-liquid coexistence.^{29,52–54} We chose to use the coexistence method over alternative approaches^{55,56} because it is straightforward to implement, converges relatively quickly, and brackets the melting point with known bounds. To determine $T_m(P)$, one performs a number of NPT simulations starting from a metastable two-phase crystal-liquid configuration (see Figure 2). Simulations were performed at a specified pressure, each with a different temperature chosen from an interval that brackets the melting point. Time histories of the cell volume exhibit negative slope during NPT simulations if $T < T_m(P)$, positive slope if $T > T_m(P)$, and a plateau at the liquid-phase equilibrium value if the crystal region completely melts on an MD timescale, here taken to be $O(10 \text{ ns})$.

The starting configuration was constructed by placing a 2D periodically infinite crystal slab in contact with molecules in a liquid-like phase at a (T, P) state point that was well below $T_m(P)$. Periodic boundaries lead to two exposed crystal surfaces in contact with liquid. We considered three cases for melting β -HMX initiated on the principal crystal faces (100), (010), and (001) in the $P2_1/n$ space group. A $6\mathbf{a} \times 4\mathbf{b} \times 5\mathbf{c}$ crystal supercell (240 molecules) was constructed using equilibrium lattice parameters $a = 6.593 \text{ \AA}$, $b = 10.534 \text{ \AA}$, $c = 7.702 \text{ \AA}$, and $\beta = 98.75^\circ$ determined from a 500 ps NPT simulation performed at 0 GPa and 400 K. A corresponding 240-molecule liquid configuration was extracted from an HMX melt simulation at 0 GPa and 800 K, which we contracted to the same $6\mathbf{a} \times 4\mathbf{b} \times 5\mathbf{c}$ cell dimensions during a 25 ps simulation with an applied thermostat at 800 K. Crystal slabs were formed by introducing a vacuum region through replication of the simulation cell along either the $\mathbf{a}$, $\mathbf{b}$, or $\mathbf{c}$ directions to respectively expose the (100), (010), and (001) surfaces. The liquid configuration was placed into the vacuum region and was thermalized through a three-stage procedure while holding the crystal molecules fixed. Three 100 ps NVT stages were performed in which the liquid was first brought to 1600 K, then cooled with a linear temperature ramp to 400 K, followed by a final equilibration at 400 K. The crystal was then thermalized at 400 K for 100 ps while holding the liquid molecules fixed, followed by a final 100 ps NVT simulation at 400 K with both the liquid and crystal region molecules treated as flexible.

2.1.3 Transport Calculations

Transport properties of HMX liquid were determined through equilibrium NVT -MD simulations performed with a cubic simulation cell containing 250 molecules. Our primary focus was to obtain reliable predictions of the shear viscosity $\eta(T, P)$, as it will influence the extent of dissipated work in fluidic sheared regions and thus the heating of hot spots. Within the Green-Kubo formalism,^{57,58} one can relate the shear viscosity to the time autocorrelation of

shear stresses sampled in the canonical (NVT) ensemble as

$$\eta(T, P) = \frac{V}{3k_B T} \int_0^\infty \sum_{\alpha\beta=xy,xz,yz} \langle \sigma_{\alpha\beta}(0) \cdot \sigma_{\alpha\beta}(t) \rangle dt. \quad (1)$$

Here, k_B is the Boltzmann constant, $\sigma_{\alpha\beta}$ are the off-diagonal components of the stress tensor, and $\langle \rangle$ denotes a time average of the stress autocorrelation function. Because the pressure dependence is parametric, the appropriate volume V must be set based on the $V(T, P)$ equation of state. Separate simulations are required for each (T, P) state point considered and the actual evaluation of Equation 1 is best performed as a post-processing step. We closely follow earlier work that determined the shear viscosity for the related molecular explosive TATB,²⁹ so we only briefly outline important considerations in the practical evaluation of Equation 1 here.

Three separate time scales are at play when evaluating η , including the sampling period t_{sample} for recording $\sigma_{\alpha\beta}$, the maximum time lag for computing the autocorrelation function t_{block} , and the total simulation time t_{sim} . The first two time scales, t_{sample} and t_{block} , are fundamentally connected to the system physics and correspond to the time scale for fluctuations in the shear stress autocorrelation and the time required for the autocorrelation to decay sufficiently close to zero. The last two terms are directly linked as the trajectory is broken into separate non-overlapping blocks, each being t_{block} in length. There must be a sufficient number of blocks to obtain an accurate time average of the autocorrelation function.

The first time scale does not present a significant hindrance in terms of computational or data storage costs. We chose to initially over sample the stresses at $t_{\text{sample}} = 1$ fs, which was found to yield practically identical results when down sampled at $t_{\text{sample}} = 5$ fs. Very large t_{block} were required for most state points, so we used $t_{\text{sample}} = 5$ fs to reduce computer memory requirements during evaluation of the autocorrelation through a fast Fourier transform.

The second and third time scales directly affect the computational cost. Higher viscosity values typically require larger t_{block} to converge and thus the minimum t_{block} required can

Figure 3: Time histories for the shear viscosity computed at 1000 K and 1 GPa using different sized block windows t_{block} . Convergence with increasing t_{block} is evident through curve overlaps at long simulation times and is plotted in the inset panel. The vertical dashed line demarcates $t = t_{\text{sim}}/2$.

be highly dependent on the state point. At the same time, $t_{\text{sim}} \gg t_{\text{block}}$. The minimum block time t_{block} , and thus the total simulation time t_{sim} required, are difficult to determine *a priori*. Convergence with t_{block} was independently verified for each state point, which we discuss in detail below, but values between 200 ps and 800 ps were sufficient in most cases. We chose t_{sim} to be large enough so that time-dependent plots of the predicted $\eta(t; T, P)$ converged to steady values for sufficiently large t_{block} . An example of $\eta(t; T, P)$ highlighting the convergence with increasing t_{block} at constant t_{sim} is shown in Figure 3. Too small of t_{block} leads to a converged prediction from the time history, but at the wrong value for the viscosity. The average and standard deviation of the time history for $\eta(t; T, P)$ were determined for times $t \geq t_{\text{sim}}/2$ and interpreted as the shear viscosity and its uncertainty.

Although the functional form for our HMX grain scale model does not require it, we nonetheless compute and report the self-diffusion coefficients for liquid HMX as they are readily obtained from the same simulations used to compute the shear viscosity. Diffusion coefficients were determined using the Einstein relation

$$D(T, P) = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle}{6t}, \quad (2)$$

which is computed in terms of the average mean-squared displacements of the molecular centers of mass $\mathbf{R}(t)$ averaged over all molecules and time origins. In practice, $D(T, P)$ was obtained through a weighted least-squares linear regression of mean-squared displacement time history data. We excluded times $t < 1$ ns and $t > t_{\text{sim}}/2$ from the regression to respectively avoid initial transients due to caging effects and poor statistical sampling at large time lags. Each contribution to the regression was weighted by the variance of the mean-squared displacement, which was computed for each time t over all molecules and time origins. These weights were propagated through the regression to yield uncertainties in the diffusion coefficients.

2.2 Grain Scale Simulations

2.2.1 General Simulation Details

The simulations of shock-wave-induced pore collapse were performed using the arbitrary Lagrangian-Eulerian finite element method, which handles large strains in regions of localized deformation using a mesh relaxation scheme. The hydrocode **ALE3D**⁵⁹ was used for this purpose. The simulations involved a 2D computational domain, where a single air-filled pore (1 μm in diameter) was placed in a slab of HMX ($18 \times 16 \mu\text{m}^2$). The pore is located 8 μm away from the drive surface ($X = 0$) and the lateral/remote boundaries are far enough away to avoid any unwanted reflections on the time scale of interest. The calculations were performed under 2D plane strain, so the pore corresponds to cylindrical cavity in 3D. A mirror plane of symmetry bisects the pore along the shock direction, so only half the slab needs to be meshed. All grain scale simulation snapshots were rendered using **VisIt**.⁶⁰

Relatively weak (≈ 3 GPa) and strong (≈ 10 GPa) shock waves were generated using a pressure drive on the boundary, which is ramped-up over a short period and held constant for a prescribed time. We considered *supported* shocks (a constant pressure drive that was sustained for the entire simulation) and *unsupported* shocks, where the pressure drive was reduced to zero after a pulse duration of 1 ns. Simulations were performed to assess the

sensitivity of results to the mesh size (see Supporting Information⁶¹). A 20 nm mesh length was found to provide sufficiently converged results based on an analysis of the post-shock melting extent and the temperature distribution around the pore.

2.2.2 Material Model

We focus on the sensitivity of pore collapse heating to melting under shock wave loading. As such, we simplified other aspects of the model to avoid complicating effects. The primary simplifications were that the HMX solid and liquid phases were taken to be (i) mechanically isotropic, (ii) locally adiabatic, and (iii) non-reactive. Although these simplifications are understood to be unrealistic for cases of interest, they enable a more precise evaluation of melting and viscous heating effects. Detailed studies of the effects of elastic/plastic anisotropy, hot spot dissipation *via* heat conduction, and coupled responses due to chemical reactions can be found in the literature.⁵

Stresses in the solid and liquid phases were respectively computed as

$$\boldsymbol{\sigma}_{\text{sol}} = -(\bar{P}_{\text{sol}} + q)\mathbf{I} + \mathbf{s}^0, \quad (3)$$

$$\boldsymbol{\sigma}_{\text{liq}} = -(\bar{P}_{\text{liq}} + q)\mathbf{I} + 2\eta\mathbf{D}, \quad (4)$$

where $\bar{P}$ is the thermodynamic pressure, q is an artificial viscous stress (commonly used in hydrocodes to smooth the discontinuity of a shock front), $\mathbf{I}$ is the second-order identity tensor, and $\mathbf{s}^0$ is an equilibrium deviatoric stress associated with the plastic flow resistance of the solid phase. The liquid phase does not support static shear stresses, but it does develop dynamic shear stresses, which are modeled using a simple viscous relation. Here η is the liquid-phase shear viscosity and $\mathbf{D}$ is the rate of deformation tensor (*i.e.*, the symmetric part of the velocity gradient). Note that this form omits contributions from a physical volume viscosity.

The elastic response of the solid phase is modeled as isotropic. The pressure-volume

response is modeled using a fitted^{5,62} Murnaghan equation of state (EOS),

$$\bar{P}_{\text{sol}} = \frac{K_0}{K_1} \left[\left(\frac{\rho}{\rho_0} \right)^{K_1} - 1 \right], \quad (5)$$

where ρ/ρ_0 is the relative density and K_0 and K_1 are the reference bulk modulus and its first pressure derivative, respectively. Elastic shear deformations were modeled as Hookean with a constant shear modulus, μ . The plastic flow behavior of the solid phase is also isotropic, with a constant yield strength, y . The flow rule used here limits the deviatoric stress according to $\sqrt{\frac{3}{2} \mathbf{s}^0 : \mathbf{s}^0} \leq y$. The artificial viscous stress, q , depends on the local mesh size and velocity gradient and is typically parameterized to spread a shock front across a few mesh elements. We utilized the *monotonic-q* formulation in ALE3D.⁵⁹

The melting criterion is based on the internal energy, e . The internal energy at which melting occurs is expressed as

$$e_{\text{m}} = e_{\text{c}} + c_V T_{\text{m}}, \quad (6)$$

where e_{c} is the cold energy (obtained from the EOS), c_V is the heat capacity at constant volume, and T_{m} is the melt temperature. In general, e_{c} , e_{m} , and T_{m} all depend on the density. Material is melted when $e > e_{\text{m}}$, ignoring the latent heat and any kinetic effects. For simplicity, the liquid phase employs the same EOS as the solid (*i.e.*, $\bar{P}_{\text{liq}} = \bar{P}_{\text{sol}}$).

The solid-phase plastic work ($\int \mathbf{s}^0 : \mathbf{D}^{\text{p}} dt$, where $\mathbf{D}^{\text{p}}$ is the plastic part of $\mathbf{D}$), the liquid-phase viscous work ($\int 2\eta \mathbf{D} : \mathbf{D} dt$), and the artificial viscous work ($-\int q \text{Tr}[\mathbf{D}] dt$) are all considered as fully dissipative. Since thermoelastic coupling is not included in the model, these three mechanisms are the only ones that raise the temperature. In the grain scale simulations, temperatures are computed as $T = (e - e_{\text{c}})/c_V$.

In Table 1, we provide a set of HMX properties that were taken from the literature. The yield strength was selected as a value between the initial flow stress determined from quasi-static single-crystal measurements⁶³ and the high-rate stresses inferred from weak shock measurements.^{64,65} The grain scale simulations presented in Sec. 3.3 consider various different

Table 1: HMX material properties used in the grain-scale simulations.

Property	Value	Refs.
ρ_0	1.900 g cm ⁻³	16
K_0	15.588 GPa	5,62
K_1	6.6 (unitless)	5,62
μ	7.06 GPa	16
y	0.050 GPa	–
c_V	1.0 J g ⁻¹	16
$T_{\text{m,ref}}$	551 K	25

representations of the melting temperature and liquid-phase shear viscosity to assess their respective contributions to pore collapse heating. In particular, we explore the influence of using a pressure dependent melt temperature $T_{\text{m}}(P)$ and pressure-temperature dependent liquid-phase shear viscosity $\eta(T, P)$ determined from our MD simulations.

3 Results and Discussion

3.1 Melt Line

We determined the melting point $T_{\text{m}}(P)$ of β -HMX at three pressures (1, 3, and 5 GPa) using *NPT*-MD phase coexistence simulations following the approach described in Section 2.1.2. Note that while β -HMX first transforms to the α and/or δ phases before melting at low pressure, it melts directly above ≈ 0.2 GPa. It is also anticipated that α and δ phases will not form from β under shock initiation conditions due to hindered kinetics in relation to the rapid ps-scale shock rise time. Initial tests revealed that surface-initiated melting occurred more quickly at 1 GPa for the (010) crystal face than for the (100) or (001) faces, so we performed all subsequent simulations using the (010) cell (see Figure 2). Temperatures were set in 20 K increments in the intervals $600 \text{ K} \leq T \leq 900 \text{ K}$ for 1 GPa, $900 \text{ K} \leq T \leq 1200 \text{ K}$ for 3 GPa, and $1200 \text{ K} \leq T \leq 1400 \text{ K}$ for 5 GPa, corresponding to 43 independent simulations. Trajectories at each state point were integrated for the lesser of either 10 ns or until the crystal slab completely melted. Crystallization was not observed on the time scales of our

Figure 4: Slopes $\Delta V(t)/\Delta t$ extracted from linear regressions of $V(t)$. Positive values indicate volume expansion that is correlated with melting. Propagated uncertainties are on the order of the symbol size or less.

simulations. Time histories for the cell volume $V(t)$ during coexistence simulations are shown in Figure S1 in the Supporting Information. To quantitatively assess trends in $V(t)$, we performed linear regressions of $V(t)$ for times $t \geq 1$ ns to estimate the rate of change $\Delta V(t)/\Delta t$. The slope parameters from these regressions are plotted in Figure 4.

State points for which the crystal region completely melts are readily identified by a plateau following a steady increase in the volume time history $V(t)$ and have a large positive time rate of change $\Delta V(t)/\Delta t$ that is off the scale in Figure 4. Visual inspection of these trajectories revealed a steady loss of order during the volume expansion phase with the melt progressing from the surface towards the center of the crystal slab. Two particular state points, namely (860 K, 1 GPa) and (1320 K, 5 GPa), partially melted within 10 ns. Longer trajectories integrated for these two states revealed a complete melt within 12 ns. The lowest temperatures for which a complete melt was observed were 860, 1140, and 1320 K for pressures of 1, 3, and 5 GPa, respectively. These three values provide upper bounds for $T_m(P)$ at their respective pressures within the assumptions and approximations of the MD model and simulation approach.

There is a distinct flattening in $\Delta V(t)/\Delta t$ at 1 GPa for temperatures below 840 K. The fact that the slope is slightly positive for (840 K, 1 GPa) may indicate that $T_m(1 \text{ GPa})$ is

Figure 5: Predictions of the melting temperature of HMX. The MD data (red circles) are fitted using the Simon-Glatzel relationship (blue line). Two melt models based on the Lindemann law (which were suggested in previous work¹⁶) are shown as solid and dashed green lines. The melting temperature (from δ -HMX) at ambient pressure²⁵ and the sub-GPa EOS-based predictions of the melting temperature of β -HMX by Myint and Nichols²⁰ are respectively shown as square and cross symbols for comparison.

below 840 K. Despite scatter in the predicted $\Delta V(t)/\Delta t$ at 3 GPa, the consistent negative values for $T \leq 1080$ K indicates that $1080 \text{ K} < T_m(3 \text{ GPa}) < 1140 \text{ K}$. Similar bracketing is evident at 5 GPa, with $1260 \text{ K} < T_m(5 \text{ GPa}) < 1320 \text{ K}$. Brackets on $T_m(P)$ indicate an uncertainty on the order of 5% for 3 and 5 GPa. A reliable lower bound on $T_m(1 \text{ GPa})$ could not be inferred due to the scatter and small magnitudes of the $V(t)$ slopes.

The atomistic predictions of the melting temperature are well-described using the empirical Simon-Glatzel relationship,^{66,67}

$$T_m(P) = T_{m,\text{ref}} \left[1 + \frac{P - P_{\text{ref}}}{a} \right]^{1/c}, \quad (7)$$

where $T_{m,\text{ref}}$ is the melting point at the reference pressure, P_{ref} , and a and c are fitting parameters. Here, we take $T_{m,\text{ref}} = 551 \text{ K}$, $P_{\text{ref}} = 0$.²⁵ Parameters a and c were fit to the upper bounds predicted by MD using least-squares optimization subject to constraints $a > 0$ and $c > 1$, which ensures that $T_m(P)$ increases with pressure but is concave down. This yields

Figure 6: Blocking analysis of viscosity predictions for state points at 1 GPa, 3 GPa, and 5 GPa. Viscosity decreases with temperature in a given panel.

$a = 0.305$ GPa and $c = 3.270$. The fitted $T_m(P)$ is plotted together with the MD predictions in Fig. 5. Also shown are melt models that are linearized in volume (Kraut-Kennedy) and pressure,¹⁶ with proportionality constants selected according to the Lindemann law^{27,28} (a common approach taken when data are absent). Both predictions based on the Lindemann law yield melting temperatures significantly lower than those from the MD simulations. The fitted $T_m(P)$ (Eq. 7) and the EOS of solid-phase HMX (Eq. 5) were used to obtain a density-based polynomial fit of the energy threshold for melting $e_m(\rho)$ (Eq. 6) for the purpose of evaluating the melting criterion in the grain scale simulations.

3.2 Liquid Properties

The temperature- and pressure-dependent equilibrium density, shear viscosity, and self-diffusion coefficients were determined for liquid HMX at 1, 3, and 5 GPa for a number of temperatures in 100 K increments above the melt line. These results are collected in Table S1 in the Supporting Information. Equilibrium densities $\rho(T, P)$ were determined from the last 250 ps of 500 ps NPT simulations. The temperature dependence for $\rho(T, P)$ is approximately linear at a given pressure with the slopes being only very weakly dependent

on pressure. Thermal expansion coefficients

$$\alpha_V = \frac{1}{V^*} \left(\frac{\partial V}{\partial T} \right)_P, \quad (8)$$

were computed at each pressure from weighted linear fits to $V(T)$ where the slope and $T = 0$ K intercept were respectively interpreted as $\partial V/\partial T$ and V^* . This yields $\alpha_V = 1.83 \times 10^{-4}$, 0.97×10^{-4} , and $0.70 \times 10^{-4} \text{ K}^{-1}$ at 1, 3, and 5 GPa, respectively, with propagated uncertainties of $0.04 \times 10^{-4} \text{ K}^{-1}$. Shear viscosity values $\eta(T, P)$ and self-diffusion coefficients $D(T, P)$ were determined following the approaches outlined in Section 2.1.3 from NVT simulations performed at the corresponding equilibrium density. Trajectory lengths t_{sim} needed to converge (or nearly converge) predictions for the viscosity are also listed in Table S1, and ranged from 6 ns to 34 ns depending on the state point.

Convergence characteristics for the shear viscosity predictions are shown as functions of the blocking time t_{block} for each (T, P) state point in Figure 6. It is immediately apparent that the results are highly sensitive to t_{block} and are generally slow to converge. Viscosity values at state points nearest the melt line, namely (900 K, 1 GPa), (1100 K, 3 GPa), and (1300 K, 5 GPa) do not fully converge even with many nanoseconds worth of contributing trajectory. Despite the fact that predictions for $\eta(T, P)$ at these state points are only partially converged, values computed using the largest t_{block} provide meaningful lower bounds. Further above the melt line, the viscosity drops quickly and the rate of convergence generally increases.

The viscosity and self-diffusion are expected to exhibit an Arrhenius temperature dependence following

$$\xi(T, P) = \xi_0 \exp[-E_{a,\xi}/k_B T], \quad (9)$$

for transport coefficient $\xi(T, P)$. Plots of the predicted viscosity values and weighted Arrhenius fits to the data are shown in Figure 7. We included our predicted lower bounds for the viscosity near the melting point in the fitting process as excluding them led to fits that fell below these lower bounds. Activation energies and pre-exponential factors extracted from

Figure 7: Viscosity as a function of temperature at selected pressures. Data points correspond to predicted values and dashed lines to Arrhenius fits. Arrhenius plots of the data and fits are shown in the inset. Fits are extrapolated down to the predicted melting point for the 1, 3, and 5 GPa cases. Results for 0 GPa were reported by Bedrov et al.²⁶

Table 2: Arrhenius parameters for the shear viscosity and self-diffusion with propagated uncertainties.

P (GPa)	η_0 (mPa·s)	$E_{a,\eta}$ (kcal·mol ⁻¹)	$D_0 \times 10^7$ (m ² ·s ⁻¹)	$E_{a,D}$ (kcal·mol ⁻¹)
1	0.067 ± 0.004	-11.6 ± 0.1	1.99 ± 0.07	14.57 ± 0.08
3	0.17 ± 0.02	-13.7 ± 0.3	1.82 ± 0.09	19.4 ± 0.1
5	0.07 ± 0.02	-19.3 ± 0.8	1.9 ± 0.2	22.5 ± 0.3

this analysis of the viscosity, and a similar analysis performed for self-diffusion, are collected in Table 2. We note that while results for self-diffusion are not plotted, the temperature response is clearly Arrhenius at each pressure.

As expected from Arrhenius kinetics, the viscosity is highly dependent on temperature. Moreover, there is a significant increase in the viscosity with increasing pressure. Extrapolating down to the melting point reveals a consistent increase in viscosity at the melting point with increasing pressure. This is matched by a systematic increase in the activation energy magnitude for viscosity $E_{a,\eta}$ with increasing pressure. Both the main panel and inset to Figure 7 indicate a possible deviation from Arrhenius behavior near the melting point, as the fits consistently underestimate the lower bounds obtained directly from MD.

There is an anomalous difference between the present results and those previously re-

Table 3: Parameters for the empirical viscosity function given in Eqs. 10 and 11 fit with $M = 2$.

Parameter	Value
η^o	4.605×10^{-4} mPa·s
P^o	1.190×10^{-1} GPa
T^*	293 K
n_P	1.330
a_0	2.551×10^1
a_1	1.473×10^{-1}
a_2	7.683×10^{-4}

ported by Bedrov et al.²⁶ for the viscosity of liquid HMX at atmospheric pressure (0 GPa). Their estimate for the viscosity very near the 0 GPa melting point ($T = 550$ K, not plotted) is significantly higher (450 mPa·s) than any of our predictions or extrapolations at higher pressures. Combined with our predicted increase in viscosity at the melting point for $P \geq 1$ GPa, this could indicate a possible minimum in a parametric plot of $\eta[T_m(P)]$ vs. P somewhere between 0 GPa and 1 GPa. Another possibility is that our lower-bound estimates may be much lower than the actual viscosity near the melting point. A physical explanation for this anomalous difference could be connected to the complicated solid-solid phase diagram of HMX below 0.2 GPa.²⁰ Two key differences in simulation and analysis protocol might also provide plausible explanations. The MD simulations performed by Bedrov et al. used practically the same force field as the one used here. However, their simulations also employed constraints on all bond-stretching motions, not just the highest frequency (C–H) ones. This almost certainly leads to a stiffer and less conformationally flexible description of the HMX molecule that may increase the viscosity. The other difference lies within the analysis of shear stress autocorrelations, as Bedrov et al. incorporated an empirical contribution from the diagonal stress components to speed up convergence.

We developed an empirical function for the pressure- and temperature-dependent viscosity for practical use in a continuum mechanics code that incorporates an Arrhenius form

with a pressure-dependent activation term. This function is

$$\eta(T, P) = \eta^o \left(1 + \frac{P}{P^o}\right)^{n_P} \exp [T_a(P)/T], \quad (10)$$

with the activation temperature expressed as a polynomial expansion to order M ,

$$T_a(P) = T^* \sum_{n=0}^M a_n \left(\frac{P}{P^o}\right)^n. \quad (11)$$

The fitting parameters in these expressions are η^o , P^o , n_P , and the coefficients a_n , while T^* is an arbitrary constant to yield dimensionless a_n . The factor of unity under n_P in Equation 10 ensures that the viscosity goes to a non-zero value as $P \rightarrow 0$. We simultaneously fit the above two functions to all of our predicted viscosity values along with the results of Bedrov et al. at atmospheric pressure. A polynomial order of $M = 2$ was found to offer the best compromise between accurately reproducing the data while yielding a robust function without anomalous extrema. The fitted coefficients are collected in Table 3. Plots of $\eta(T, P)$ and additional comparisons for fits with different polynomial orders are provided in Figure S2 in the Supporting Information.⁶¹

3.3 Grain Scale Simulations

3.3.1 Baseline Material Model

Our baseline model for HMX incorporates a constant yield strength ($y = 0.050$ GPa) that governs plastic flow of the solid phase, a constant melt temperature ($T_m = T_{m,\text{ref}} = 551$ K), and an inviscid liquid phase ($\eta = 0$). Snapshots of pressure and temperature fields obtained from pore collapse simulations involving supported and unsupported shocks are shown in Figure 8. These simulations consider a low-amplitude shock (3 GPa) generated by a time-dependent boundary pressure (see Section 2.2). In the supported case (Figure 8(a)), the leading edge of the shock reaches the pore at $t = 2.1$ ns. At 2.4 ns, a release wave emanates

radially from the pore as it begins to collapse. By 2.7 ns, the pore is pinched completely shut, which generates a higher-amplitude pulse that moves radially away from the initial pore. At later times, the pressure in the vicinity of the initial pore tends to equilibrate. As shown in the Figure, a small low-pressure region develops in the wake of the shock and persists for some time; this is created by localized vortical flow, which puts material at the eye of the vortex into tension ($\rho/\rho_0 < 1, p < 0$). In the unsupported case (Figure 8(b)), a release wave trails behind the leading edge of the shock by a few micrometers and at later times ($t > 3.0$ ns) the pore gradually reopens.

Although not clearly depicted here, small pools of liquid-HMX form in the pore collapse region. The temperature rise is due to solid-phase plastic work and dissipative q -work as thermoelastic coupling is neglected and the liquid-phase is inviscid. Thus, the temperature rise is limited to $\approx T_{\text{m,ref}}$ as the material’s flow resistance (strength) is lost upon melting. Detailed descriptions of pore collapse, jetting, dynamic fracture, and dissipation mechanisms are provided elsewhere, in particular for cases involving supported shocks.^{2,5,8,9,23,65,68–71} Although many have considered pore collapse mechanics under supported shock wave loading, we are unaware of any previous work that considers the attendant heating associated with a short compressive pulse followed by release.

3.3.2 Comparison of Melting Temperature Models

We first consider the heating effects associated with different melting models. Here, the baseline model ($T_{\text{m}} = T_{\text{m,ref}}$) is compared to a model with a pressure-dependent melting point $T_{\text{m}}(P)$ obtained by fitting the Simon-Glatzel relation to our MD predictions (Eq. 7). Figure 9 shows results obtained from these two melting models for supported and unsupported shocks with either a 3 or 10 GPa pressure drive. Plotted here are time histories of (i) the relative melt mass and (ii) the volume-averaged pressure in a sample volume around the pore. The melt mass is normalized by the *pore mass* (i.e., the equivalent mass of solid HMX at ambient conditions that would fit inside the initial pore) and the sample volume is the Lagrangian

Figure 8: Pressure and temperature fields generated by (a) supported and (b) unsupported shocks (3 GPa) using the baseline material model. The fields are shown for a small window around the pore (the full slab of HMX is much larger) with the shock wave moving from left to right. The time origin corresponds to the start of the pressure drive.

volume that falls within 5 radii of the initial pore center. Small oscillations in the melt mass are due to the mesh discretization, as a mesh element is considered as either fully solid or fully melted. Therefore, advection of mass through the mesh can change the total amount of melted material in small discrete increments.

Figure 9: Extent of melting in simulations of supported and unsupported shocks at 3 and 10 GPa. Vertical dashed lines indicate times at which the histograms shown in Figure 10 were computed.

Inspecting first the responses at 3 GPa in the top row, the supported shock shown in panel (a) yields melting for the case of $T_m = T_{m,\text{ref}}$, but no melting whatsoever for $T_m(P)$. In the latter case, there is not enough plastic work done in the vicinity of the pore to reach the elevated melting temperature. However, when the shock pressure is released as in panel (b), both models predict melting. In fact, the model with $T_m(P)$ exhibits more melting because more plastic work can be done under pressure prior to the loss of strength. Responses at 10 GPa are shown in the bottom row. The supported 10 GPa shock shown in panel (c) produces significant amounts of melted HMX if $T_m = T_{m,\text{ref}}$, but melting is completely suppressed with $T_m(P)$. If the 10 GPa shock is unsupported as in panel (d), the case with

Figure 10: Temperature histograms for supported shocks at (a) 3 GPa and (b) 10 GPa. The solid-phase bin midpoints are connected by solid lines; the liquid-phase bin midpoints are marked by filled symbols.

$T_m(P)$ again displays melting as the pressure is released. In comparison to the weaker shock, more material is melted with $T_m = T_{m,\text{ref}}$. The step-like production of melted material in the case of $T_m = T_{m,\text{ref}}$ is largely due to q -heating associated with the impact of a strong jet on the downstream side of the pore.

Figure 10 shows temperature histograms that were computed for the Lagrangian sample regions in the 3- and 10-GPa supported shock cases. The solid and liquid phases were treated separately and the histograms were binned by relative mass, where the normalizing mass is the pore mass. The times at which these histograms were computed are indicated in Fig.9.

At 3 GPa, the model with a constant melt temperature yields a distribution that extends up to approximately $T_{m,\text{ref}}$. The melt mass stays at approximately this temperature because the liquid phase is strengthless and inviscid ($\eta = 0$). Some of the liquid is heated to slightly above $T_{m,\text{ref}}$ *via* dissipative q -work. The model with $T_m(P)$ does not exhibit melting, but small amounts of solid reach higher temperatures mostly due to increased amounts of strength-based plastic work. At 10 GPa, the model with a constant melt temperature exhibits a liquid-phase distribution that extends well beyond $T_{m,\text{ref}}$, which is contrary to the physical expectation. This is again a q -heating effect, which is substantially more pronounced for the 10 GPa shock, even for the fine mesh used here. Although the artificial viscosity may represent some unresolved physical process, the lack of specificity for this amount of dissi-

pation is unsettling. This perhaps highlights the uncertainty of temperature calculations for strong shocks in heterogeneous materials. The case with $T_m(P)$ exhibits no melting, but has a solid-phase tail that extends to considerably higher temperatures. This high-temperature tail results from a combination of solid-phase plastic work and dissipative q -work.

Accurately capturing the pressure-dependence of the melting point thus appears to be an important consideration. In supported shocks, the pressure-dependence of $T_m(P)$ suppresses melting in the pore collapse region and yields a temperature distribution that extends to significantly higher values. Depending on the kinetics of solid- and liquid-phase decomposition reactions, such differences may have an impact on predictions of explosive behavior.

3.3.3 Comparison of Liquid Viscosity Models

We now consider heating effects associated with different models of the liquid-phase shear viscosity. In these simulations, we use our fitted pressure-dependent melting model, $T_m(P)$, and compare cases with (i) $\eta = 0$, (ii) a temperature-dependent shear viscosity $\eta(T)$ determined at 1 atm in previous work²⁶ (see Figure 7, 0 GPa curve), and (iii) the temperature- and pressure-dependent shear viscosity $\eta(T, P)$ that was determined in the current work (Eq. 10). Figure 11 shows time histories of the melting extent predicted using these three viscosity models for unsupported shocks at 3 and 10 GPa along with temperature histograms. The analysis was identical to that used for Figures 9 and 10.

For the 3 GPa unsupported shock shown in the top row of Figure 10, both viscous-liquid models exhibit more melting than the inviscid model (see panel (a)) and reach higher temperatures (see panel (b)). While higher temperatures in the liquid phase were anticipated, the increased amount of melting in these locally adiabatic simulations was not. The increased level of melting is caused by a drag effect in the solid-liquid interaction. As the viscous liquid in the hot spot flows over the surrounding solid, it exerts a drag force that drives additional plastic work, which melts more material. The pressure-dependence of the shear viscosity does not have a significant effect for the weak shock case, as the material around the pore

Figure 11: Effects of liquid-phase shear viscosity on pore collapse heating and melting in unsupported shocks at 3 GPa (a, b) and 10 GPa (c, d). In the histograms, the solid-phase bin midpoints are connected by solid lines; the liquid-phase bin midpoints are marked by filled symbols.

melts at relatively low pressures. From panel (a), melting starts at a sample-average pressure of ≈ 0.5 GPa and progresses as the pressure is further reduced.

For the 10 GPa unsupported shock shown in the bottom row of Figure 10, the pressure-dependence of the shear viscosity now increases the amount of dissipative heating. As can be seen in panel (c), there is a similar drag effect, where more material is melted if the liquid phase has a higher shear viscosity. Perhaps more interesting is the effect on the temperature distribution shown in panel (d). Since the liquid viscosity increases with pressure and a significant quantity of material around the pore melts with $P > 0$, there is more viscous dissipative work for the case of $\eta(T, P)$ in comparison to the others. This serves to push the high-temperature tail of the distribution to well above 1000 K. In the case of $\eta(T, P)$, the amount of liquid hotter than the maximum temperature of the $\eta(T)$ distribution is equal to

Figure 12: Fields predicted around a partially collapsed pore for an unsupported 10 GPa shock at late time (well after the pressure has been released). These results were obtained using our most sophisticated model ($T_m(P)$ and $\eta(T, P)$). The snapshots illustrate (a) the solid, liquid, and gas phase regions on the mesh and the velocity vector field, (b) the Mises stress field, and (c) the temperature field with pressure contours superposed. Note that the simulations employ a symmetry plane, so the snapshots correspond to the top half of the pore collapse region.

$\approx 15\%$ of the pore mass. The pressure-dependence of the viscosity makes a larger difference in the 10 GPa case because the material melts at higher pressures during the release. From panel (c), melting starts at a sample-average pressure of ≈ 5 GPa (compared to 0.5 GPa for the 3 GPa shock) and higher pressures are experienced during the growth of the melt pool.

An enlarged view of selected field variables is shown in Fig. 12 for the stronger unsupported shock (10 GPa). These fields were computed using our most sophisticated material model ($T_m(P)$ and $\eta(T, P)$). These snapshots correspond to the same instant in time ($t=4.2$ ns) as the histogram plotted in Fig. 11(d). At this point, the compressive pulse has moved well past the pore and the pressure is mostly released (see Fig. 8(b)).

The melt pool formed in the pore collapse region is shown as dark grey in panel (a). The superposed velocity vector field reveals circulation of molten HMX about the air pocket that remains open. Indeed, parts of the melt pool spin around as it moves in the shock direction.

Deviatoric stress magnitudes are captured by the Mises effective stress $\sqrt{\frac{3}{2}\mathbf{s}:\mathbf{s}}$ in panel (b). The Mises stress is discontinuous across the solid/liquid boundary because the solid flow stress is limited to $y = 0.050$ GPa, whereas the deviatoric stress in the liquid depends on the shearing rate and shear viscosity. Although the pressure is approximately zero at the air/liquid interface, the pressure tends to increase with distance from the surviving air pocket (see the pressure contours in panel (c)). These modest pressures are generated by inertial forces associated with the vortical flow of the liquid around the air pocket. The finite shearing of the liquid layer and the pressure sensitivity of the shear viscosity then lead to substantial deviatoric stresses in the liquid phase, especially near the solid/liquid interface. This combination of liquid viscous dissipation, solid plastic dissipation, and q -dissipation produces a temperature field that is highest near the air pocket. We note that the vortical flow observed here may be more relevant to elongated crystal defects (similar to the cylindrical cavity studied here) as compared to more compact defects such as spherical cavities. However, the increased level of shock focusing in quasi-spherical pore collapse may give rise to greater levels of turbulence with pressure-enhanced viscous dissipation.

4 Conclusions

Grain scale models of solid high explosives are rapidly increasing in their complexity, with various efforts seeking to address (anisotropic) elastic and plastic responses, phase transformations, transport, and chemistry. However, parameters for many of these physics terms are not well characterized and thus have only reasonable placeholder values that are frequently treated as constants. Here we examine two aspects of HMX response: the melting point and liquid shear viscosity, which are expected to influence hot spot formation at defect sites during shock compression. We place these terms on firmer physical grounds by connecting with all-atom molecular dynamics modeling to predict the pressure-dependent melting point $T_m(P)$ and the temperature- and pressure-dependent shear viscosity $\eta(T, P)$ up to 5 GPa.

A phase coexistence approach was taken to bracket $T_m(P)$ and equilibrium simulations were combined with the Green-Kubo relation to obtain $\eta(T, P)$. Practically usable functions for these parameters are provided that can be readily incorporated into grain scale models and that smoothly extrapolate to higher state points.

Starting from a simplified grain scale model, we systematically increase the complexity of treatments for T_m and η to isolate specific influences on heating during shock-induced pore collapse. Two shock strengths are considered (3 and 10 GPa) and we explore effects that manifest for both supported and unsupported shocks. The behavior under pressure release has not been well-studied, but is anticipated to be relevant to modern ultrafast experiments, where compressive pulses are typically limited to < 1 ns.²⁴ We find that using a physics-based $T_m(P)$ completely suppresses melting for supported shocks, which is in contrast to the significant melting exhibited when T_m is treated as a constant equal to its value at atmospheric pressure. Suppressed melting leads to significantly hotter hot spots as more plastic work is done to the solid. Unsupported shocks are predicted to produce sizable melt pools even with a physics-based $T_m(P)$. Including a temperature- and pressure-dependent liquid viscosity is shown to have a significant effect on the response for unsupported shocks. Higher viscosity values reached under even modest pressures lead to (i) increased melting due to a drag effect in the liquid/solid interaction, and (ii) peak temperatures that are higher by hundreds of Kelvin due to dissipative work in the liquid phase.

Our results provide a baseline for constructing more advanced material descriptions and for understanding and interpreting predictions from these models. In particular, the strength model employed here is quite simple and more sophisticated treatments (which account for anisotropic elastic/plastic responses and detailed deformation mechanisms) could be pursued in future work. For example, the material surrounding a pore could become disordered through other atomic-scale mechanisms, which are more closely related to dislocation locking and lattice breakdown/instability³⁷ rather than plastic-work-based heating. Accurately capturing the extent of melting and the respective temperatures of each phase could also

plausibly influence the decomposition rate. The complicated multiphysics couplings identified here with our comparatively simple model point to an increased need for a systematic approach to grain scale model construction.

Acknowledgement

The authors thank Nithin Mathew and Tommy Sewell for many useful discussions. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 (LLNL-JRNL-xxxxxxx).

Supporting Information Available

The following files are available free of charge.

- Figures S1-S3, Table S1, and extra details concerning the melt line calculation, fitted shear viscosity function, and mesh sensitivity analysis (PDF)

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Graphical TOC Entry

Supporting Information: Sensitivity of pore collapse heating to the melting temperature and liquid-phase shear viscosity of HMX

Matthew P. Kroonblawd^{*,†} and Ryan A. Austin[‡]

[†]*Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory,
Livermore, CA 94550, United States*

[‡]*Engineering Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94550,
United States*

E-mail: kroonblawd1@llnl.gov

Figure S1: Time histories of the simulation cell volume during NPT coexistence simulations at 1, 3, and 5 GPa. Curve colors denote simulation temperature, repeat cyclically every 100 K, and are respectively teal, orange, purple, cyan, and black for temperature values ending in 00, 20, 40, 60, and 80 K. Simulations above or near the melt point are indicated by color-coded temperature labels.

1 Melt Line

Time histories of the cell volume $V(t)$ during NPT phase coexistence simulations are shown in Figure S1. Increases in $V(t)$ indicate melting and plateaus indicate that the system has reached a completely melted state. Comparison of the three panels reveals a distinct change in $V(t)$ responses with increasing pressure. At 1 GPa, most of the volume curves for temperatures below 860 K exhibit no significant positive or negative slope. This is in contrast to the response at 3 GPa, where two simulations at 1100 K and 1120 K have negligible slope and simulations with $T < 1100$ K have distinct negative slopes. A similar split between negligible and negative slope is seen at 5 GPa for $T < 1260$ K. One possibility is that the melt point lies between the temperatures that bracket a transition from negligible to negative slope in $V(t)$.

Table S1: Liquid-phase HMX properties.

	T (K)	t_{sim} (ns)	ρ (kg·m ⁻³)	η (mPa·s)	D (Å ² ·ns ⁻¹)
$P = 1$ GPa	900	20	1720 ± 5	56 ± 4	5.31 ± 0.09
	1000	25	1692 ± 5	22.4 ± 0.4	13.2 ± 0.2
	1100	20	1665 ± 6	13.2 ± 0.6	26.6 ± 0.4
	1200	20	1640 ± 6	8.9 ± 0.2	46.4 ± 0.7
	1300	20	1615 ± 6	5.7 ± 0.4	73 ± 1
	1400	20	1594 ± 7	4.7 ± 0.3	105 ± 1
	1500	15	1571 ± 6	3.3 ± 0.2	140 ± 3
	1600	10	1549 ± 6	2.56 ± 0.06	180 ± 5
$P = 3$ GPa	1100	20	1908 ± 4	101 ± 7	2.40 ± 0.04
	1200	20	1890 ± 4	42 ± 2	5.24 ± 0.08
	1300	20	1873 ± 4	34 ± 1	10.3 ± 0.2
	1400	20	1857 ± 4	23 ± 1	16.8 ± 0.3
	1500	20	1841 ± 4	21.3 ± 0.5	26.5 ± 0.4
	1600	18	1827 ± 4	12.4 ± 0.6	41.0 ± 0.7
	1700	10	1812 ± 5	7.7 ± 0.2	51 ± 2
$P = 5$ GPa	1300	34	2017 ± 3	124 ± 5	3.10 ± 0.03
	1400	28	2003 ± 4	70 ± 2	6.29 ± 0.07
	1500	18	1990 ± 4	38 ± 3	9.8 ± 0.2
	1600	12	1977 ± 4	31 ± 2	15.8 ± 0.4
	1700	6	1965 ± 4	22 ± 2	23 ± 1

2 Liquid Properties

Values reported in Table S1 correspond to the viscosity value obtained with the largest t_{block} plotted for each state point in Figure 6 of the main article.

Figure S2: Liquid shear viscosity functions $\eta(T, P)$ of the form given in Equations 10 and 11 of the main article with different polynomial expansion orders M (columns) that were obtained from global fits to the MD data at 0, 1, 3, and 5 GPa. Isobars shown in the top row include the MD data (points) and the fitted $\eta(T, P)$ at the corresponding pressures (lines). Surfaces of $\eta(T, P)$ shown in the bottom row include the MD-predicted melting point $T_m(P)$. A polynomial order of $M = 2$ was found to yield the best compromise between reducing the root-mean-squared error with respect to the MD data while generating a $\eta(T, P)$ function that did not exhibit aphysical features.

Figure S3: The sensitivity of simulated melting extent and temperature distribution in the pore collapse region to the mesh size.

3 Mesh Sensitivity Analysis

Grain-scale simulations of pore collapse were carried out to assess the mesh-size dependence of the results of interest. These simulations considered a pressure pulse of 10 GPa (unsupported), the MD-predicted melt curve $T_m(P)$, the liquid-phase shear viscosity $\eta(T, P)$, and mesh sizes of 40, 20, and 10 nm. In Figure S3, we plot the extent of melting and the temperature distribution around the pore for different mesh sizes. Although the finite element formulation employed here never converges in an absolute sense, the results obtained using a mesh size of 20 nm are sufficient for our purposes.

Acknowledgement

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 (LLNL-JRNL-809399-DRAFT).