

Molecular dynamics simulations of void defects in the energetic material HMX

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Abstract A molecular dynamics (MD) simulation was carried out to characterize the dynamic evolution of void defects in crystalline octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine (HMX). Different models were constructed with the same concentration of vacancies (10 %) to discuss the size effects of void. Energetic ground state properties were determined by annealing simulations. The void formation energy per molecule removed was found to be 55–63 kcal/mol⁻¹, and the average binding energy per molecule was between 32 and 34 kcal/mol⁻¹ according to the change in void size. Voids with larger size had lower formation energy. Local binding energies for molecules directly on the void surface decreased greatly compared to those in defect-free lattice, and then gradually increased until the distance away from the void surface was around 10 Å. Analysis of 1 ns MD simulations revealed that the larger the void size, the easier is void collapse. Mean square displacements (MSDs) showed that HMX molecules that had collapsed into void present liquid structure characteristics. Four unique low-energy conformers were found for HMX molecules in void: two whose conformational geometries corresponded closely to those found in HMX polymorphs and two, additional, lower energy conformers that were not seen in the crystalline phases. The ratio of different conformers changed with the simulated temperature, in that the ratio of α conformer increased with the increase in temperature.

Keywords Void defect · Dynamic evolution · Molecular conformation

Introduction

Defects in solid and crystalline energetic materials are known to exert a significant influence on impact and initiation sensitivity. To date, theoretical investigations into the crystal defects of energetic materials have been done mainly by Kuklja et al. [1–10], who conducted first-principle investigations into the effects on the optical band gap, electronic properties, and degradation reactions of the energetic materials of defects such as vacancy complexes, a single vacancy, edge dislocation, and voids, etc. From these calculations, they concluded that compression of the 1,3,5-trinitro-1,3,5-triazacyclohexane (C₃H₆N₆O₆, RDX) crystal in the presence of defects reduces the optical band gap of this material appreciably; N–NO₂ homolysis is the dominating reaction in octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (C₄H₈N₈O₈, HMX) containing surfaces, interfaces, voids, or vacancies, and these imperfections will also lower activation barriers and accelerate kinetics. Manna [11] investigated the influence of high pressure and molecular vacancies on the electronic structure of solid nitromethane using the self-consistent charge density-functional tight-binding method. Due to the complicated structures of molecular crystals with defects and related deformations, which remove some of the symmetry of the crystal structure, expensive computer resources are required to run periodic ab initio calculations. Therefore, despite the efforts cited above, only a few first-principles studies are available.

Molecular dynamics (MD) simulations can reveal changes in atomic and electronic structure that may not be captured by static calculations. For example, Boyd et al. [12] characterized void defects in crystalline RDX using this method, carried out energetic analysis and investigated the thermal behavior of void, but void evolution with runtime

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was not addressed in their work. The effects of molecular vacancies on the decomposition mechanisms and reaction dynamics of crystalline β -HMX at high temperature were studied using ReaxFF MD simulations [13]. The dynamic response to shock wave loading of energetic materials containing defects has been studied using large-scale MD simulations [14]. Nevertheless, to the best of our knowledge, minimal work has been carried out to investigate the evolution of void with runtime without any external stimuli (e.g., impact or shock). It can be predicted that such investigations might provide a theoretical foundation for the improvement of crystal quality as well as improved storage and aging of energetic materials.

Generally, it is believed that initiation of combustion in energetic materials is associated with so-called “hot spots” [2, 15]—local regions of a crystal (crystal defects or deformations) in which the energy of shock compression is trapped, leading to chemical chain reactions of decomposition. Voids, molecular vacancies, dislocations, impurities, pore, and other types of defects play a crucial role in such initial reactions. However, which one of the many different defects present in a crystal is responsible for sensitivity remains as yet undetermined, and hot-spot formation mechanisms are still controversial. Some authors insist that the mechanism of collapse of voids is one of the most important mechanisms that can lead to ignition in pressed explosives. Some theoretical calculations have established another possible explanation that void/vacancy-induced weakening of N–NO₂ bonds in proximity to hot spot energy could promote detonation [10, 16, 17]. So, a knowledge of the structure and nature of voids is of great importance to understanding the “hot-spot” formation mechanism. The dynamic evolution characteristic of voids should affect the chemical reaction and initiation of denotation in energetic materials significantly. Such investigations are also valuable in furthering our understanding of how the formation of hot spots leads to detonation.

In this research, which was aimed at understanding the evolution and characteristics of voids, we present MD simulations of crystalline β -HMX containing voids. As one of the most important energetic materials, HMX is applied widely in many fields, such as explosives, rocket propellants, airbag inflators, etc. The HMX crystal has a complex structure built out of 28-atom molecules, and often serves as a good model system for molecular materials.

Computational method

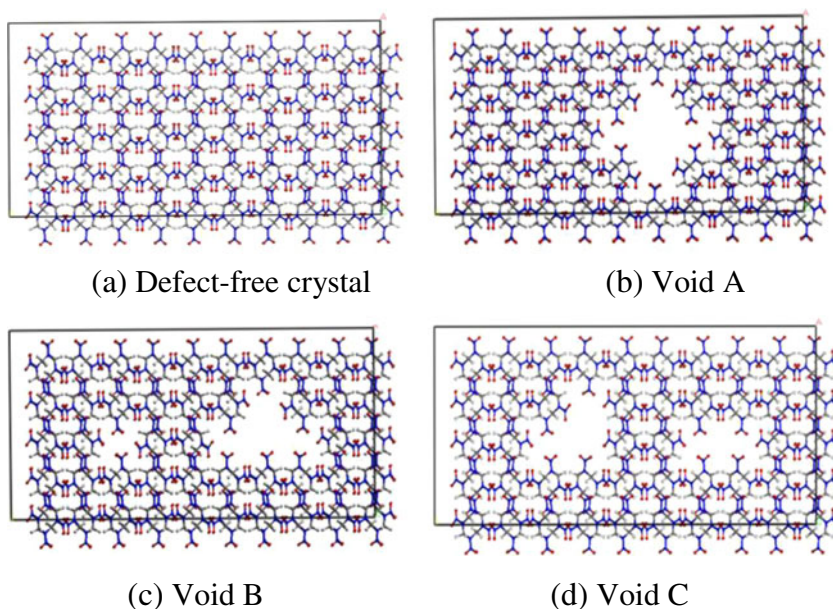
According to neutron diffraction experiments of β -HMX [18], the unit cell model is constructed. Molecular mechanics potential-energy minimization is performed on the unit cell (Smart minimizer, optimization of the cell parameters, and

“fine” quality). Then, we extend the unit cell to a supercell consisting of $5 \times 5 \times 5$ unit cells. Since there are two HMX molecules per unit cell, the supercell includes 250 molecules and 7,000 atoms. A (100) view of the supercell is shown in Fig. 1a. After that, cohesive voids are introduced by removing 25 molecules from the 250-molecules supercell, first one and its neighbors over an increasing distance; this corresponds to a 10 % concentration of vacancies in the material. In order to explore the size effects of void, models are constructed as follows: (1) model has only a void containing 25 molecules, denoted as void A; (2) model includes two voids with 10 and 15 molecules, or 5 and 20 molecules, respectively, as void B or void C [see Fig. 1b–d]. Through the design of void B and void C, if possible, we can also study the transfixion of voids through the interaction of voids, except the size effects.

The defect-free supercell and all models were optimized using the same method of unit cell optimization. Based on the optimized structures, annealing dynamics were performed to allow the lattice parameters to adjust to the internal stress distribution, modified by the presence of the void and allowing the molecules to relax around the void. The lowest energy structures from each complete annealing cycle were optimized by the “smart” method with quality “fine” before they were output to the trajectory. In the annealing dynamics run, the initial and mid-cycle temperatures were 300 K and 400 K, respectively; the number of annealing cycles was specified at 5; heating ramps per cycle was set to 5; dynamics steps per ramp was set 10,000. The NVT ensemble was applied with a time step of 1 fs. For potential energy calculations, the Coulombic and van der Waals interactions were calculated by employing the standard Ewald method with quality “fine” [19]. The temperature was controlled using the Nose thermostat by applying the default Q ratio [20–22].

The Compass force field [23] was applied in the MD simulations. Compass is a powerful *ab initio* force field supporting atomistic simulations of condensed phase materials and stands for condensed-phase optimized molecular potentials for atomistic simulation studies. The force field can be divided into two categories: valence terms including diagonal and off-diagonal cross-coupling terms, and nonbond interaction terms. The valence terms represent internal coordinates of bond (b), angle (θ), torsion angle (ϕ), and out-of-plane angle (χ), and the cross-coupling terms include combinations of two or three internal coordinates. The nonbond interactions include an LJ-9-6 function for the van der Waals (vdW) term and a Coulombic function for an electrostatic interaction. This force field was used successfully in [24–27], including MD simulations for crystal surfaces of HMX [24], the interfaces of HMX and RDX and fluorine polymers [25, 26], and the polymorph transformation of HMX crystal [27]. This shows that the COMPASS force field can be applied effectively to theoretical simulations for HMX.

Fig. 1 (100) Views of the defect-free system **(a)** and void models: **b** one void with size 25 molecules denoted as void A, **c** two voids with sizes 5 and 20 molecules (void B), and **d** two voids with size 10 and 15 molecules (void C)



Based on the void structure with the lowest energy after anneal dynamics run, 1-ns MD simulations were performed to characterize the dynamic evolution of voids. Other parameters were the same as those mentioned above for annealing dynamics simulations. All calculations were run with the commercial molecular modeling software package Materials Studio 3.0 [28].

Results and discussion

Energetic calculations for voids

Applying the void structure with the lowest energy after the annealing dynamics run, we calculated the formation energy of a void defect E_f , the average binding energy per molecule E_b , and local binding energy. The formation energy E_f is calculated using the following equation:

$$E_f(n) = E_{\text{sys}}(n) + nE_{\text{mol}} - E_{\text{sys}}(0) \tag{1}$$

where $E_{\text{sys}}(n)$ is the ground state energy of the system with a void of size n , E_{mol} is the energy of an isolated β -HMX molecule, and $E_{\text{sys}}(0)$ is for the ideal crystal. This calculation takes account of the subsequent relaxation of the surrounding lattice, and $E_f(n)$ represents the energy required to remove and separate n molecules.

The average binding energy per molecule E_b is that needed to separate the lattice into isolated molecules. It can be calculated by

$$E_b = \frac{[(N-n)E_{\text{mol}} - E_{\text{sys}}(n)]}{N-n} \tag{2}$$

where N is the number of molecules in the absence of any vacancies, and n is the void size. Calculated energetic results are presented in Table 1. From the energy calculations of different models, it was found that the formation energy per molecule removed increased when a large void was divided into two small voids. Furthermore, the larger the void size, the smaller the formation energy. The formation energy was determined by the pair interactions of the removed molecules in all directions. For large voids, the numbers and strengths of interactions were decreased relative to those in small size voids.

Since the void size investigated here represents 10 % of the molecules in either lattice, their effects on E_b are small, at between 32 and 34 kcal/mol⁻¹ for all the systems considered. This value is close to the calculated lattice energy of HMX, 35.64 kcal/mol⁻¹, using the same force field and method. Relative to the experimental value, 40.71 kcal/mol⁻¹ [29], the relative error is 12 %.

The local binding energy at a specific lattice site x , $E_n(n, x)$, is calculated by the following Eq. (3), including the intermolecular interactions and the conformational relaxation:

$$E_n(n, x) = E(n, x) - E(n) \tag{3}$$

where $E(n, x)$ and $E(n)$ are the total energies in the system with void size n and the same system with an additional molecule

Table 1 Energetic calculations for the void models (in kcal/mol⁻¹)

	Void A	Void B	Void C
E_f/n	55.80	60.80	62.20
E_b	33.40	32.85	32.69

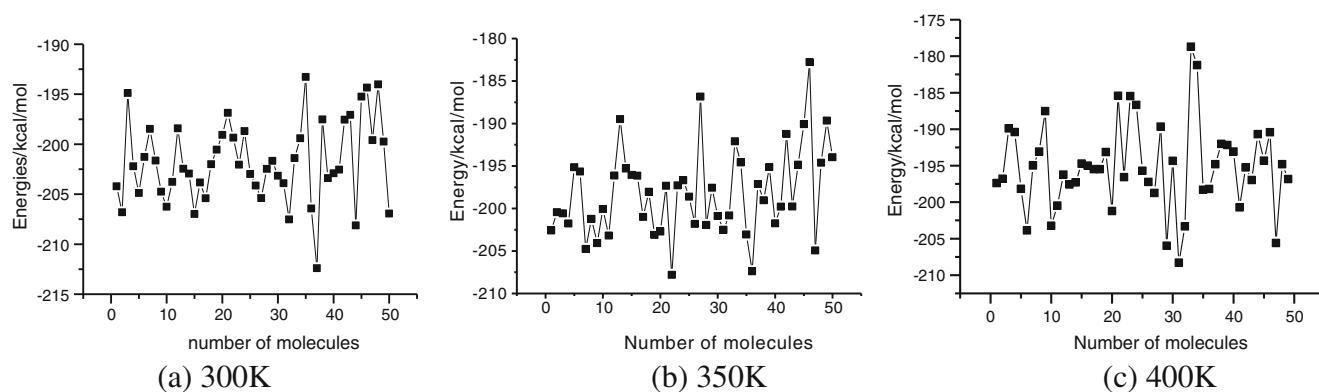


Fig. 2a–c Energy distributions of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ($C_4H_8N_8O_8$) (HMX) molecules collapsed into void A simulated at different temperatures. **a** 300 K, **b** 350 K, **c** 400 K

removed at site x . Here, we calculated only $E(n, x)$ for void A to account for the energy change resulting from void formation. For molecules located at or near the surface of a void, the average value for $E(n, x)$ is calculated to be $264.32 \text{ kcal/mol}^{-1}$. A large decrease was observed compared to the $300.34 \text{ kcal/mol}^{-1}$ in the defect-free lattice, which is caused mainly by the decreased interactions of surface molecules with fewer neighbors and conformational change. Thereafter, $E(n, x)$ increases with the distance away from the void surface. When the distance is increased up to around 10 \AA , $E(n, x)$ fluctuates around $300 \text{ kcal/mol}^{-1}$, indicating that the structure is very close to that of a defect-free lattice. In addition, the structure includes a few molecules whose local binding energies are much higher than in the bulk crystal.

Thermal behavior of HMX molecules in void A

We used the “void A” model as an example to investigate the effect of temperature on the dynamics evolution characterization of void. MD simulations were performed at three temperatures, 300 K, 350 K, and 400 K. Temperatures were set based on the following considerations: (1) below the melting temperature of β -HMX crystal; and (2) no polymorph transformation during MD simulation. As we know, the melting point of β -HMX is in the range of 540–550 K depending on the method used to determine it. Landers and Brill [30] suggested by experimental studies that if $P < 0.12 \text{ GPa}$, the $\beta \rightarrow \delta$ transformation occurs when $T = 422\text{--}463 \text{ K}$; if $P > 0.12 \text{ GPa}$, β -HMX is stable until the temperature exceeds 551 K. Using the ReaxFF force field, Zhou et al. predicted that β -HMX is stable in the temperature ranges of 303–423 K at atmospheric pressure [31]. Therefore, we chose 300 K, 350 K, and 400 K as the temperatures for the simulation.

The simulation results revealed that void collapsed completely along with evolving run time. The higher the simulation temperature is, the faster the void collapses. Approximately 50 HMX

molecules collapsed into the void. For these collapsed molecules, we calculated the energy of each molecule at different temperatures, and the energy distributions are shown in Fig. 2. The energy of single molecule fluctuates about the average value of $-201.82 \text{ kcal/mol}^{-1}$ at 300 K, $-198.19 \text{ kcal/mol}^{-1}$ at 350 K, and $-195.17 \text{ kcal/mol}^{-1}$ at 400 K. It was found that molecules at high temperature have higher energies, which may be associated with the conformation change discussed in the next section.

From the mean square displacements (MSDs) for the centers of mass of HMX molecules (Fig. 3), we can see that the HMX molecules transporting into the void show characteristics of a liquid structure. The behavior of MSD as a function of time is used to discriminate between solid and liquid phase. For a fluid with no underlying regular structure, the MSD gradually increases with time. For a solid, the MSD oscillates about a mean value. The increase of the MSD with time is observed clearly from the curves in Fig. 3. At 350 K and 400 K, the movement rate of molecules is very close, and much faster than that at 300 K. Besides, molecular diffusion becomes faster and faster with increasing runtime, especially after 800 ps. This may be caused by variation in the number and strength of the interactions due to evolution of the void. Without the lattice-bound

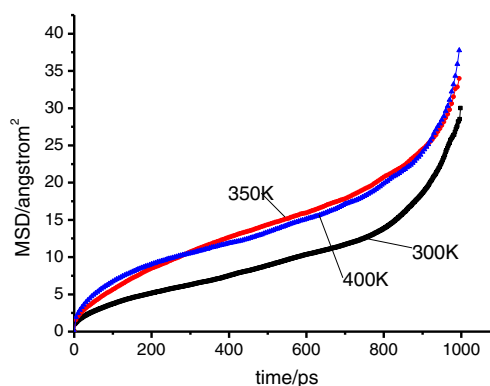


Fig. 3 Mean square displacements (MSDs) of collapsed HMX molecules in void A at different temperatures

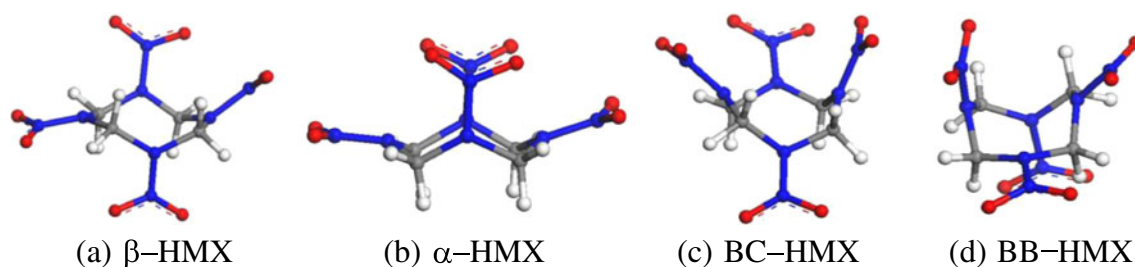


Fig. 4a–d Different conformations of HMX molecules collapsed into voids. **a** β -HMX, **b** α -HMX, **c** boat–chair (BC)-HMX, **d** boat–boat (BB)-HMX

structure, fast moving liquid-state HMX molecules may accelerate the degradation reaction of HMX.

Conformation of HMX in voids

As we know, the “ α ” conformer, with C_2 symmetry, corresponds to the molecular geometry found in the α polymorph of crystalline HMX and is quite similar to the conformations found in the γ and δ forms, while the “ β ” conformer, with C_i symmetry, is the conformation found in the β form. In addition to these conformers, another two low-energy conformations of HMX were found by Smith et al. [32] through theoretical calculation, namely, the global minimum boat–chair (BC) conformer with C_1 symmetry and the boat–boat (BB) conformer with C_2 symmetry. Similarly, four conformations of the HMX molecule were found in our simulations (Fig. 4) and their ratios in all collapsed molecules are presented in Table 2. Due to the distortion, these conformations have no symmetry and are judged only by the relative orientation of the nitro groups.

Conversion of conformation was observed for the liquid HMX molecules. In the “void A” model, the four conformations shown in Fig. 4 were all found with different percentages. At 300 K, the BC conformer occupies the largest ratio, at 52.9 %, followed by the β conformer. α -HMX represents very few of the total collapsing molecules. It can be seen that the molecule trends to a low-energy state without the lattice boundary. In all four conformations, BC and BB represent

the global minimum conformer. Therefore, the reaction of β -HMX to BC and BB is exothermic, while to α -HMX it is endothermic. With the increase in temperature, the ratio of α -HMX increases greatly. Secondly, the percentage of BB-HMX also increases, while that of the BC conformation clearly decreases. It can be predicted that the number of α -HMX conformers will increase greatly with a further increase of temperature. High-energy α -HMX molecules in the void may lower the activation barrier for the N–NO₂ bond-breaking reaction and accelerate kinetics, resulting in a higher sensitivity to initiation of chemical degradation. Because the conversion from the β conformer to α -HMX is endothermic, the rise in temperature favors this reaction. As for the ratio change of BC and BB, according to our Compass force field calculations, the energy of BB is lower by 0.6 kcal/mol⁻¹ than that of BC. So, increasing the temperature may allow the conversion from β to the lower-energy BB. This conversion may also be related to the reactive energy barrier. The conformation change is caused by anisotropic interactions between molecules near a void with others in their vicinity.

With the decrease in void size, void collapse becomes difficult. For the void B and void C models, the small voids with sizes of 5 and 10 molecules effectively do not collapse, only the radius of void becomes small. For the void with size 20, the main conformation is still the β conformer (48.8 %), with the BC conformation in second place (39.5 %) in the 43 collapsed HMX molecules. The α -HMX molecules occupy

Table 2 Ratios of different conformations for octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (C₄H₈N₈O₈) (HMX) molecules collapsed into voids

		n^a	R_β^b	R_α	R_{BC}	R_{BB}
Void A (300 K)		50	35.3	2	52.9	9.8
Void A (350 K)		50	28	10	50	12
Void A (400 K)		50	31.4	16.3	34.7	16.3
Void B (300 K)	Void 1 with size 5	0	0	0	0	0
	Void 2 with size 20	43	48.8	2.3	39.5	9.3
Void C (300 K)	Void 1 with size 10	0	0	0	0	0
	Void 2 with size 15	5	0	0	40	60

^a Number of HMX molecules collapsed into void

^b Percentage of different conformation HMX molecules

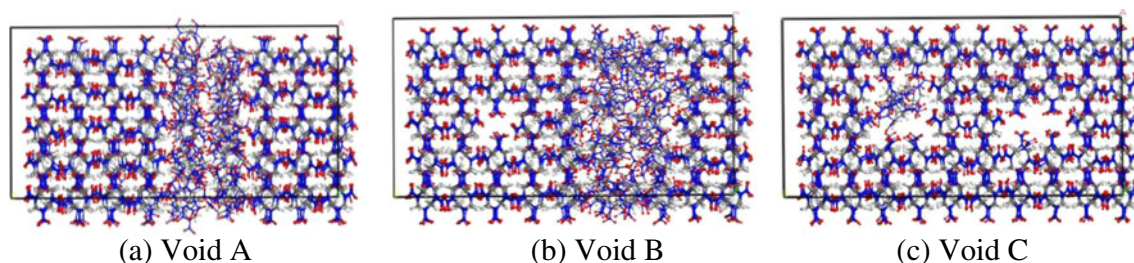


Fig. 5a–c (100) Views of void geometries after 1 ns MD simulations. **a** Void A, **b** void B, **c** void C

only 2.3 % (see Table 2 and Fig. 5b). For the void with size 15, five molecules are transported into the void (see Fig. 5c), of which three molecules represent the BB conformation, and two the BC conformation. This further confirms that the HMX molecules tend towards lower-energy BB and BC conformations without a lattice boundary, for example, gas and liquid phase molecules. Furthermore, the small void does not collapse easily. Clearly, the molecular strain near small voids is decreased substantially compared with that in large voids, so the net force drawing molecules into the void becomes small. Besides, for voids B and C, the expected transformation phenomenon cannot be observed within the range of the simulated time.

Generally, a void inserted into the crystal tends to change the equilibrium lattice parameter. A study by Boyd et al. [12] indicated that changes in lattice parameters accompanying void formation were less than 0.3 % over the entire range of void size. The largest was a decrease of 0.29 % in a for $n=30$. In our work, due to applying the NVT ensemble in which volume is held constant, the formation of void necessarily increases the simulated pressure. Table 3 shows the pressure values for different models determined from our MD simulations. Compared to atmospheric pressure, the system pressure is largely increased. Namely, void collapse is also promoted by system pressure to some extent. Besides, as seen from Table 3, the pressure increases with the increase in simulated temperature, and void collapse decreases the system pressure. Furthermore, in the light of the experimental results of Landers and Brill [30], β -HMX is stable in the simulated temperature range of 300–400 K under these pressures.

Table 3 Pressure values (GPa) for different models during the MD simulated process

	Initial	Final	Average
Void A (300 K)	0.427	0.029	0.053
Void A (350 K)	0.466	0.110	0.100
Void A (400 K)	0.535	0.487	0.162
Void B (300 K)	0.412	0.209	0.233
Void C (300 K)	0.392	0.340	0.418

Boyd et al. [12] observed no collapse even if the void size was up to 30 with a concentration of vacancies 13.9 % for a smaller system of 216 RDX molecules. We think that the difference is caused mainly by simulated temperature and pressure. Boyd et al. [12] adopted stepwise simulated annealing to quench the system from an initial 250 to 10 K at a pressure of 1 atm over a total time of 500 ps. NPT molecular dynamics trajectories were sampled for different properties. Thus, the simulated temperature and pressure all are lower than those of our work. Secondly, other simulation conditions, including force field and MD parameter set, and quality of the equilibrium, may have some effect on the simulated results.

Furthermore, our energy calculations for four different conformational HMX molecules show that the Compass force field does a credible job in reproducing the quantum chemistry conformational energies for HMX. Taking the HMX molecules collapsed in Void A at 400 K as an example, HMX conformer energies are tabulated in Table 4. Relative to the BC conformer, the force field accurately reproduces the energy of the β conformer. In our force field calculations, the relative energy of the β conformer is 0.9 kcal/mol⁻¹, and 0.8 kcal/mol⁻¹ at the B3LYP/6-311G**//MP2/6-311G** geometry/energy level [32]. For the application of the force field to crystalline HMX, it is important that the difference in energy between the α and β conformers is well represented. According to our field force calculations, this difference is 2.8 kcal/mol⁻¹. Quantum chemistry calculations give a value of 3.5±1.0 kcal/mol⁻¹ at the MP2 level [32]. Besides, in contrast to quantum chemistry, the force field yields an energy for the BB conformer that is lower than that of BC.

Table 4 HMX conformer energies (in kcal/mol⁻¹)

	α	β	BC	BB
ff ^a	3.7	0.9	0	-0.6
qc ^b	4.3	0.8	0	0.5

^a Average force field energies calculated in our work

^b Quantum chemistry energies at the B3LYP/6-311G**//MP2/6-311G** level cited from Ref. 32

Conclusion

The dynamic evolution characterization of void defects was explored by means of MD modeling of crystalline β -HMX. From the formation energies of different void models with the same concentration of vacancies (10 %), it was found that the larger the void size, the smaller the formation energy. Average binding energies for different models were between 32 and 34 kcal/mol⁻¹, close to the calculated lattice energy of HMX (35.64 kcal/mol⁻¹). A considerable decrease in the local binding energies for the molecules at or near the void surface was observed and this continued until the distance away from the surface of void was equal to approximately 10 Å.

MD simulations revealed that the larger the void is, the more easily it collapses. The HMX molecules transported into the void show liquid structure characteristics, and have higher energies and faster motion rate with the increase in temperature. Molecular conformational changes and reorientations were found for molecules that had collapsed into the void. In addition to the two conformations (α and β) found in crystalline HMX, we found two lower-energy conformations of HMX not seen in the crystalline phase: BB and BC. The ratios of the four conformations changed with the simulation temperature, with the ratio of the α conformer increasing with the increase in temperature. It can be predicted that all HMX molecules may adopt the high-energy α conformer when the temperature increases sufficiently, which will greatly increase the sensitivity to initiation of chemical degradation.

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