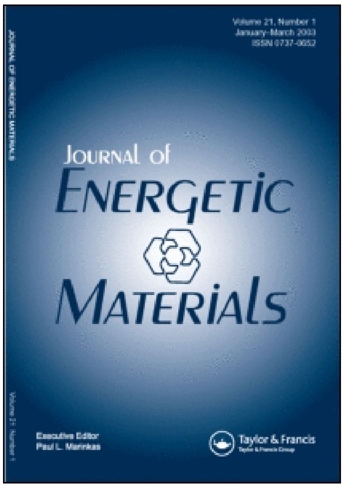

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Numerical Model for Dislocation Mechanism of Detonation

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A mechanism of explosive decomposition during plastic deformation of high explosive crystals was developed. Plastic deformation proceeds through the formation and motion of dislocations, which form shear bands. The mechanism consists of two stages: shear band ignition and burning. The first reaction is decomposition of the explosive molecules in the core of a dislocation during its motion. The density functional theory quantum mechanical method was used to study the physics of this process. The constitutive equations for its description are given. The burning stage represents the process of surface burning of explosive between ignited shear bands. This physical model of the dislocation mechanism is transformed into a numerical model, which was incorporated into a hydrodynamic computer code. The test simulations demonstrate the predictive power of this dislocation model.

Keywords: detonation, dislocation, explosive decomposition

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Introduction

During the last 10 years, great efforts have been made in the development of high-accuracy hydrodynamic computer codes. Nevertheless, these codes cannot predict the process of high explosive initiation by fragment impact in practical applications. The pressure generated by a low moving fragment in an explosive is about 10–15 kbar. The hot spot mechanism does not work at such low pressures. Only one mechanism of high explosive decomposition applies to this case—the dislocation mechanism.

The dislocation mechanism was postulated 25 years ago [1,2]. Coffey [3] and Coffey and Sharma [4] then developed the main phenomenology for this mechanism; that is, the plastic deformation that occurs during shock compression of an explosive crystal proceeds by means of formation and motion of dislocations, and dislocation motion causes decomposition of explosive molecules. This correlates with a great deal of experimental data. However, the detailed physics of the dislocation mechanism was unknown. Therefore, we could not introduce this mechanism into an up-to-date hydrodynamic computer code and that significantly limited its applicability. Thus, a study of detailed physics of the dislocation mechanism has been needed since its introduction. A rigorous numerical model for the dislocation mechanism has also been needed.

Quantum Mechanical Study of the Dislocation Mechanism

The main events of the dislocation mechanism take place in the dislocation core. Therefore, it is necessary to study it at molecular level by quantum mechanical methods. We use the density functional theory (DFT) quantum mechanical method [5,6], which is often used to calculate properties of systems with large numbers of electrons. The molecules of interest are sufficiently large: RDX ($C_3H_6N_6O_6$) has 21 atoms and HMX ($C_4H_8N_8O_8$) has 28 atoms. Moreover, we need to calculate molecular crystals of RDX and HMX. For example, the unit cell of RDX crystal has 8 molecules and contains 168 atoms.

To study the dislocation mechanism, we chose RDX. There is extensive experimental data on its crystalline structure and on its plastic deformation under compression [7]. It is a crystal with orthorhombic space group *Pbca* and with eight molecules per unit cell. The measured lattice parameters are

$$\mathrm{a} = 13.182\ \text{Å}; \mathrm{b} = 11.574\ \text{Å}; \mathrm{c} = 10.709\ \text{Å};$$
$$\alpha = \beta = \gamma = 90 \text{ degrees}$$

Our quantum mechanical calculations reproduce this structure. For a compressed crystal at 50 kbar pressure, our calculations give the following structure:

$$\mathrm{a} = 12.231\ \text{Å}; \mathrm{b} = 10.544\ \text{Å}; \mathrm{c} = 10.016\ \text{Å};$$
$$\alpha = \beta = \gamma = 90 \text{ degrees}$$

Experiments [8] show that RDX single crystal has a slip system of the type {**021**} [**100**]. That means that the slip plane is the {021} plane and the slip direction is the [100] direction (see Fig. 1).

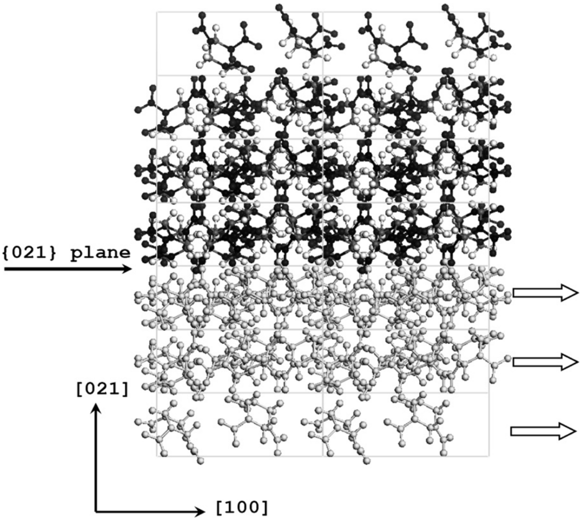


Figure 1. A slip system of the type {**021**} [**100**] in the RDX crystal.

We are interested in the molecular processes during dislocation motion. Let us extract from the large crystal only three layers at the slip boundary. Dislocation within its core has the following structure and stages of motion (see Fig. 2). Now we consider the interaction of two molecules, A and B, in the dislocation core. This interaction defines the dislocation mechanism. The compression of crystal from 0 to 50 kbar leads to overlapping of electronic clouds of molecules A and B. This significantly changes the character of intermolecular interaction from weak to strong and creates important consequences.

During dislocation motion, an RDX molecule makes a jump inside the core. The velocity of the molecule at this jump

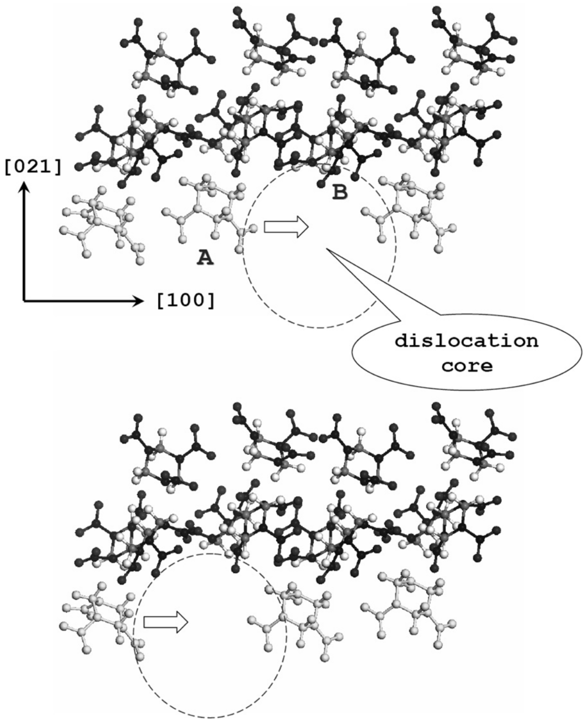


Figure 2. Consecutive steps of dislocation motion in the RDX crystal.

depends on the intensity of the shock wave loading and is between 0 and 10 km/s. To begin the study of the interaction of two selected molecules in the dislocation core, we have performed molecular dynamics simulations. For the calculation of energy, we used the semiempirical method AM1, which is based on the neglect of diatomic differential overlap (NDDO) approximation [9,10]. During shock compression of the explosive crystal, the dislocation velocity is about 2–3 km/s [11]. We have made calculations for several velocities: 0.5, 1, 2, and 5 km/s. The typical examples of the *MD/QC* simulations of molecular collision have the following images (snapshots) for the crystal at $P = 0$ kbar and $P = 50$ kbar (see Fig. 3). In the compressed crystal, we have a breakup of an N-NO_2 bond.

Thus, in the dislocation core we have a new type of dissociation process (see Fig. 4). Collision of two RDX molecules causes large deformation of the N-NO_2 bond that significantly changes its strength. Moreover, motion of the NO_2 group is accompanied by a bombarding molecule up to the moment of a complete break of a N-NO_2 bond. It is a new type of chemical reaction, namely, a mechanically activated reaction. We have used a precise DFT method for calculation of the reaction pathway of the synchronous dissociation process presented in Fig. 4. We found that, at low collision velocity, the energy needed for bond breaking is about 15 kcal/mol (Fig. 5). As the velocity increases, the energy drops to zero and even becomes negative. This is a fundamental result. It explains zero activation energy for chemical processes under pressure and shear (in other words, under compression + deformation) [12–14].

Now it is possible to describe the main features of the decomposition process under high pressure and shear deformation. The compression of a solid explosive decreases distance between molecules, creates conditions for strong interaction between them, and blocks the rotation of molecules at collision. Shear deformation proceeds through the generation and motion of dislocations. Collision of the molecules inside a dislocation core causes molecule deformation and decreases to zero the energy required for bond decomposition, which proceeds in a synchronous manner.

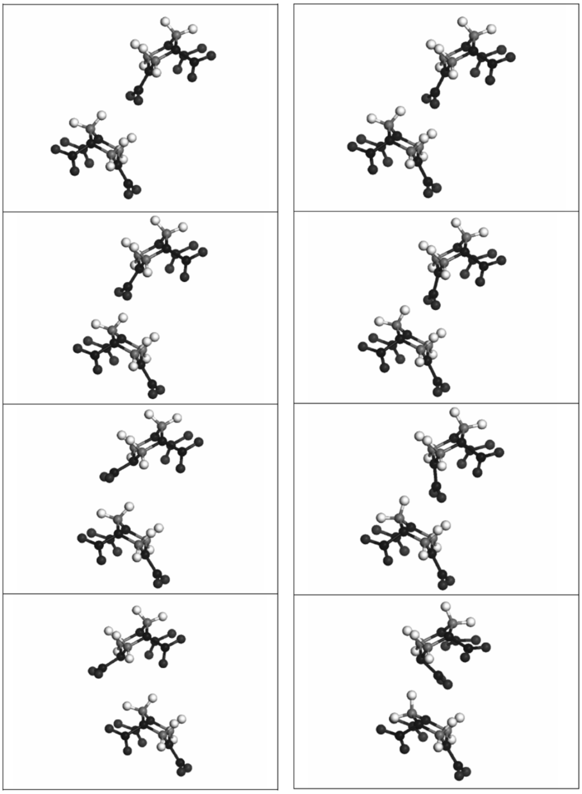


Figure 3. A collision of RDX molecules at dislocation motion; crystal at $P = 0$ kbar (left) and $P = 50$ kbar (right).

Thus, we have developed a mechanism of molecular decomposition during the motion of dislocations in the RDX crystal; that is, we have studied the physics of the dislocation mechanism. One can suppose that the same mechanism works at shock compression of the HMX crystal, because an HMX molecule is very similar to an RDX molecule.

Numerical Model for the Dislocation Mechanism

To introduce the dislocation mechanism into a hydrodynamic code, it is necessary to develop a numerical model. The quantum

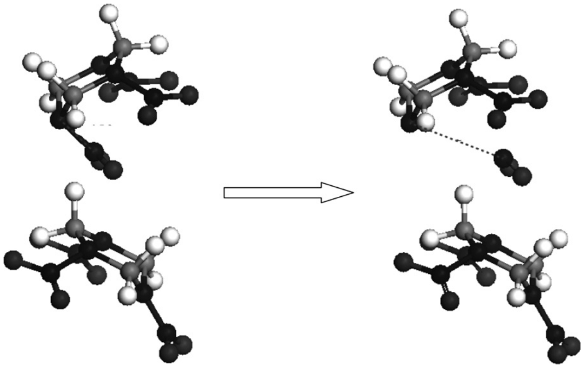


Figure 4. A breakup of the N$-$NO$_2$ bond at collision of molecules (synchronous breakup).

mechanical investigation gave us detailed physics of RDX molecule breakup. It is the first step of RDX decomposition. We now derive the governing expression for this step.

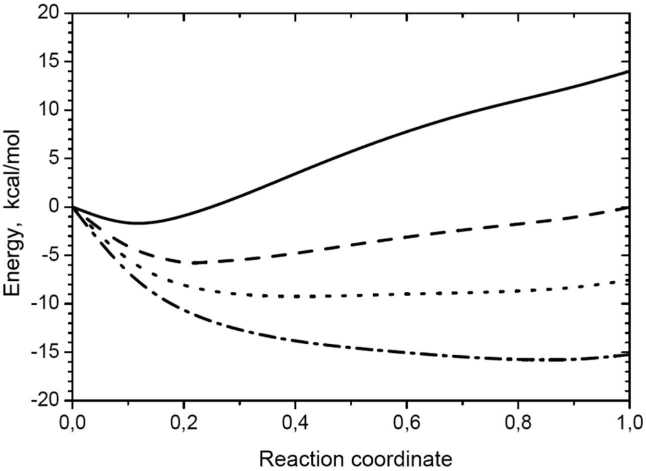


Figure 5. Energy of dissociation of the N$-$NO$_2$ bond for a process inside the dislocation core: collisions with velocities 0.5 km/s (solid line), 1.0 km/s (dash line), 2.0 km/s (dotted line), and 5 km/s (dash-dotted line).

The first reaction, which actually initiates decomposition process, is breaking of the N$-$NO$_2$ bond and formation of the primary radicals. We understand the physics of this process and can prepare a formula to describe it. It is typical bimolecular process. Therefore, one can write the following classical expression for it:

$$\left(\frac{d[R]}{dt}\right)_{dis} = K[A][A]$$

where K is the rate constant:

$$K = Z\exp\left(-\frac{E_{dis}}{RT}\right)$$

Here Z means frequency of molecule collisions (1/s) and exp $(-E_{dis}/RT)$ means the probability of reaction (bond dissociation) for each collision.

Let us consider frequency of collisions Z. It is proportional to shear stain rate $\dot{e}_{ij}$ and to some function of the collision parameter χ.

$$Z = a\ \dot{e}_{ij}F(\chi)$$

Here a is a proportionality coefficient. The physical meaning of the collision parameter is given in Fig. 6. At $\chi \rightarrow 0$, the effectiveness of a collision $F(\chi) \rightarrow 1$. The parameter χ decreases with the compression of a crystal and can be calculated from the Hugoniot curve as a function of shock pressure $\chi = f(P)$. Our estimations for the RDX crystal show that $\chi \rightarrow 0$ at a pressure P of 8–10 kbar. In our hydrodynamic code simulations we use the following approximation of the collision effectiveness $F(\chi)$ on pressure P (Fig. 7).

Parameter E_{dis} decreases with increasing collision velocity (see Fig. 5). The collision velocity is proportional to dislocation velocity, which increases with shock wave intensity and is approximately equal to shear wave velocity. Thus, E_{dis} can be

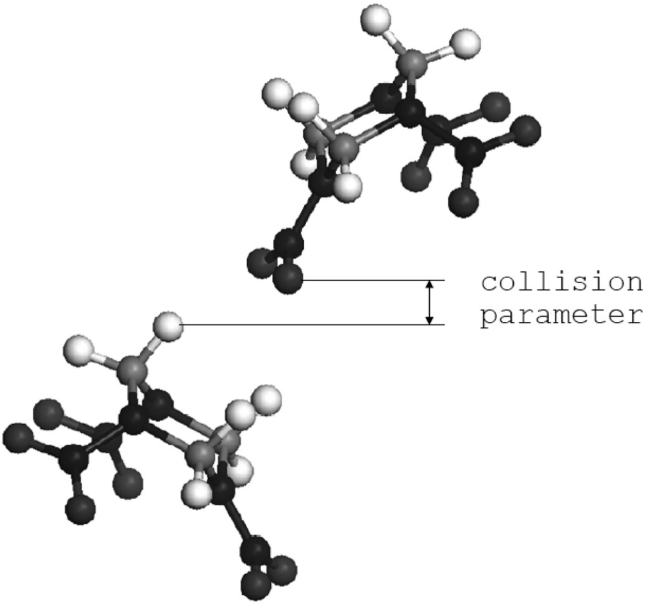


Figure 6. A collision parameter.

expressed as a function of shear wave velocity $E_{dis} = f(V_s)$. In the region of our interest, pressure $P > 5$ kbar and $V_s > 1$ km/s. Therefore, $E_{dis} = 0$ and in this case the exponential term in the rate constant $\exp(-E_{dis}/RT) = 1$. This means that the process does not depend on temperature. This agrees totally with observations of classical mechanochemistry, which are

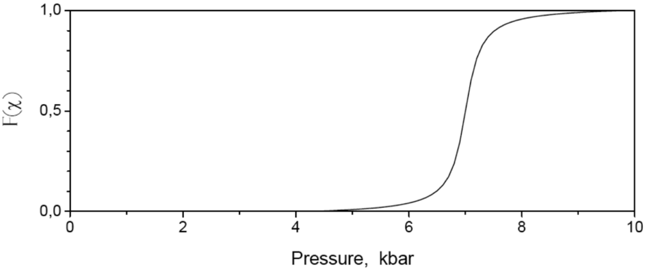


Figure 7. Dependence of the collision effectiveness $F(\chi)$ on pressure P.

reactions under pressure and shear [12–14]. We obtain the following expression for rate of radical generation:

$$\left(\frac{d[R]}{dt}\right)_{dis} = K\,[A]\,[A] = a\,\dot{\gamma}\,F(\chi)\,[A]\,[A]$$

Here a is a calibrated parameter.

The primary radicals generated at dislocations motion activate some sequence of reactions that gives final products. In our calculations we use the following kinetic scheme:

1. $\mathbf{A} \rightarrow \mathbf{R}$ (at dislocation motion)
2. $\mathbf{R} \rightarrow \mathbf{I}$
3. $\mathbf{I} \rightarrow \mathbf{C}$
4. $\mathbf{A} + \mathbf{I} \rightarrow \mathbf{R} + \mathbf{I}$

Here A represents the initial RDX molecule, R is a radical, I is an intermediate product, and C is a final product. The reaction (4) represents an autocatalytic reaction. One can write a formulation for calculating the rates of change of all the components as:

$$\frac{d[A]}{dt} = -\left(\frac{d[R]}{dt}\right)_{dis} - K_4[A]\,[I]$$

$$\frac{d[R]}{dt} = \left(\frac{d[R]}{dt}\right)_{dis} - K_2[R] + K_4[A][I]$$

$$\frac{d[I]}{dt} = K_2[R] - K_3[I]$$

$$\frac{d[C]}{dt} = K_3[I]$$

where K_2, K_3, and K_4 are rate constants for appropriate reactions (2)–(4)

$$K_i = Z_i \exp\left(-\frac{E_i}{RT_{band}}\right)$$

E_i is the activation energy, Z_i is the preexponential factor, T_{band} is the temperature in the shear band, and $\left(\frac{d[R]}{dt}\right)_{dis}$ is the rate of radical generation by moving dislocations (process 1). Clearly, the process described by (1)–(4) is a purely homogeneous mechanism. It acts in the shear band region. The generation of temperature in the shear band is a result of shock compression and additional heating due to plastic work. The increase in temperature due to the shear process is calculated by the formula:

$$\Delta T_{plas} = \frac{\Delta Q}{C_v} = \frac{1}{C_v}\int \left(\frac{dQ}{dt}\right)_{plas} dt = \frac{1}{C_v}\int S_{ij} \cdot \dot{e}_{ij} dt$$

where S_{ij} is deviatoric stress, $\dot{e}_{ij}$ is deviatoric strain rate, μ is viscosity, and C_v is heat capacity.

Now let us move from the microlevel to the mesolevel. Real explosive compositions consist from grains, which in turn consist of explosive crystals. During deformation of an explosive crystal, the moving dislocations create shear bands. The decomposition process in shear bands starts with radical generation and proceeds according to the homogeneous process (1)–(4) until the

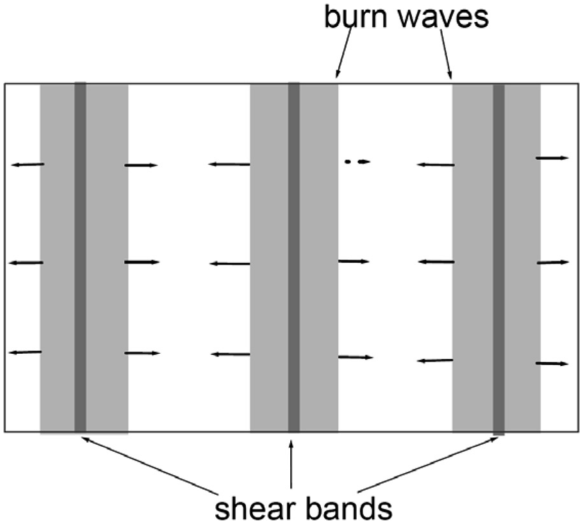


Figure 8. Burning of explosive between ignited shear bands.

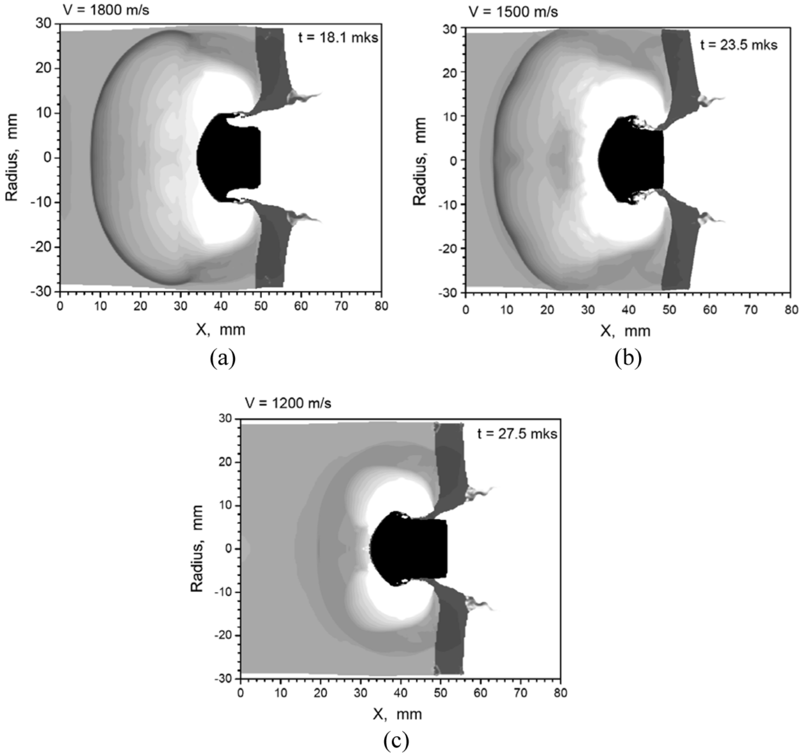
total exothermic reaction sequence ignites shear bands. Then these ignited shear bands undergo classical surface burning.

Thus, the overall decomposition mechanism (called the *dislocation mechanism*) has two stages:

1. Ignition stage (homogeneous process)
2. Burning stage (heterogeneous process)

This can be presented schematically as in Fig. 8. The decomposition rate is calculated as

$$\frac{d\lambda}{dt} = \frac{V}{b_o/2} = \frac{2\,V}{b_o}$$



(a) (b)

(c)

Figure 9. Initiation of detonation at bullet velocity $V = 1{,}800\,\text{m/s}$ (a) and $V = 1{,}500\,\text{m/s}$ (b) and failure of detonation at bullet velocity $V = 1{,}200\,\text{m/s}$ (c).

where V is the surface burning rate (i.e., burn front velocity) and b_o is the distance between shear bands. There exists a classical expression for dependence of V on pressure

$$V = V_o(P/P_o)^n$$

Here V_o is the rate at the reference pressure P_o. There are enough experimental data for V_o.

This numerical model for the dislocation mechanism has been incorporated into the RUSS-2D hydrodynamic code [15]. This model was calibrated to the Composition B explosive composition. The model reproduces the experimental data [16,17] well. Typical results of numerical simulations are presented in Fig. 9.

In conclusion, development of the dislocation mechanism and its numerical model turns a new page of numerical modeling of applied explosive processes, in particular in computer simulations of explosive initiation by fragment impact.

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