Thermal conductivity of liquid octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from molecular dynamics simulations

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Abstract

The thermal conductivity of liquid octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) has been determined from imposed heat flux non-equilibrium molecular dynamics (NEMD) simulations using a previously published quantum chemistry-based atomistic potential. The thermal conductivity was determined in the temperature domain $550 \leqslant T \leqslant 800$ K, which corresponds approximately to the existence limits of the liquid phase of HMX at atmospheric pressure. The NEMD predictions, which comprise the first reported values for thermal conductivity of HMX liquid, were found to be consistent with measured values for crystalline HMX. The thermal conductivity of liquid HMX was found to exhibit a much weaker temperature dependence than the shear viscosity and self-diffusion coefficients. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Plastic-bonded explosives (PBX) are highly filled composite materials comprised of explosive crystallites (the fill material) suspended in a polymeric binder (the matrix). It is important to understand the safety and performance characteristics of PBXs on the basis of the fundamental physical and chemical interactions among the constituents under a given set of conditions (stress state, temperature, and strain rate), and to incorporate this physics-based under-standing into constitutive models suitable for use in continuum hydrodynamic simulation codes. One approach for this is the use of mesomechanics models in which a PBX is studied at the level of explosive filler suspended in the binder matrix (see Ref. [1]). (Given the typical particle sizes in a PBX, this requires consideration of a piece of material roughly 1 or a few millimeters on a side.) The advantage of such a method is that it enables a detailed sensitivity assessment of the various microscopic dissipative mechanisms that will determine the ultimate response of the PBX to some external stress, e.g., weak shock loading. A necessary condition for the development of successful mesoscale models is the availability of reliable values for the physical param-

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eters that appear in their mathematical formulation. Examples of these include mechanical, viscoelastic, and viscoplastic properties of the constituents; strengths of the interfaces between them; equilibrium transport properties; and kinetic rate laws for chemical reactions.

The high explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is the energetic constituent in several PBX formulations, e.g., PBX-9501 [2]. One of the goals of our research is to use atomistic molecular dynamics (MD) simulations to predict many of the thermophysical and mechanical properties of HMX required for improving the mesoscale descriptions of the mechanics of HMX-containing PBX formulations. We believe that atomistic MD simulations can provide such information for thermodynamic states where direct experimental measurement is difficult or impossible. In previous work [3] we presented calculations of the shear viscosity and self-diffusion coefficients of liquid HMX in the temperature domain $550 \leqslant T \leqslant 800$ K, which approximately spans the existence limits of the liquid phase under atmospheric pressure. The calculations were based on equilibrium MD simulations and linear response theory. We found that both self-diffusion and shear viscosity are well described by an Árrhenius temperature dependence with a rather large activation energy.

In this Letter we present the first predictions of the thermal conductivity and its temperature dependence for liquid HMX. The results were obtained from imposed heat flux non-equilibrium molecular dynamics (NEMD) simulations described below. The thermal conductivity is needed for a complete mesomechanical description of PBXs as well as for various combustion models (e.g., Ref. [4]), since it largely determines the rate at which heat generated locally is dissipated to the surrounding material. No direct measurements or calculations of thermal conductivity have been performed for liquid HMX; therefore, this work represents the first report of that property.

2. Molecular dynamics simulation details

Calculations of thermal conductivity from MD simulations can suffer significant difficulties due to complications in determining the microscopic heat flux [5] $J(t)$, especially for molecular fluids, which are often characterized by long-range interactions (e.g., Coulomb). While the microscopic definitions of mass flux (self-diffusion) and momentum flux (viscosity) involve only self-particle or self- and inter-particle static correlations, respectively, the heat flux involves inter-particle dynamic correlations requiring evaluation of pair velocities [5,6]. Long-range static correlations can be effectively treated using Ewald and related methods; however, no equivalent method exists for handling long-range dynamic correlations. Since the force field for the polar HMX molecule contains partial atomic charges and therefore includes long-range interactions (and perhaps long-range correlations) we chose to employ a MD simulation method that does not involve calculation of the microscopic heat flux and hence does not suffer from the complications mentioned above.

Recently, Müller–Plathe suggested a NEMD method [7] for calculation of thermal conductivity that was subsequently adapted and applied by some of us to molecular liquids with long-range interactions [8]. The idea of the method is to impose an exactly known heat flux on the system and then determine the resulting steady-state temperature gradient in the direction parallel to the heat flux. The thermal conductivity λ can be expressed as

$$\lambda = \frac{\langle J_z(t) \rangle}{2tA\langle \mathrm{d}T/\mathrm{d}z \rangle} , \qquad (1)$$

where $\langle J_z(t) \rangle$ is cumulative heat flux imposed during the simulation in the z direction, $\langle \mathrm{d}T/\mathrm{d}z \rangle$ is the resultant temperature gradient in this direction, A is the surface area perpendicular to the z-axis, and t is the total simulation time. The heat flux is created by exchanging the center-of-mass velocities of molecules in 'cold' and 'hot' slabs located in the middle of the simulation box and adjacent to one of the simulation box boundaries [8]. Specifically, the velocity exchange involves the 'hottest' molecule in the cold slab and the 'coldest' molecule in the hot slab, where 'temperature' is defined by molecular center-of-mass velocities. Performing this exchange with a frequency W results in the heating up of the hot slab and cooling down of the cold slab and

eventually yields a steady-state temperature gradient in the z direction due to thermal conduction through slabs separating the cold and hot ones. The temperature gradient can be easily measured by calculating the local temperature in each slab. The imposed heat flux is given exactly by the relationship

$$\langle J_z(t) \rangle = \sum_{\text{transfers}} \frac{m}{2} \left(v_c^2 - v_h^2 \right), \qquad (2)$$

where v_c and v_h are the translational velocities of the identical mass molecules that participate in the exchange procedure in the cold and hot slabs, respectively. The reader is referred to Refs. [7,8] for more details about the methodology and implementation of the imposed heat flux NEMD method.

In previous work [9] we developed a classical, explicit-atom force field for flexible HMX molecules using the results of high-level quantum chemistry calculations for conformational energies and geometries of gas-phase HMX and other related nitramine compounds [10]. Good agreement was obtained between measured thermophysical properties of the α, β and δ polymorphs of HMX and predictions based on this potential [11]. Here, we utilize this potential in imposed heat flux NEMD simulations carried out for the HMX melt at six temperatures (550–800 K, in 50 K intervals) and atmospheric pressure. For each temperature, standard equilibrium isothermal-isobaric (NpT) MD simulations were performed for 4 ns in order to establish equilibrium densities. Subsequently 1 ns isothermal-isochoric (NVT) equilibration runs were conducted using NEMD to establish the initial temperature gradient along the z direction, followed by 6–8 ns (depending upon temperature) production runs. The Nosé–Hoover thermostat [12] with a 1 fs time integration step and constrained bond lengths [13] was used to control the overall temperature. The Ewald summation method [14] was employed to evaluate long-range electrostatic interactions. Each system contained 100 HMX molecules and periodic boundary conditions were employed. The orthorhombic simulation box, extended in the z direction, was subdivided into 10 equal slabs with width of about 5.0 Å and cross-sectional area of about 625.0 Å^2. The molecular center-of-mass velocities were exchanged every 500 fs ($W = 0.002$ fs^{-1}) for pairs of molecules belonging to 'cold' and 'hot'

slabs. This choice of the W was based on our previous experience with simulations of liquid *n*-butane and water [8], where the same value of W was found to provide accurate predictions of thermal conductivity over a wide temperature domain.

3. Results and discussion

The thermal conductivity of liquid HMX at atmospheric pressure is summarized in Table 1. Also shown are the equilibrium density ρ, shear viscosity η and self-diffusion coefficient D, which were obtained previously using equilibrium MD simulations with the same potential [13]. The thermal conductivity exhibits a much weaker temperature dependence than that found for the other transport properties. Whereas the shear viscosity and self-diffusion coefficients vary by orders of magnitude, the thermal conductivity only varies by $\sim 40\%$ over the same domain. Such behavior is consistent with experimental data on aromatic hydrocarbons [15] and can be explained by differences in the energy, momentum and mass transfer mechanisms. In order to transport energy a molecule need only oscillate in its local 'cage', interacting with its neighboring molecules without disrupting the local structure. As the primary mechanism for energy transport does not involve long-range molecular transport, the thermal conductivity is relatively insensitive to temperature. In contrast, (zero frequency) momentum and mass transfer require hopping of the molecules from cage to cage, a process involving severe disruption of the local structure. This process is thermally activated with a

Table 1
Thermophysical properties of liquid HMX

T (K)	ρ (kg m^{-3})[a]	$D \times 10^9$ (m^2 s^{-1})[a]	η (Pa s)[a]	$\lambda \times 10^4$ (cal cm^{-1} s^{-1} K^{-1})[b]
550	1650.9	0.006	0.450	9.28
600	1614.4	0.018	0.120	7.51
650	1586.9	0.040	0.040	6.90
700	1554.5	0.094	0.022	6.24
750	1520.1	0.225	0.010	6.30
800	1488.2	0.325	0.0055	6.40

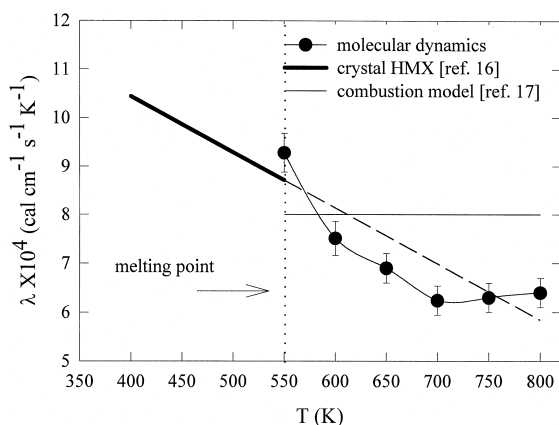[a] From Ref. [3].
[b] This work.

Fig. 1. The thermal conductivity of HMX is shown as a function of temperature. Symbols: this work (liquid phase); solid bold line: experiment (crystal phase); solid thin line: semi-empirical form used in some combustion models. The dashed line is an extrapolation of the experimental data for HMX crystal into the liquid region.

large activation energy (14.5 kcal/mol) [3], resulting in a strong temperature dependence of the viscosity and self-diffusion coefficients.

In Fig. 1 we show a comparison of the thermal conductivity for liquid HMX obtained from NEMD with measured values for crystalline HMX [16] as well as values used in combustion models for HMX [17]. Despite being weak, the temperature dependence of the thermal conductivity of liquid HMX is not featureless. The thermal conductivity exhibits a sharp drop in the temperature domain from the melting point (550 K) up to 650 K. At higher temperatures the thermal conductivity manifests almost no temperature dependence. The predicted value at 550 K is consistent with the HMX crystal data [16]. The thermal conductivity used in some combustion models [17] agrees to within about 25% with our NEMD predictions over the entire temperature domain.

4. Conclusions

We report the first direct predictions of the thermal conductivity of liquid HMX at atmospheric pressure for $550 \leqslant T \leqslant 800$ K. The predictions were obtained using a previously published flexible-molecule force field for HMX in conjunction with imposed heat flux NEMD simulations. Unlike the shear viscosity and self-diffusion coefficients calculated in our previous work, the thermal conductivity exhibits a weak temperature dependence in the domain investigated. The predicted thermal conductivities are consistent with the value used in some combustion models. The present predictions validate the semi-empirical value of this parameter for those models, but also provide an opportunity to improve the models by taking into account a more realistic temperature dependence of the thermal conductivity.

Acknowledgements

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