

Temperature-dependent shear viscosity coefficient of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX): A molecular dynamics simulation study

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Equilibrium molecular dynamics methods were used in conjunction with linear response theory and a recently published potential-energy surface [J. Phys. Chem. B **103**, 3570 (1999)] to compute the liquid shear viscosity and self-diffusion coefficient of the high explosive HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) over the temperature domain 550–800 K. Predicted values of the shear viscosity range from 0.0055 Pa *s at the highest temperature studied up to 0.45 Pa *s for temperatures near the melting point. The results, which represent the first publication of the shear viscosity of HMX, are found to be described by an Arrhenius rate law over the entire temperature domain studied. The apparent activation energy for the shear viscosity is found to scale with the heat of vaporization in a fashion consistent with those for a wide variety of simple nonmetallic liquids. The self-diffusion coefficient, which requires significantly shorter trajectories than the shear viscosity for accurate calculation, also exhibits an Arrhenius temperature dependence over the simulated temperature domain. This has potentially important implications for predictions of the shear viscosity at temperatures near the melting point. © 2000 American Institute of Physics. [S0021-9606(00)50613-8]

INTRODUCTION

Plastic-bonded explosives (PBXs) and propellants are highly filled composite materials comprised of grains of a high explosive (HE) held together by a polymeric binder. There has been an increasing effort in recent years to understand and predict the macroscopic behavior of these composites on the basis of fundamental thermophysical and mechanical properties of, and interactions among, the constituents. This poses a severe challenge due to both the large domain of spatial and temporal scales that must be spanned and the distinct classes of materials that must be described within a single modeling framework.

One approach to this problem is the use of mesomechanical simulations that resolve the composite at the level of individual grains suspended in a binder,¹ thereby providing, in principle, a bridge between molecular-level information and the continuum constitutive laws required by large-scale engineering codes. Another important use for mesomechanical modeling in the context of high explosives is as a tool to clarify ignition sensitivity and to understand the effect of hot spots on HE burn (e.g., the efficacy of viscous heating in melt zones as a mechanism for initiation under weak shock loading). Although the input to such models would ideally include information about the size distribution of explosive grains along with various thermophysical and mechanical properties of the constituents, much of this

information is unavailable for the materials of interest. Moreover, for explosives, the material reacts at sufficiently short time scales as to make experimental determination of some of these material properties extremely difficult, if not impossible. In such cases, recourse is usually made to either a “best guess” strategy or the use of a more approximate model formulation. Increasingly, however, a judicious application of molecular simulation tools is emerging as a viable source for some of this information.²

In this paper we present calculations of the atmospheric pressure shear viscosity for liquid HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) as a function of temperature $550\text{ K} \leq T \leq 800\text{ K}$. HMX is the energetic constituent in several high-performance military PBX formulations, e.g., PBX-9501.³ The predictions are based on the application of linear response theory to multianosecond molecular dynamics trajectories obtained using a recently published quantum chemistry based force field for HMX.⁴ The lower-temperature limit of 550 K is close to the melting point of HMX.⁵ The shear viscosity has been identified as one of the important thermophysical parameters in certain models of weak shock initiation.⁶ However, it has yet to be measured for HMX, nor do there appear to be any preceding theoretical or computational predictions in the literature. Thus, the present predictions of the temperature-dependent shear viscosity of HMX should serve as a useful constraint on this important yet previously undetermined parameter in mesomechanics models.

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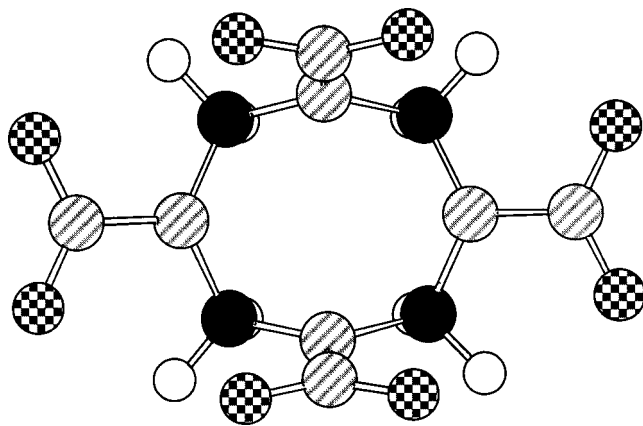


FIG. 1. Conformation of the HMX molecule in the α form. Solid atoms are carbons, cross-hatched are nitrogens, patterned are oxygens.

FORCE FIELD AND SIMULATION METHODOLOGY

In previous work⁴ we developed a classical, explicit-atom force field for flexible HMX molecules using results of high-level quantum chemistry calculations for conformational energies and geometries of gas-phase HMX (one of the optimal geometries is illustrated in Fig. 1) and other nitramine compounds [1,3-dimethyl-1,3-dinitro methyl diamine (DDMD)⁴ and dimethylnitramine (DMNA)⁷]. The lack of experimental data for liquid HMX precludes direct validation of the developed force field. However, good agreement between experimental results and simulation predictions was obtained for thermophysical properties of gaseous and liquid DMNA.⁷

Molecular dynamics (MD) simulations were carried out at six different temperatures (550–800 K, at 50 K intervals) and atmospheric pressure. Isothermal-isobaric (NpT) simulations were performed for 4 ns in order to establish the equilibrium density, using the final configuration from a higher-temperature equilibration as the starting point for the next lower temperature. Isothermal-isochoric (NVT) production runs of 10–30 ns duration (depending upon temperature) were performed using the Nosé–Hoover thermostat⁸ with an integration step size of 1.0 fs. Periodic boundary conditions were employed. The standard Shake algorithm⁹ was used to constrain bond lengths. The Ewald summation method¹⁰ was employed to evaluate long-range electrostatic interactions. All simulation cells contained 50 HMX molecules.

VISCOSITY CALCULATION

The shear viscosity η can be calculated using equilibrium fluctuations of the off-diagonal components ($\sigma_{\alpha\beta}$) of the stress tensor.¹⁰ It was shown by Daivis and Evans¹¹ that, for an isotropic system, the convergence of viscosity calculations can be improved by including equilibrium fluctuations of diagonal components of the stress tensor. In this case the generalized Green–Kubo formula is applied to the symmetrized traceless portion ($P_{\alpha\beta}$) of the stress tensor with appropriate weight factors for diagonal and off-diagonal elements:

$$\eta = \frac{V}{10k_B T} \int_0^\infty \sum_\alpha \sum_\beta q_{\alpha\beta} \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt, \quad (1)$$

where V and T are volume and temperature of the system, k_B is the Boltzmann constant, $q_{\alpha\beta}$ is a weight factor ($q_{\alpha\beta} = 1$ if $\alpha \neq \beta$, $q_{\alpha\beta} = \frac{4}{3}$ if $\alpha = \beta$), and $P_{\alpha\beta}$ is defined as

$$P_{\alpha\beta} = (\sigma_{\alpha\beta} + \sigma_{\beta\alpha})/2 - \frac{\delta_{\alpha\beta}}{3} \left(\sum_\gamma \sigma_{\gamma\gamma} \right), \quad (2)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta.

Einstein relations are often used in place of the Green–Kubo expression for the calculation of transport coefficients. Haile¹² has shown that in a system with periodic boundary conditions the viscosity cannot be calculated using the conventional Einstein formula,¹⁰ which involves atomic coordinates and velocities. However, it can be employed after slight modifications,^{12,13} yielding

$$\begin{aligned} \eta &= \lim_{t \rightarrow \infty} \frac{V}{20k_B T t} \left\langle \sum_\alpha \sum_\beta q_{\alpha\beta} [A_{\alpha\beta}(t) - A_{\alpha\beta}(0)]^2 \right\rangle \\ &= \lim_{t \rightarrow \infty} \frac{V}{20k_B T t} \left\langle \sum_\alpha \sum_\beta q_{\alpha\beta} [\Delta A_{\alpha\beta}(t)]^2 \right\rangle, \end{aligned} \quad (3)$$

where

$$\Delta A_{\alpha\beta}(t) = \int_0^t P_{\alpha\beta}(t') dt'. \quad (4)$$

It was shown by Mondello and Grest¹³ that Eqs. (3) and (4) give the same results as the Green–Kubo formulation for MD simulations of short-chain alkanes. We considered both forms [Eqs. (1) and (3)] for the shear viscosity of HMX and found the results to differ by two percent or less. Thus, all results reported below were obtained using the Einstein relations defined in Eqs. (3) and (4). In addition, the self-diffusion coefficient D was computed using the standard Einstein relationship¹⁰

$$D = \lim_{t \rightarrow \infty} \frac{\langle [R_{\text{cm}}(t) - R_{\text{cm}}(0)]^2 \rangle}{6t}, \quad (5)$$

where $R_{\text{cm}}(t) - R_{\text{cm}}(0)$ is the time-dependent center-of-mass displacement of a given molecule.

The choices of integration time step and sampling frequency are important for obtaining accurate results from MD simulations. Previous experience involving simulations of explicit-atom systems (e.g., DMNA,⁷ ethers,¹⁴ and polystyrene¹⁵) with bond constraints has shown that a 1 fs integration time step is sufficiently short to yield accurate integration of the equations of motion. In order to determine how often the stress tensor should be sampled during production runs to yield reliable calculations of the shear viscosity we performed a short (2 ns) simulation at high temperature (750 K), recording the stress tensor at every time step (1 fs). The time history of one of the elements of the stress tensor is shown in Fig. 2, where it is plotted at inter-

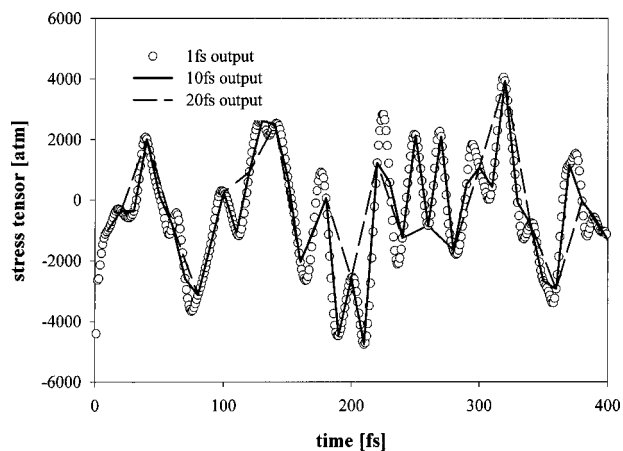


FIG. 2. Representation of the stress tensor evolution using different output frequencies for one of the off-diagonal components at 750 K.

vals of 1, 10, and 20 fs. (Note that a time integration step of 1.0 fs is used in each case; only the frequency of stress tensor output is varied). As would be expected for an atomic representation,¹³ the stress tensor exhibits strong oscillatory behavior. It is clear that a sampling frequency of 20 fs results in loss of information, whereas a 10 fs time step captures all but the fastest oscillations. In order to further ensure that a 10 fs sampling interval does not influence the viscosity calculations, we computed the apparent shear viscosity versus time [Eq. (3)],¹⁶ sampling the stress tensor at intervals of 1, 10, 20, and 40 fs from the 2 ns run at 750 K. The results, which are shown in Fig. 3, indicate a nearly imperceptible difference between a sampling interval of 10 fs versus 1 fs. It is interesting to note that, although sampling the stress tensor at 20 fs intervals led to significant differences in the apparent time history (Fig. 2), the resulting shear viscosity is only weakly affected. We tentatively attribute this to cancellation of errors during integration in Eq. (4). Based on the preceding considerations, the stress tensor was sampled at an interval of 10 fs in all simulations. The center-of-mass positions of the molecules were recorded at intervals of 1 ps for use in calculating the self-diffusion coefficients.

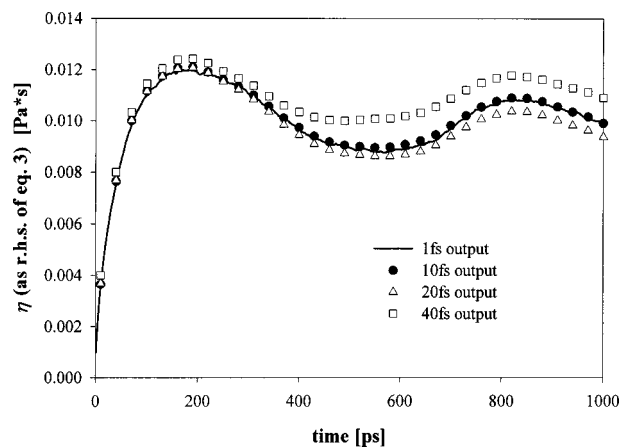


FIG. 3. Influence of the stress tensor output frequency on the rhs of Eq. (3) as a function of time at 750 K.

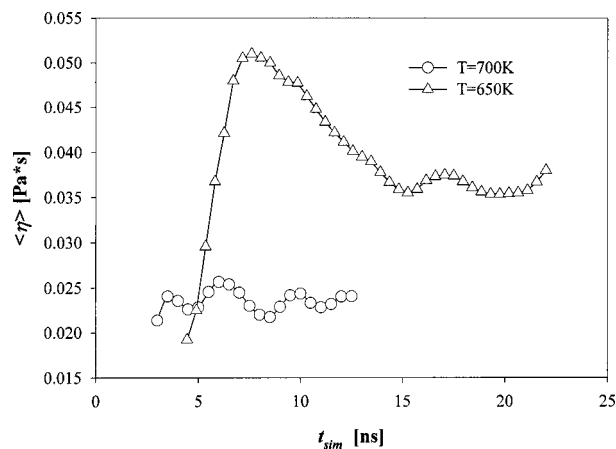


FIG. 4. Average viscosity (see the text for a definition) obtained from MD simulation as a function of trajectory length for 650 and 700 K.

The length of the trajectory (t_{sim}) required for the calculation of a given property is another important, but difficult to estimate, parameter in MD simulations. In order to obtain accurate transport coefficients from equilibrium MD methods, the length of the trajectory should be much longer than any relevant characteristic relaxation times of the system. Mondello and Grest¹³ showed that for *n*-alkanes the rotational diffusion time (τ_R) is the longest relevant relaxation time for viscosity calculations. Dysthe *et al.*¹⁷ pointed out that other relaxation times could be important for small molecules, e.g., the mean time for a molecule to move one molecular diameter (τ_D). HMX does not resemble a long polymeric chain, but neither can it be considered a “simple” molecule. Thus, it is difficult to predict which of the characteristic times will most closely correlate with the shear viscosity for liquid HMX; and hence which will determine the length of the simulation required to obtain accurate values of the shear viscosity. However, one can define a viscosity relaxation time τ_η as¹⁷

$$\eta(\tau_\eta) = (1 - e^{-1}) \eta(t_{\text{sim}} \rightarrow \infty). \quad (6)$$

For very long trajectories (minimal statistical error), we expect the rhs. of Eq. (3) to be time dependent for times $t \sim \tau_\eta$ and independent of time for $t \gg \tau_\eta$. Hence, τ_η is a characteristic time for the approach of the rhs. of Eq. (3) to a constant value, and simulations must be much longer than τ_η in order to obtain reliable values for the shear viscosity.

While the criteria $t_{\text{sim}} \gg \tau_\eta$, $t_{\text{sim}} \gg \tau_D$, and $t_{\text{sim}} \gg \tau_R$ provide guidance in determining the length of the simulation trajectories t_{sim} required to obtain accurate values of the shear viscosity, in practice, we used the following ultimate criterion in determining when to discontinue the simulation for a particular temperature. Using Eq. (3), we calculate the viscosity by averaging values of the rhs of Eq. (3) for $10\tau_\eta < t < t_{\text{sim}}/2$ as a function of the length of the simulation, t_{sim} . In Fig. 4 we show the dependence of the average viscosity as function of trajectory length for 650 and 700 K. It can be seen that, after some t_{min} additional simulation time results in minor fluctuations (less than 10% from some mean value) of the average viscosity. We define t_{min} as the trajectory length such that (1) the time-dependent average viscos-

TABLE I. Relaxation times and transport coefficients of liquid HMX obtained from MD simulations.

T (K)	t_{\min} (ns)	t_{sim} (ns)	τ_{η} (ps)	τ_R (ps)	τ_D (ps)	ρ (kg m ⁻³)	$D \times 10^9$ (m ² s ⁻¹)	η (Pa s)
550		20	1250	310.0	1664	1650.9	0.006	0.450
600	25.0	30	520	70.0	675	1614.4	0.018	0.120
650	17.5	20	270	33.6	304	1586.9	0.040	0.040
700	8.0	15	120	20.7	129	1554.5	0.094	0.022
750	6.0	15	40	12.9	54	1520.1	0.225	0.010
800	4.0	10	20	9.5	37	1488.2	0.325	0.0055

ity (Fig. 4) has at least two maxima in the interval $10\tau_{\eta} < t < t_{\min}$ and (2) after t_{\min} further simulation time does not change the average viscosity by more than 10%. Therefore, for all temperatures except 550 K, our conservative estimate of the uncertainty in the shear viscosity is $\pm 10\%$ or less. At 550 K, the simulation was too short to allow estimation of uncertainty in the viscosity.

RESULTS AND DISCUSSION

Characteristics relaxation times

In Table I we report, for each temperature, t_{\min} , t_{sim} , and τ_{η} , as defined in Eq. (6); the rotational diffusion correlation time, obtained by fitting the ‘‘end-to-end’’ vector autocorrelation function [$T_1 = \langle \cos \theta(t) \rangle$] for nitro group nitrogen atoms on opposite sides of the molecule to a simple exponential decay law,

$$T_1 = \exp\left(-\frac{t}{2\tau_R}\right); \quad (7)$$

and τ_D calculated as

$$\tau_D = \frac{\langle R_g^2 \rangle}{6D}, \quad (8)$$

where D is the HMX center-of-mass self-diffusion coefficient determined from Eq. (5) and $\langle R_g^2 \rangle$ is the average squared radius of gyration (7.3 Å²). With the exception of 550 K, each trajectory was at least 45 times longer than the largest relaxation time at a given temperature. The system at 550 K would have required upward of 70 ns by these criteria, which is beyond the practical limits imposed by our computational resources. Therefore we stopped the simulations at this temperature after 20 ns, which is sufficient to accurately calculate the self-diffusion coefficient.

Viscosity and self-diffusion

The atmospheric pressure, temperature-dependent shear viscosity and self-diffusion coefficients for liquid HMX in the temperature domain 550 K $\leq T \leq$ 800 K are summarized in Table I. We also include the equilibrium density for each temperature. The shear viscosity is predicted to range from 0.0055 Pa*s at 800 K up to 0.45 Pa*s at 550 K.

The temperature dependence of the shear viscosity and self-diffusion coefficients are well described by Arrhenius expressions, as shown in Fig. 5. There is no evidence for the onset of nonArrhenius behavior over the temperature domain considered, which extends down to near the melting point of

HMX. The calculated apparent activation energies are 14.4 and 14.5 kcal/mol for self-diffusion and shear viscosity, respectively. The Eyring rate expression for dense fluids¹⁸ indicates that the viscosity activation energy is proportional to the energy of vaporization. For more than 100 substances, including associated liquids, the simple relation ($\Delta E_{\text{vap}} = n\Delta E_{\text{vis}}$, where $2 \leq n \leq 5$) holds.¹⁸ Assuming that the energy of vaporization is approximately equal to the cohesive energy, it is possible to compare ΔE_{vap} and ΔE_{vis} determined directly from MD simulations. We obtain $\Delta E_{\text{vap}} = 36.3$ kcal/mol from simulation (800 K), yielding a ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}} = 2.5$. The large value for the viscosity activation energy is consistent with the high energy of vaporization of HMX.

Correlation of viscosity with diffusion and rotation of HMX

In this section, based on the MD simulation results, we examine correlations between the temperature dependence of viscosity with that of other dynamic properties, in particular self-diffusion and rotational diffusion. There are many empirical, semiempirical, and theoretically based relations to describe the correlation between these thermophysical properties. Most of these correlations can be represented as

$$\eta_D = K \frac{\rho T}{D} \quad (9)$$

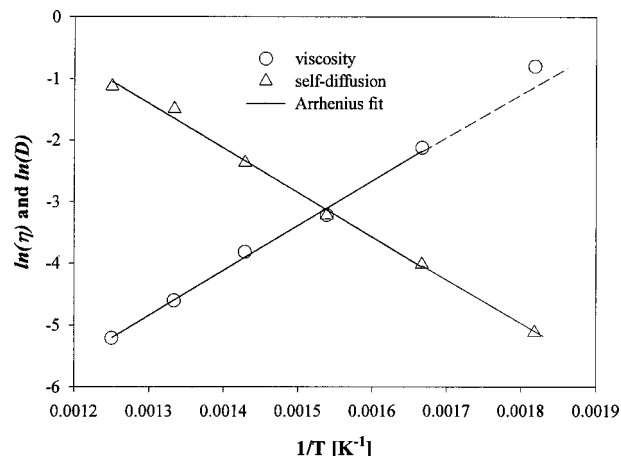


FIG. 5. Arrhenius fit (solid lines) of viscosity in the temperature domain 600–800 K and self-diffusion in the temperature domain 550–800 K obtained from MD simulations (symbols) and extrapolation of viscosity fit to 550 K (dashed line).

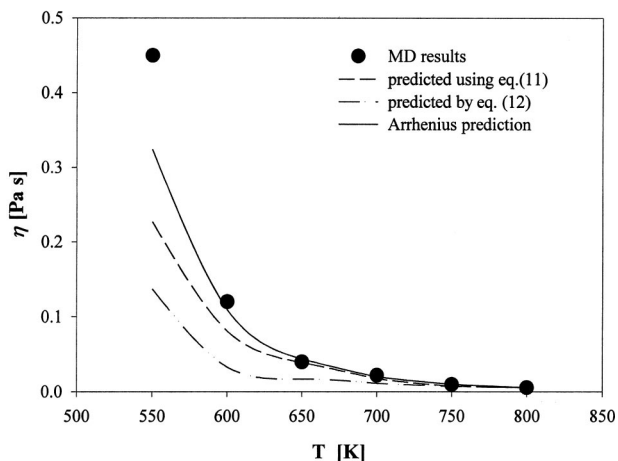


FIG. 6. Temperature dependence of viscosity obtained from the MD simulation, Arrhenius fit, and correlation equations (11) and (12).

or

$$\eta_{\tau_R} = K \rho T \tau_R, \quad (10)$$

where K is a constant that depends on the particular model involved in the derivation of the relation. If we have an accurate value of viscosity η_0 at some temperature T_0 , then the temperature dependence of the viscosity can be established from the temperature dependence of the self-diffusion coefficient (D) or rotational diffusion time (τ_R) using one of the following relationships:

$$\eta_{D_1} = \eta_{D_0} \frac{\rho_1 T_1 D_0}{\rho_0 T_0 D_1} \quad (11)$$

or

$$\eta_{\tau_1} = \eta_{\tau_0} \frac{\rho_1 T_1 \tau_{R1}}{\rho_0 T_0 \tau_{R0}}. \quad (12)$$

The practical advantage of these relations is that, in MD simulations, single molecule properties like the self-diffusion coefficient and rotational relaxation times converge much faster than system properties due to additional averaging over the number of molecules in the ensemble. We applied Eqs. (11) and (12) to our MD results using data at 800 K as a reference point in order to predict the viscosity over the entire temperature domain. In Fig. 6 we compare the predicted values with those obtained from simulation. It appears that in the temperature domain 600–800 K predictions of Eq. (11) are more consistent with MD results than are the predictions of Eq. (12). This leads us to conclude that the viscosity temperature dependence in liquid HMX is more correlated with molecular center-of-mass diffusion than with the molecular rotational relaxation time.

Also shown in Fig. 6 is the prediction of viscosity by the Arrhenius equation

$$\eta = \eta_0 \exp\left(-\frac{\Delta E_{\text{vis}}}{RT}\right), \quad (13)$$

with parameters (ΔE_{vis} and η_0) determined using MD viscosity results at 800 and 750 K. This allows us to test how accurately the low-temperature viscosity can be predicted

based on the faster converging MD simulations at a higher temperature if Arrhenius behavior is assumed. It is clear that in the temperature domain 600–800 K, the predictions from the Arrhenius equation are in essentially quantitative agreement with results obtained from MD. Since our simulation at 550 K is too short to estimate the uncertainty in the viscosity, we have more confidence in the viscosity value obtained using Eq. (13) at this temperature.

CONCLUSIONS

We have performed extensive MD simulations of liquid HMX in the temperature domain $550 \text{ K} \leq T \leq 800 \text{ K}$ and atmospheric pressure to obtain predictions of the shear viscosity and molecular self-diffusion coefficient. Simulation times ranging from 10 to 30 ns were required in order to obtain converged results for the shear viscosity. Although the shear viscosity appears as a parameter in some mesomechanical models for high explosives, this work contains the first real predictions for that property.

The predicted shear viscosities are 0.0055 and 0.45 Pa*s at the highest and lowest temperatures, respectively, and increase rapidly as HMX approaches its melting point. Both the shear viscosity and self-diffusion coefficient were found to obey Arrhenius behavior over the entire temperature domain studied, thus allowing for easy prediction of those quantities within a mesomechanical modeling framework. Although direct calculations of the shear viscosity require large amounts of CPU time, the self-diffusion coefficient can be reliably computed using much shorter trajectories. This suggests an approach in which a few values of the shear viscosity and self-diffusion coefficient are obtained at high temperatures in conjunction with low-temperature calculations of the self-diffusion. If the self-diffusion coefficient is found to obey Arrhenius behavior over the entire temperature domain, then one might assume similar behavior for the shear viscosity and thereby obtain low-temperature values for that parameter by extrapolation.

Two correlation formulas directly relating the self-diffusion and shear viscosity coefficients were tested against our predictions. Specifically, expressions used for long-chain polymers (η proportional to the end-to-end rotational relaxation time τ_R) and for “simple” molecules (η proportional to the inverse self-diffusion coefficient) were considered. Qualitative agreement was obtained, the viscosity/diffusion correlation yielded better agreement. However, neither of these was found to be of predictive value.

The present calculations further demonstrate the ability of molecular dynamics methods, judiciously applied to appropriate problems, to provide practical information of direct use to modelers working at larger spatial and temporal scales.

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¹⁶We refer to the rhs of Eq. (3) as the time-dependent apparent shear viscosity. The shear viscosity itself is defined as the long-time limit of the rhs Eq. (3) and is independent of time.

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