Review Article

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Molecular dynamics application of cocrystal energetic materials: A review

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Abstract: Cocrystallization is an important method to obtain high-energy and low-sensitivity explosives. Therefore, the synthesis, structures, and properties of cocrystal energetic materials have become a highly active research topic. Studying the physical and chemical properties of cocrystal energetic materials by molecular dynamics is of great significance for the in-depth understanding and design/synthesis of new cocrystal energetic materials. This review introduces the method of molecular dynamics, the cocrystal energetic materials synthesized successfully to date, and the application of molecular dynamics to cocrystal energetic materials. The existing problems and future development directions are discussed. We hope that this review will encourage researchers interested in the field to design and synthesize high-energy and low-sensitive energetic materials with practical application value.

Keywords: cocrystal, energetic materials, molecular dynamics

1 Introduction

Energetic materials such as explosives, gunpowder, and propellants play an important role in the military field. Energy and sensitivity are important parameters for evaluating energetic materials, but they are often mutually inclusive [1]. Generally, higher energy comes with higher sensitivity and thus, poorer safety. Therefore, energetic materials with high energy and low sensitivity are highly desired [2].

Cocrystallization [3] combines different energetic molecules into a lattice. The interactions between molecules are hydrogen bonding [4], π–π stacking [5], van der Waals forces, and other non-covalent interactions (such as halogen bonding), *etc*. Due to the addition of molecules, the oxygen balance, detonation performance, and safety of the explosives are improved [6]. Therefore, the design, synthesis, and application of cocrystal energetic materials have become a highly active research topic in the field of energetic materials [7].

In general, X-ray diffraction single-crystal data are difficult to obtain for cocrystal explosives. The formation of cocrystal explosives can only be confirmed by infrared spectroscopy, X-ray powder diffraction, differential scanning calorimetry, and so on. It is necessary to combine molecular dynamics simulations with practical experiments to study the formation of high-energy cocrystal materials. Regarding an atom as a mass point, the molecular dynamics calculates the positions and velocities of atoms at different times by Newton's laws of motion. It provides detailed information on the mechanical properties [8], gas fluid mechanics [9], molecular structure changes, and chemical reactions [10] from a microscopic point of view. Therefore, it plays an important role in the field of energetic materials.

In this review, the method of molecular dynamics is introduced, synthesized cocrystal energetic materials are collected, and current research into the molecular dynamics of cocrystal energetic materials is summarized. Thus, our review provides important information on the development status and future trends in this field.

2 Molecular dynamics

In 1957, Alder and Wainwright of the Lawrence Livermore laboratory in the United States used the classical Newton's

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law of mechanics to study the interaction between hard sphere atoms and proposed the molecular dynamics method for the first time [11]. They simulated and calculated the equation of state of hard spheres of 32 molecules and 108 molecules, respectively, with periodic boundary conditions, and the results showed good agreement. Due to the large errors in the calculation of migration coefficients of non-equilibrium materials, Lees and Edwards [12] proposed a periodic boundary condition to study the conductivity under strong shear to establish the early non-equilibrium molecular dynamics (NEMD). These two belong to classical molecular dynamics, that is, the interaction between particles is described by potential function. Obviously, the description of the interaction between atoms directly determines the quality of the calculation results in molecular dynamics. Therefore, many potential functions and force fields have been developed in recent years, such as CHARMM, COMPASS, and ReaxFF reactive force fields [13,14], *etc*. However, the determination of the potential function and its parameters describing the interaction between atoms is very complex.

In order to avoid the complicated work of describing the interatomic forces, the first principle molecular dynamics was developed. Car and Parrinello proposed a method to unify molecular dynamics and density functional theory (DFT), referred to as CPMD [15]. It optimizes the wave function only in the first-time step, and is applicable to systems with small energy transfer between atomic and electronic subsystems. However, for metal systems, the transfer of energy is difficult to control. Kresse and Hafner raised *ab initio* molecular dynamics (AIMD) for liquid metals, which calculate the electronic ground state and Hellmann–Feynman forces in the local-density approximation at each molecular-dynamics step [16]. Subsequently, density functional tight bound molecular dynamics (DFTB–MD) and self-consistent charge density functional tight bound molecular dynamics (SCC–DFTB–MD) were developed. The DFTB used in these methods is a semi empirical tight binding method, which has high computational efficiency than the ordinary DFT method. In short, the results of first principle molecular dynamics calculation are more accurate than those of classical molecular dynamics. Nevertheless, due to the huge calculation burden, only small-scale molecular systems can be calculated at present.

Currently, molecular dynamics is an important method for studying the structure and properties of molecular systems, which is widely used in carbon nanotubes [17], solar cells [18], energetic material [19], biomedicine [20], and so on.

3 Cocrystal explosives

3.1 Synthetic methods

Cocrystal explosives have been synthesized in a variety of ways, including the solvent evaporation, spray drying, vacuum freeze-drying, ball milling, electron spray deposition, self-assembly, and so on. Liu *et al.* [21] prepared hexanitrohexaazaisowurzane (CL-20)/DNDAP cocrystals by slow evaporation and spray drying methods. Nano-CL-20/1,3,5,7-tetrachitro-1,3,5,7-tetrachitroheterocyclic octane (HMX) and CL-20/2,4-DNI cocrystals were prepared also by spray drying method [22,23]. Gao *et al.* [24] applied vacuum freeze-drying method to prepare nano-CL-20/NQ Cocrystal. Qiu *et al.* [25] synthesized nanoscale CL-20/HMX high explosive cocrystal by bead milling. Nano-CL-20/2,4,6-trinitrotoluene (TNT) cocrystal explosives were obtained by mechanical ball milling with 0.38 mm grinding beads [26]. The electron spray deposition was applied to prepare a series of nanosized CL-20-based energetic cocrystals [27]. Liu *et al.* [28] prepared CL-20/DNDAP cocrystals *via* an efficient self-assembly in slightly soluble-medium. By the same method, CL-20 and HMX nanocrystals were also obtained [29]. In addition, there are some improved new methods. For example, when prepared pure CL-20/HMX crystal, solvent evaporated from a saturated solution of the stoichiometric mixture in the presence of a high boiling anti-solvent [30]. Li *et al.* [31] developed a microchannel-confined crystallization strategy, by which CL-20/HMX cocrystal with desired shape and size was prepared.

3.2 Species

The first cocrystal explosive, CL-20/TNT, was synthesized with a molar ratio of 1:1 (as shown in Figure 1a) by Bolton and Matzger in 2011 [32]. It has been proved by experiments that an approximate doubling of the impact stability is achieved than that of CL-20, which indicates the successful application of cocrystal technology in the field of energetic materials. In 2012, they synthesized CL-20/HMX cocrystals (as shown in Figure 1b) with a molar ratio of 2:1, which exhibit greater power than HMX and maintain the same impact safety as HMX [33].

Currently, a large number of cocrystal explosives have been prepared successfully. Table 1 summarizes the cocrystal energetic materials successfully prepared in recent years. From Table 1, not only ordinary energetic

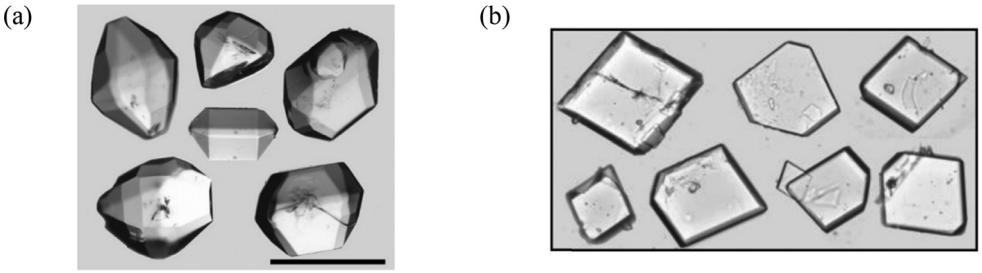

Figure 1: Prismatic habits of cocrystals: (a) CL-20/TNT with a molar ratio of 1:1 [32]; (b) CL-20/HMX with a molar ratio of 2:1 [33].

material molecules (such as TNT, HMX, PETN, NTO, CL-20 *etc*.) but also energetic ionic salts, solvents, and insensitive components were combined with explosive molecules to form cocrystals. For example, CL-20/1-AMTN cocrystals are prepared by composing CL-20 and an energetic ionic salt [34]. TNT/aniline is a cocrystal solvate [35]. CL-20/polyvinyl acetate (PVAc) or PVB are composited CL-20 with insensitive agents [36]. In addition, there are a series of cocrystals based on BTO [37], BTN [38], DADP [39], and DNBT [40], and even some new substances, such as 4*H*,8*H*-difurazano[3,4-*b*:3′,4′-*e*] pyrazine/hydroxylamine [41] and (DDTO + PCL–)/DDTO [42].

CL-20 is a relatively new explosive with high energy density. Due to its high sensitivity, its practical application is limited. Therefore, it is not difficult to see from Table 1 that the synthesis of CL-20 cocrystal explosives has become a current research hotspot. Fortunately, the experimental tests of most CL-20 cocrystal samples showed that its sensitivity is significantly lower than that of CL-20 explosives.

Table 1: Cocrystal energetic materials successfully prepared in recent years

Cocrystals	Molar ratio	Authors and references	Year	Cocrystals	Molar ratio	Authors and references	Year
TNT/TNB	1:1	Ma *et al.* [43]	2017	CL-20/FOX-7	2:1	Ghosh *et al.* [55]	2020
TNB/TNCB	1:1	Tan *et al.* [44]	2021	CL-20/NM	1:2	Zhang *et al.* [56]	2021
HMX/PNO	1:1	Lin *et al.* [45]	2017	CL-20/TATB	3:1	Xu *et al.* [57]	2015
HMX/BTNEN	2:1	Zohari *et al.* [46]	2021	CL-20/DNP	2:1	Goncharov *et al.* [58]	2015
HMX/ANPyO	4:1/8:1	Xue *et al.* [47]	2021	CL-20/DNG	1:1		
PETN/TKX-50	1:1	Xiao *et al.* [48]	2019	CL-20/MDNT	1:1	Stephen *et al.* [59]	2016
NTO/TZTN	1:1	Wu *et al.* [49]	2015	CL-20/TKX-50	1:1	Xiao *et al.* [48]	2019
DNAN/NA	1:1	Sun *et al.* [50]	2019	CL-20/DNT	1:2	Liu *et al.* [60]	2016
DNAN/DNB	1:1			CL-20/DNT	1:1	Liu *et al.* [61]	2018
FTDO/BTF	3:1	Zelenov *et al.* [51]	2020	CL-20/1,4-DNI	2:1	Tan *et al.*[62]	2019
CTA/BTF	2:1	Foroughi *et al.* [52]	2020	CL-20/2,4-DNI	1:1	Liu *et al.* [23]	2019
DAF/ADNP	1:1	Bennion *et al.* [53]	2017	CL-20/DNDAP	2:1	Liu *et al.* [21]	2018
BTO/ATZ	1:2	Zhang *et al.* [54]	2016	CL-20/MTNP	1:1	Ma *et al.* [63]	2017
BTO-based	—	Tao *et al.* [37]	2018	CL-20/MDNI	1:1	Yang *et al.* [64]	2018
BTN-based	—	Ma *et al.* [38]	2019	CL-20/4,5-MDNI	1:1		
DADP-based	—	Landenberger *et al.* [39]	2015	CL-20/MMI	1:2/1:4	Liu *et al.* [65]	2019
DNBT-based	—	Bennion *et al.* [40]	2015	CL-20/TFAZ	1:1	Liu *et al.* [66]	2019
4*H*,8*H*-difurazano[3,4-*b*:3′,4′-*e*]pyrazine/hydroxylamine	1:2	Nyder *et al.* [41]	2021	CL-20/ benzaldehyde	1:2	Bao *et al.* [67]	2020
TNT/Aniline	1:1	Fondren *et al.* [35]	2020	CL-20/PVAc or PVB	3:1/2:1/1:1/ 1:2/1:3	Li *et al.* [36]	2022
(DDTO $^{+}$ PCL^{-})/DDTO	1:1	Feng *et al.* [42]	2022	CL-20/1-AMTN	1:1	Zhang *et al.* [34]	2018

4 Application of molecular dynamics

4.1 Design and synthesis of cocrystals

4.1.1 Electric field intensity prediction

In the experiment, applied electric field is used in the desolvation of cocrystal to avoid the danger caused by heating. Wang and Zhu [68] simulated the polarization and electric-field-assisted desensitization of CL-20/DMF solvent Cocrystal by molecular dynamics, and verified that the electric-field-assisted desolvation of the CL-20/DMF cocrystal is more favorable in the electric field strength range of 0.2 –0.4 V/Å.

4.1.2 Temperature determination

Temperature has a great influence on the quality of cocrystal energetic materials. Molecular dynamics was used to simulate the crystal growth process to predict the suitable temperature for the synthesis experiment. Han *et al.* [69] studied the CL-20/HMX-isopropanol (IPA) interface modeling at different temperatures by molecular dynamics simulations, and indicated that IPA molecules are more likely to aggregate on cocrystal surfaces at lower temperatures. With the increase in temperature, the strength of hydrogen bond interaction between cocrystal and solvent gradually increases. The hydrogen bond strength of (100) and (011) interface models is the highest at 335 K. Molecular dynamics results of Zhu *et al.* showed that the temperature of CL-20/MTNP cocrystal synthesis should be lower than 313 K, in order to avoid ethanol solvent from attaching to the cocrystal surface [70]. For the formation of DNP/CL-20 cocrystal, considering the influence of methanol and ethanol solvent, the temperature should be controlled at 308 K [71].

4.1.3 Solvent selection

Solvent plays a key role in the preparation of cocrystal energetic materials. The optimal solvent for the synthesis can be predicted by molecular dynamics. Liu *et al.* [72] carried out molecular dynamics simulations of the cocrystal formation process in different solvents. Compared with ethyl acetate and acetone, NTO/TZTN cocrystal is easier to be prepared with methanol as solvent. However, for CL-20/HMX cocrystal, the mixed solvent dimethyl sulfoxide(DMSO)/acetonitrile(ACN) is preferred to grow and is more stable [73]. Zhang *et al.* [74] simulated and analyzed the interaction between a CL-20/HMX cocrystal surface and DMSO/ACN co-solvent by establishing a CL-20/HMX solvent interface model, showing that CL-20/HMX cocrystals tend to form when the solvent molar ratio of DMSO to ACN is 1:3. Wu *et al.* [75] studied the effects of six solvents on the formation and morphology of CL-20/TNT cocrystal explosive. The results show that CL-20/TNT is easier to form cocrystal in medium polar solvents ethanol and acetonitrile. Sha *et al.* [76] explored the effects of the water layer on the CL-20/TNT cocrystal surfaces, and suggested that the (002) face was identified as the least affected by water erosion.

4.1.4 Compositional proportion

The molar ratio of components directly determines the formation of cocrystals. It is predicted by molecular dynamics and guides the feeding ratio of synthetic experiments. Hang *et al.* [77] studied CL-20/TNAD cocrystal with different component ratios, indicating that the component ratio of 1:1 is more stable and insensitive. According to the results of Wu *et al.* [78], CL-20/MDNI cocrystals may have better mechanical properties and stability when the molar ratio is 3:2. A molecular dynamics study by Ding *et al.* [79] showed that CL-20 and nitroguanidine (NQ) at a molar ratio of 1:1 present a large binding energy and good mechanical properties (as shown in Figure 2 and Table 2). Therefore, CL-20 and NQ form a stable cocrystal structure

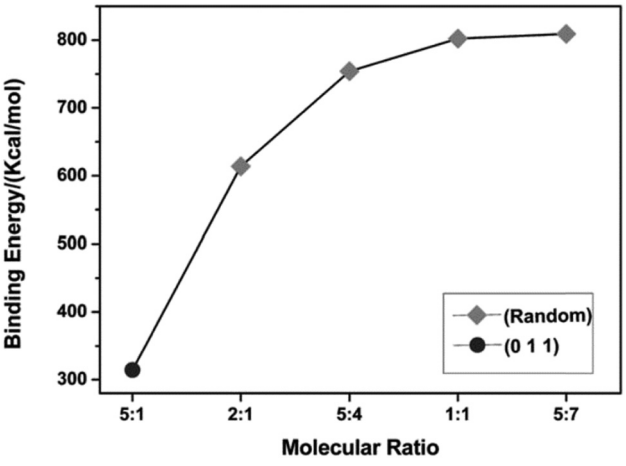

Figure 2: Change rules of binding energy at different faces and ratios [79].

Table 2: Mechanical properties of CL-20/NQ cocrystal models with different molecular ratio[a] [79]

Complex	5:1	2:1	5:4	1:1	5:7
C_{11}	17.118	9.404	10.915	11.268	6.924
C_{12}	5.200	4.885	3.502	5.547	3.925
C_{13}	6.270	4.049	3.101	5.409	3.475
C_{14}	−0.509	−0.468	−0.311	0.530	0.311
C_{15}	−0.911	−0.423	−0.349	−0.121	−0.626
C_{16}	−0.127	0.160	−0.249	−0.023	−0.193
C_{22}	8.764	7.914	10.319	10.688	8.220
C_{23}	3.587	3.475	4.143	4.440	4.156
C_{24}	−1.179	0.015	0.395	0.020	0.233
C_{25}	0.110	−0.122	0.217	−0.279	−0.219
C_{26}	−0.531	−0.228	0.537	0.537	0.081
C_{33}	15.654	8.972	8.347	10.306	7.088
C_{34}	−0.096	0.012	−0.112	0.221	−0.323
C_{35}	3.665	0.628	−0.189	0.188	0.587
C_{36}	−0.463	0.099	−0.013	−0.318	−0.024
C_{44}	2.263	2.964	1.088	2.217	2.845
C_{45}	0.327	−0.095	0.115	0.158	0.340
C_{46}	−0.910	−0.227	0.252	−0.102	0.451
C_{55}	3.874	2.384	2.347	1.628	2.817
C_{56}	−0.190	−0.320	−0.516	0.352	−0.231
C_{66}	5.222	3.486	3.390	3.424	1.231
Bulk modulus (K)	7.227	5.641	5.824	4.966	4.998
Shear modulus (G)	3.386	2.586	2.290	1.754	1.894
$C_{12}-C_{44}$	2.937	1.921	2.414	3.330	1.080
Poisson's ratio (γ)	0.298	0.301	0.326	0.342	0.332
Tensile modulus (E)	8.803	6.730	6.073	4.708	5.046
K/G	2.135	2.181	2.543	2.831	2.639

[a] All values are in GPa.

with a molar ratio of 1:1. Han *et al.* [80] predicted that HMX/MDNI cocrystals form more easily at a molar ratio of 1:1. The molecular dynamics calculation results of Song *et al.* [81] and Feng *et al.* [82] show that various Cocrystals with different molecular ratios formed by CL-20, HMX, FOX-7, TATB, NTO, and DMF are most stable at low molar ratios, such as 2:1, 1:1, 1:2, and 1:3. Xie *et al.* [83] calculated binding energy and mechanical properties and found that HMX/2-picoline n-oxide cocrystal was easier to form at molar ratios of 1:1, 2:1, and 3:1. The results of Wei *et al.* [84] show that HMX/FOX-7 cocrystal formed at 1:1 molar ratio has good mechanical properties. Li *et al.* [85] calculated the binding energy between five growth planes and another random plane of HMX in 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane/nitroguanidine (HMX/NQ) cocrystals with different molecular molar ratios, indicating that HMX and NQ mainly form cocrystals with a molar ratio of 1:1 on the (020) and (100) crystal planes. Shi *et al.* [86] reported that HMX/RDX cocrystals with a molar ratio of 1:1 have good thermal stability and mechanical properties. Hang *et al.* found that CL-20/HMX [87], CL-20/FOX-7 [88], and CL-20/RDX [89] with a molar ratio of 1:1 have higher binding energies and better mechanical properties. They also reported that when the molar ratio is 2:1, 1:1, or 1:2, CL-20/NTO cocrystals form more easily [90], and when the molar ratio of CL-20/TNT/HMX cocrystals is 3:1:2 or 3:1:3, the binding energy is higher and the stability is better [91].

In conclusion, the optimal experiment conditions required for synthesis of cocrystals are simulated and predicted by molecular dynamics. It reduces the experimental cost and improves the efficiency, which is of great significance to the design and synthesis of cocrystal explosives.

4.2 Structures and properties of cocrystals

4.2.1 Structures and formation mechanism

The structure of a material determines its mechanical properties and is closely related to its application [92,93]. As a relatively new type of energetic material, the structures and formation mechanism of cocrystal explosives have become active research topics. Li *et al.* [94] established six interface structures between HMX and LLM–105, and researched the interaction energies ($-E_{int}$), radial distribution function (RDF), and mechanical properties by isothermal and isobaric molecular dynamics. It signified that the (1 1 −1)/(1 1 0) interface governed by the O···H hydrogen bond and strong van der Waals forces exhibits excellent ductility and fracture strength. Duan *et al.* [95] discussed molecular structure and intermolecular interaction of CL-20/DNDAP, CL-20/DNT, and CL-20/MDNT cocrystals, and showed that the structure of cocrystal is determined by non-covalent bond interaction. Zhang *et al.* [96] indicated that the interaction between H···O and C···O is the main driving force of the formation, and O···O contributes to the stability for CL-20/TNT cocrystal. Shi *et al.* [97] researched the terahertz (THz) absorption spectra of CL-20/TNT cocrystal and found the presence of C–H···O hydrogen-bonding stretching and bending vibrations. Besides, they concluded that the CL-20 in cocrystal is the same as that in the β-polymorph, other than the initial conformation of ε-CL-20. Xiong *et al.* [98] showed the presence of hydrogen bonds and van der Waals interactions in the TKX-50/RDX cocrystals. Here the hydrogen bonding is mainly between the H atoms of

TKX-50 and the O or N atoms of RDX (as shown in Figure 3). Subsequently, they studied TKX-50/HMX cocrystals, and found that the structure of TKX-50 substituted by HMX is more stable on the plane of slow crystal growth of TKX-50/HMX cocrystals [99]. Furthermore, the molecular dynamics results of Shi *et al.* showed that the binding energies of RDX/HMX [100] and CL-20/1-AMTN [101] decrease with increase in the temperature and that the two cocrystals have good stability.

4.2.2 Mechanical properties

The mechanical properties of energetic materials are not only important parameters to ensure the performance of weapons, but also related to the safety of weapons. The mechanical properties obtained by molecular dynamics simulations are encouraging research. The molecular dynamics results of Hang *et al.* [102] showed that adding TNT into CL-20 improves the mechanical properties of

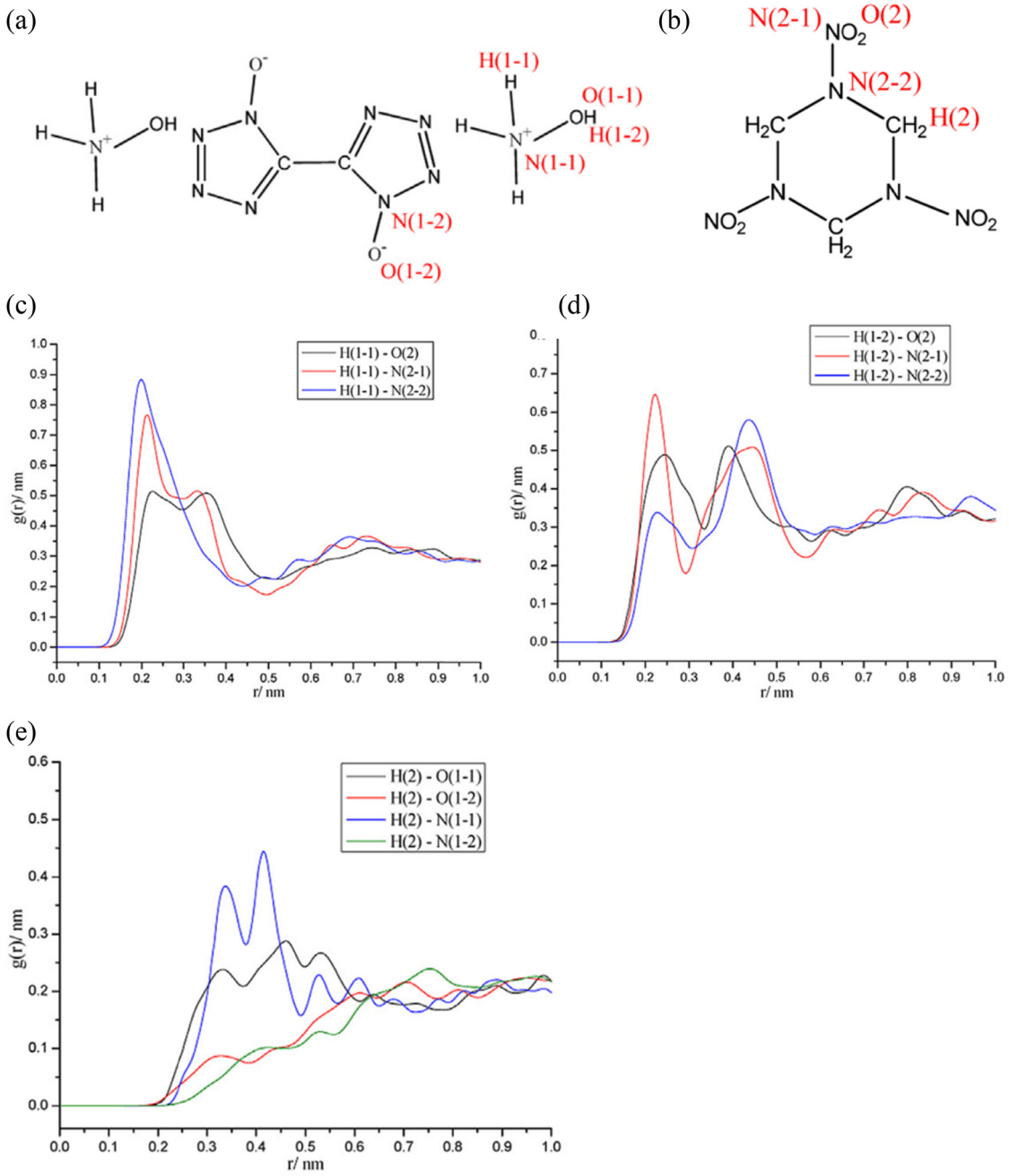

Figure 3: Explanation of hydrogen bonds in TKX-50/RDX cocrystal. (a) Molecular structure of TKX-50. (b) Molecular structure of RDX. (c–e) RDF spectra of different types. H, O, N atoms of TKX-50 were recorded as H(1-1), H(1-2), O(1-1), O(1-2), N(1-1), and N(1-2); H, O, N atoms of RDX were recorded as H(2), O(2), N(2-1), and N(2-2) [98].

CL-20 effectively. According to the molecular dynamics simulation results of Li *et al.* [103], the 2:1 ratio of LLM-105/HMX cocrystal has the highest binding energy, highest cohesive energy density (CED), shortest maximum N–NO_2 bond length (L_{max}), and greatest ductility. Duan *et al.* [104] concluded that the rigidity and stiffness of the CL-20/DNDAP cocrystal and composite decrease compared to that of CL-20, while the ductility and elasticity are better than that of the two pure components [105].

There are often internal defects such as vacancies, twins, and dislocations during the crystallization process, and bubbles, impurities, holes, and density discontinuities in the process of press-fitting and casting lead to changes in the physical properties. For CL-20/TNT cocrystals, doping defects improve the mechanical properties but have an adverse impact on its sensitivity and stability [106].

In practical application, the mechanical properties of energetic materials are mainly adjusted by adding polymer binder. Molecular dynamics studies indicated that the stability of polymer-bonded explosives (PBXs) was related to its CED, and the mechanical properties of poly-(phthalazinone ether ketones)/ε-CL-20 cocrystal are obviously better than ε-CL-20 [107]. According to the simulation results of Wang and Xiao, the stiffness of the ε-CL-20/HMX cocrystal-based PBXs with HTPB is weaker and its ductility is better than those of the cocrystal [108]. Cao *et al.* [109] showed that adding a small amount of polymer adhesive reduces the modulus of CL-20/TNT cocrystals, while among the four polymers, fluororubber (F_{2311}), fluororesin (F_{2314}), PVAc, and polystyrene (PS), only F_{2311} and F_{2314} increase ductility. For CL-20/DNB cocrystals, among the six fluoropolymers, CL-20/DNB/F_{2311} has the best mechanical properties, the highest intermolecular interaction energy, the best compatibility, and highest stability [110]. Zhang *et al.* [111] believed that hydrogen bond interactions play a major role between PEG and CL-20/DNB cocrystal, and CL-20/DNB cocrystal-based PBXs with PEG have buffer action for external stimuli. Li *et al.* [112] found that with the increase in F_{2311} content, the rigidity of CL-20/TNT-based PBXs decreased, and the toughness improved.

4.3 Sensitivity and decomposition mechanism of cocrystals

Sensitivity is an important index to measure the stability of explosives. It is related to the intermolecular forces. Sha and Zhang [113] simulated the process of water molecules adsorbed onto the surface of CL-20/TNT cocrystals, indicating that hydrogen bonds are formed between water molecules in the air and molecules in CL-20/TNT cocrystals, resulting in a reduction in energy required for N–N bond fracture. In this scenario, the sensitivity of the CL-20/TNT cocrystals is improved but the safety is reduced. To research the shock sensitivity of CL-20 cocrystals, Zhang *et al.* found that the coupling of heat and pressure drives the shock reaction, and the vibration spectrum, specific heat capacity, and the strength of the triggering bond are the determinants of the shock sensitivity. In addition, intermolecular hydrogen bonding effectively buffered the heat of the system, resulting in delayed decomposition reaction and reduced shock sensitivity [114].

The decomposition mechanism of cocrystal provides more microscopic information for understanding initiation mechanism and sensitivity. The thermal decomposition of HMX/DMF and HMX/DNDAP cocrystals represents that the reactivity of HMX molecules with DNDAP is higher at low temperatures, but higher with DMF at high temperature [115]. For CL-20/HMX cocrystals, the C–N bonds of CL-20 molecules in cocrystals are cleaved at lower temperatures under a strong constant field. While for an oscillating field, the thermal effect is strong, but the effect on sensitivity is weak [116]. Under the shock, for CL-20/TNT cocrystal, the polymerization reaction is more likely to occur to form larger clusters, which is not conducive to decomposition [117].

Numerous studies have been performed to investigate why the sensitivity of CL-20-based cocrystals is lower than that of single crystal by analyzing the chemical reaction mechanism of cocrystals and single crystal components using molecular dynamics. Based on the ReaxFF reactive force field, Guo *et al.* found that the decrease in CL-20/TNT cocrystal sensitivity is related to the carbon-rich clusters generated during thermal decomposition of TNT [118] (as shown in Figure 4) and that molecular steric hindrance is the main source of sensitivity anisotropy [119] (as shown in Figure 5). Ren *et al.* [120] showed that the interaction between TNT and intermediate products significantly delays further exothermic chain reaction during the thermal decomposition of CL-20/TNT cocrystals. In addition, the slow decomposition of CL-20/HMX and CL-20/TNT cocrystals is related to the change in decomposition kinetics for CL-20, especially the fracture of N–NO_2 bonds and the decomposition of the molecular skeleton [121]. Furthermore, Zhang *et al.* [122] reported that the initial decomposition step for CL-20/TNT cocrystals under impact is the same as that for its component single crystal. Since the decomposition rate of CL-20 is higher than that of TNT, the heat

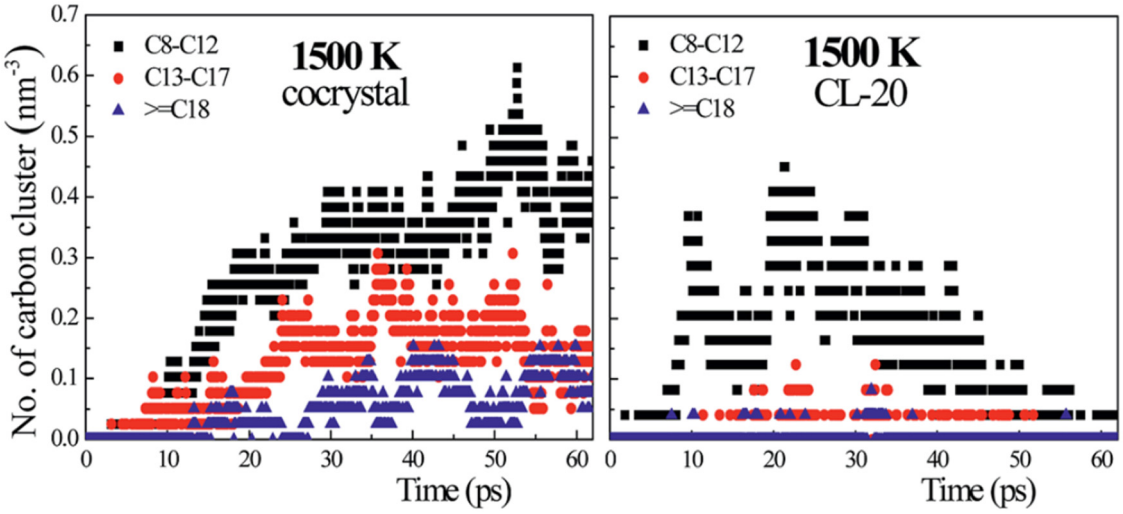

Figure 4: Time evolution of three types of carbon cluster for cocrystal and CL-20. Larger and more carbon aggregates, which slow energy release in chemical reactions, were observed in the cocrystal system [118].

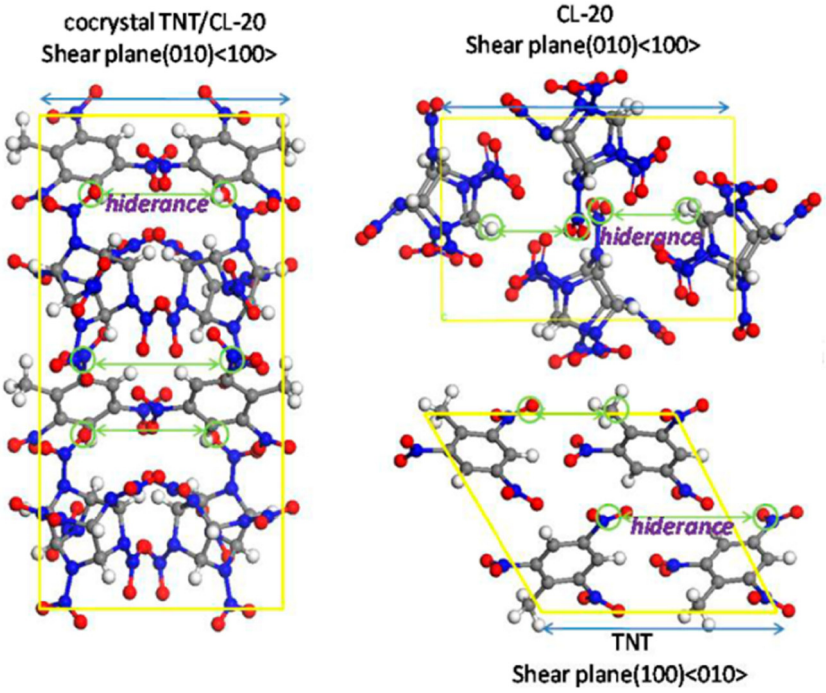

Figure 5: Unit cells of the cocrystal TNT/CL-20 (left), CL-20 crystal (upper right), and TNT crystal (lower right) including schematic illustrations of molecule contacts during shear deformation [119].

released by CL-20 decomposition accelerates the decomposition of TNT, thus reducing its own decomposition rate. Xue *et al.* [123] proposed that the improvement in the stability of CL-20/HMX cocrystals is due to the increased stability of CL-20 and HMX molecules and their enhanced intermolecular interaction. In summary, the sensitivity decrease in cocrystal may be related to many factors, such as the types of molecules and the external stimulations. For example, the shock wave acting on explosives causes not only high temperature and high pressure [124], but also a directional mechanical stress loading [125,126]. The reason for the sensitivity reduction in cocrystal may be more complex than that under the heat. As a consequence, the

decrease in sensitivity of cocrystals compared with that of single crystal is not yet fully understood and requires further study.

5 Conclusion and future directions

5.1 Conclusion

Molecular dynamics based on quantum chemical calculations can reveal the interactions between atoms through the Schrödinger equation or by density functional theory directly. The results are very accurate, but a huge amount of calculation is required, meaning that such methods can only be used to study systems with a limited number of molecules. In classical molecular dynamics, a potential function with empirical parameters is used to calculate the interaction between atoms, improving the calculation efficiency greatly. Therefore, systems with millions of atoms can be considered. However, the applicability of the force field parameters to the research object must be pre-verified.

Molecular dynamics is used widely in research on cocrystal explosives. The material models can refer to perfect, defected, and PBX explosives. External stimuli such as high temperature, shock, and electric field can be considered. Research in the field is currently focused on design and synthesis, structure and properties, the reaction mechanism of decomposition, and sensitivity reduction.

Overall, molecular dynamics simulation results provide detailed micro-level information for in-depth understanding of the structure and properties of cocrystal energetic materials. Accordingly, this review introduces the application of molecular dynamics to cocrystal energetic materials, and the purpose is to encourage researchers interested in the field to design and synthesize high-energy and low-sensitivity energetic materials with practical application value.

5.2 Existing problems

Although many studies on the structure, properties, and chemical reactions of cocrystal energetic materials have been performed, there are still many problems to be solved. For example, there are very few cocrystal energetic materials that can be used in practice. Furthermore, the essence of the stable existence of cocrystals and the essential reason for the relative reduction in cocrystal sensitivity need to be studied further. In addition, potential functions are the key of molecular dynamics. Thus, developing potential functions suitable for more complex models and general force fields suitable for various systems is an urgent requirement.

5.3 Future development directions

The preparation and synthesis of new high-energy and low-sensitivity cocrystal energetic materials with practical application value are research undertakings with great development potential. The formation mechanisms, initiation mechanisms, and sensitivity-reduction mechanisms of cocrystal energetic materials are also topics worthy of in-depth analysis and discussion in the future. In addition, the application of molecular dynamics to cocrystal energetic materials and the establishment of more complex models and general force fields are also likely directions of future research.

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