

Detonation initiation in a model of explosive: Comparative atomistic and hydrodynamics simulations

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Abstract. Here we extend consistent simulations to reactive materials by the example of AB model explosive. The kinetic model of chemical reactions observed in a molecular dynamics (MD) simulation of self-sustained detonation wave can be used in hydrodynamic simulation of detonation initiation. Kinetic coefficients are obtained by minimization of difference between profiles of species calculated from the kinetic model and observed in MD simulations of isochoric thermal decomposition with a help of downhill simplex method combined with random walk in multidimensional space of fitting kinetic model parameters.

1. Introduction

As atomistic simulation indicates, the thermal decomposition of condensed phase explosive PETN [1,2] and AB model explosive [3,4] is initiated by chemical reactions within a picoseconds timescale after several atomic oscillations. We developed the kinetic model of chemical reactions observed in a molecular dynamics (MD) simulation. Kinetic coefficients are obtained by minimization of the mean-square deviation between profiles of species calculated from the kinetic model and observed in MD simulations of isochoric thermal decomposition. An approximation of self-sustained detonation wave [3,5] simulation in AB model explosive [4] with optimal parameters of the kinetic model provides verification. MD gives full information about all atoms: coordinates and velocities, therefore an equation of state can be obtained, kinetic processes such chemical reactions, viscosity, heat transport naturally appear as properties of the interatomic potential. However, the detonation initiation requires scales of sample sizes about millimeters and associated microseconds timescales [6], which are unachievable using nowadays computational facilities in a reactive MD.

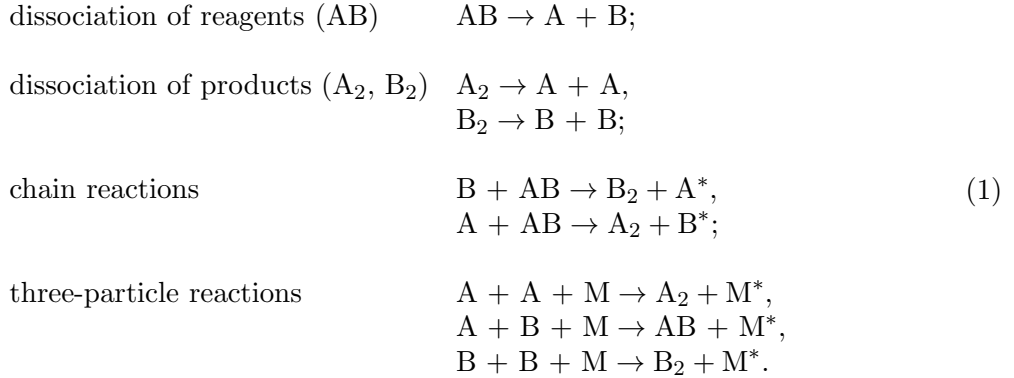
Obtained in this work reaction rates could be naturally used in hydrodynamics modeling of detonation.

2. Two component kinetic model

From analysis of MD simulation a two component kinetic model was proposed [3]. Chemical reactions of reagents AB and products A₂ and B₂ dissociation, chain reactions, and three-particle



collisions with a partition of two radical types A or B are presented in the scheme:



Lets consider a description of AB explosive decomposition where first, second order and back reactions are taken into account:

$$\dot{n}_f = k_1(0.5 - n_f) - k_b n_f + k_2(0.5 - n_f)n_f, \tag{2}$$

where n_f is a concentration of products. The molecule is associated to products after the AB molecule decomposition. In fact radicals A and B were observed in reactions of dissociation AB, A₂, B₂ [5]. These radicals are go in exothermal chain and in three particle reactions with a partition of two radicals [3]. The molecular concentration measured in units of full number of atoms in system and additionally normalized on the amount of atoms in a specific molecule $N_i, i = \text{A+B, AB, A}_2+\text{B}_2$, $n_i = N_i/(a_i N_{\text{tot}})$, where $N_{\text{tot}} = N_{\text{A+B}} + N_{\text{AB}} + N_{\text{A}_2+\text{B}_2}$, a_i is the number of atoms in i -th type of molecule, $a_i = 1$, when $i = \text{A+B}$ and $a_i = 2$, when $i = \text{AB, A}_2+\text{B}_2$; then number of atoms of reacted AB is $N_f = N_{\text{A+B}} + N_{\text{A}_2+\text{B}_2}$. Therefore maximum of molecular concentration in case of diatomic molecules is 0.5 from the atomic concentration. Kinetic coefficients were calculated using the Arrhenius form with a modification of pre-exponential factor by additional power variation of temperature and activation energy dependence on density of energetic material:

$$k_i = \Lambda_i (T/T_D)^{y_i} \exp \frac{E_i^{(a)}(\rho)}{RT}, \tag{3}$$

where $i = 1, 2$ or b associated with rates of 1st, 2nd order and back reactions respectively, $T_D = 10^4$ K is the dimensional factor, time-dependent profiles of temperature and density were taken from MD. An empirical dependence of reactions barrier on density was proposed:

$$E_i^{(a)}(\rho) = E_i^{(a)} \frac{(\rho/\rho_0 - 2.74)^2}{((\rho/\rho_0 - 2.74)^2 + (\rho/\rho_i^{(G)})^{y_i^{(\rho G)}})}, \tag{4}$$

where $E_i^{(a)}$, $\rho_i^{(G)}$, $y_i^{(\rho G)}$ are varied parameters. The dependence in numerator of fraction associates with absence of the barrier when dimensionless density $\rho/\rho_0 = 2.74$, as it has been observed in MD simulation of AB explosive isothermal compression at temperature $T = 40$ K.

Coefficients of chemical reactions were obtained with the help of downhill simplex minimization method [7, 8] and random walk in multi-dimensions. The dimensionality of parameters space $N_d = 15$ was defined by the number of varied parameters: Λ_i , $E_i^{(a)}$, y_i , $\rho_i^{(G)}$, $y_i^{(\rho G)}$, where $i = 1, 2$ or b . As a target function the mean-square deviation of products curves from observed in MD simulation of isochoric thermal decomposition was chosen:

$$Z = \sum_k \sum_{t_{i,k}} \frac{(n(t_{i,k})_k^{(\text{MD})} - n(t_{i,k})_k^{(\text{fit})})^2}{n(t_{i,k})_k^{(\text{MD})} + n(t_{i,k})_k^{(\text{fit})} + \epsilon}, \tag{5}$$

Table 1. Initial states for the simulation of thermal decomposition. The states obtained by MD simulation and calculated from Hugoniot curve [5] for different densities are indicated with (MD) and (H) superscripts, respectively.

ρ/ρ_0	$P^{(MD)}$ (GPa)	$T_0^{(MD)}$ (kK)	$P^{(H)}$ (GPa)	$T_0^{(H)}$ (kK)
1.857	15.68	1076.2	15.65	1012.4
1.95	19.64	1476.6	20.99	1550.07
1.96	21.96	1624.5	21.8	1641.7
1.98	21.77	1660.4	23.41	1797
2	23.77	1804.3	24.78	1937.23
2.03	24.24	1836.5	27.4	2207.42
2.08	27.17	2076.4	31.6	2640.61
2.1	28.37	2231.3	33.48	2836.84

where $\epsilon = 10^{-4}$, k indicates a specific simulation in the series of simulations (8) with annealing temperature T_0 and initial states presented in the table 1, $\{t_{i,k}\}$ the moment of program output for the simulation k , N is the full amount of outputs in all simulations for series. Indexes (MD) and (fit) are associated with results obtained in MD simulations and integration of the kinetic model equation 2. The step of result output τ for densities $\rho < 1.75\rho_0$ was $\tau = 0.3$ ps; for $\rho \geq 1.75$, $\tau = 0.07$ ps correspondingly. Parameters of absolute value less then 10^{-12} were set to zero, $y_b = 0$ in all optimization calculations. Some parameters were obligated to limitation of variation: $\rho_i^{(G)} \leq 12$, $y_i^{(G)} \leq 12$. Penalties of target function (5) were considered for reaction barriers:

$$\begin{aligned} |E_1^{(a)} - 1.5| > 1, & \text{ then } Z = Z + (E_1^{(a)} - 1.5)^2, \\ E_2^{(a)} > 2, & \text{ then } Z = Z + (E_2^{(a)} - 2)^2, \\ E_3^{(a)} > 3, & \text{ then } Z = Z + (E_3^{(a)} - 3)^2. \end{aligned} \quad (6)$$

For parameters $y_i^{(\rho G)}$ analogues limitations were considered:

$$|y_i^{(\rho G)} - 1| > 0.5, \text{ then } Z = Z + (y_i^{(\rho G)} - 1)^2. \quad (7)$$

The solution of equation (2) were obtained numerically. Initial conditions were taken from MD simulation. Formal macrokinetics in hydrodynamics uses a mass fraction of solid phase, therefore the kinetic coefficient of second order reactions must be renormalized by dividing on number of atoms in the reagent molecule AB $k_2 = k_2/2$ when A and B molecules have equal masses. In a recently published work pre-exponential factors in the reaction rates are replaced by their natural logarithm in tables with results, these coefficients should be taken as a power of exponent to get a pre-exponent in ps^{-1} .

3. Simulation techniques

An atomistic simulation of detonation in AB model explosive was studied actively since Brenner and co-workers developed a reactive empirical bond-order (REBO) potential [4]. We use the AB model [5] with maximal half-reactions $A + AB \rightarrow A_2 + B + 3 \text{ eV}$ and $B + AB \rightarrow B_2 + A + 3 \text{ eV}$ barrier $E_b = 0.198 \text{ eV}$, which still provides a stable planar detonation front [5]. Recently developed kinetic model [3] which proposed in this work need to run atomistic simulations of isochoric thermal decomposition of AB explosive with different densities. A molecular FCC crystal with AB molecules initially orientated in $x = [100]$ direction had unit cell volume 0.141 nm^3 which corresponds density $\rho_0 = 1.3 \text{ g/cm}^3$ and $P = 0$ ($T = 40 \text{ K}$). The sample was placed to the box $L_x \times L_y \times L_z = 10 \times 10 \times 8 \text{ nm}^3$ with imposed periodic boundary conditions.

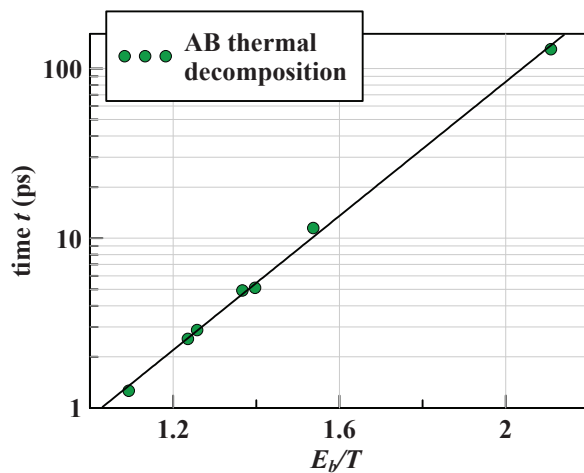


Figure 1. The time needed to reach 50% of products is approximated by Arrhenius law with the activation energy $E_a = 0.88647$ eV and preexponential factor $\Lambda_a = 93.3$ ps $^{-1}$ for reactions observed in series of MD simulations. The material was prepared initially to the state associated with a shock compression to densities more then $1.85\rho_0$ (table 1). An inversed temperature is normalized by the reaction barrier E_b [5].

Concentration of atoms in the sample $n_0 = 5.67376 \times 10^{21}$ cm $^{-3}$ associates to $N \approx 30000$ atoms. In a case of study thermal decomposition in samples with different densities of model explosive, a set of samples were prepared using Langevine thermostat with temperature $T_0 = 1400$ K and worked 2–8 ps after that the thermostat was turned off:

$$\rho/\rho_0 \in \{1, 1.25, 1.5, 1.75, 1.95, 2, 2.5\}. \quad (8)$$

FCC molecular crystals with densities ρ and lattice constant a ($a^3 = a_0^3 \rho_0 / \rho$, where $a_0 = 0.522$ nm) were created. The sample size and boundary conditions were as for the density ρ_0 , therefore number of atoms varied in range $N \approx 30$ –132 thousands. The initial velocity dispersion of atoms in generated crystal corresponds with temperature $T = 2400$ K. Densities of explosive $\rho > \rho_0$ lead to faster reaction start then in a sample of density ρ_0 . As simulations showed fractions of product molecules A_2 and B_2 from all atoms $\lambda_{A_2+B_2} = N_{A_2+B_2}/N_{\text{tot}} \leq 5 \times 10^{-3}$, note that thermostat parameters were varied for each density of the sample. Geometrical sizes of samples were chosen to satisfy a condition of statistically significant number of reacted molecules A_2 and B_2 when $\lambda_{A_2+B_2} \approx 10^{-2}$ has already formed.

Series of AB explosive thermal decomposition at the initial state corresponded to Hugoniot of non-reacted AB [5] with different compression ratios V/V_0 were simulated, where V_0 —is a unit volume of the FCC lattice for $P_0 \approx 0.5$ GPa, $T_0 = 40$ K. All samples in the series were placed to periodic boundary condition box of size: $L_x \times L_y \times L_z = 10 \times 16 \times 16$ nm 3 and contained approximately 277–300 of atoms. The Langevine thermostat with adjustable target temperature to minimize modulus of Hugoniot function was used to relax samples:

$$H = \epsilon(P, V) - \epsilon(P_0, V_0) - P(V - V_0), \quad (9)$$

where ϵ is total energy of the system in MD. MD samples had been relaxed by thermostat for $\tau = 0.5$ ps, then the thermostat was turned off. The pressure in samples was lower then Hugoniot curve predicts. A comparative table with results of samples preparation associated with (index (MD)) and approximation of pressure and temperature for shock compressed AB material (index (H)) [5] are presented in the table 1.

The relaxation time is limited by fast start in ≈ 1 ps of exothermal reactions. The time needed to reach 50% of products observed in MD simulations series of thermal decomposition initially prepared sample (as in table 1) on reversed initial temperature has an exponential dependence. Arrhenius law parameters were achieved from fitting of the dependence:

$$k = \Lambda_a e^{-E_a/T}, \quad (10)$$

the result is presented on the figure 1.

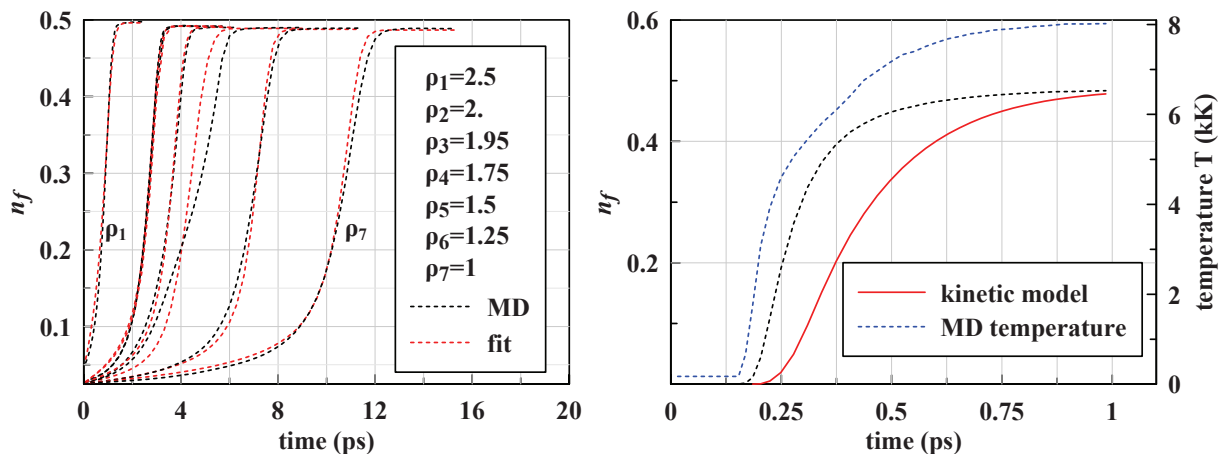


Figure 2. On the left: Products fitted using kinetic model (section 2) in a series of isochoric thermal decomposition of AB model explosive with different densities ρ_i in units of density $\rho_0 = 1.3 \text{ g/cm}^3$ in the uncompressed AB. Initial temperature of all AB samples is $T_0 = 1400 \text{ K}$. On the right: An approximation of kinetics in a self-sustained detonation wave using optimal reaction rate parameters provides agreement of final state after detonation front. However, the reaction rates in the MD simulated detonation front, which are shown by dashed lines, result in faster kinetics than our kinetic model optimized by low-rate isochoric thermal decomposition.

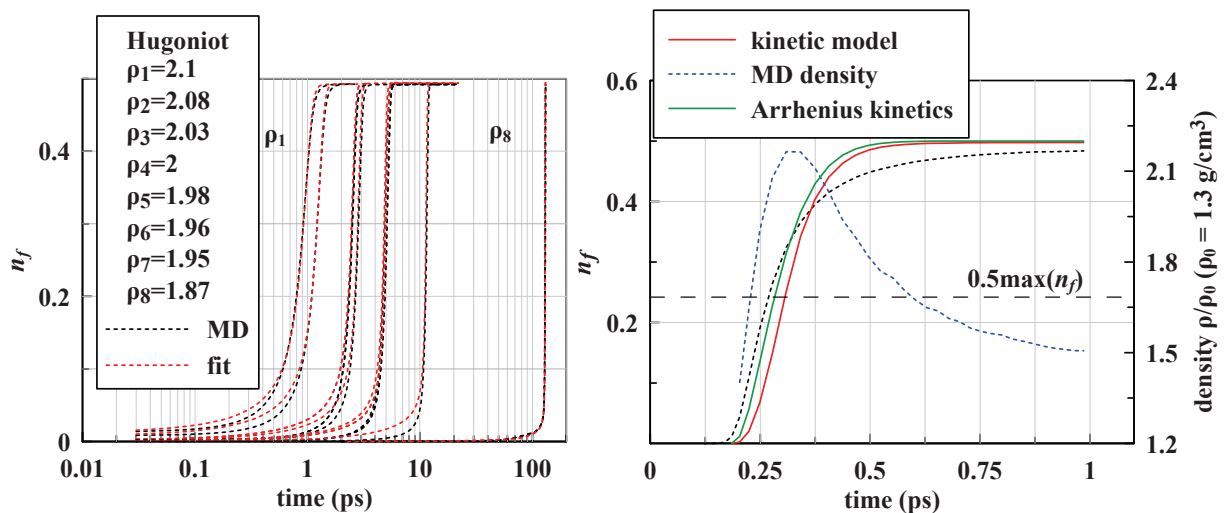


Figure 3. On the left: Fit of products concentration from MD simulation of isochoric thermal decomposition of AB material using optimization of reaction rates in only 1st order kinetics where material was prepared in a state associated with shock compression (1). On the right: An approximation of kinetics in a self-sustained detonation wave by using optimal reaction rate parameters for thermal decomposition of associated to shock-compressed initial states of AB material provides more precise fit of products than ones obtained for parameters achieved from fitting of thermal decomposition with different densities and the same initial temperature (figure 2).

4. 1D steady self-sustained detonation wave approximation

Stationary planar detonation front was performed with moving-window molecular dynamics (MW-MD) [5, 9, 10]. The sample is simulated in moving coordinates, where detonation

front is immovable and uncompressed reagents flow into the front at the detonation velocity $D = 7.54$ km/s [5]. Obtained 1D time-averaged profiles in self-sustained detonation wave were used to get time-dependent fractions of explosive compounds and thermodynamic parameters using a velocity profile in a coordinate system of detonation front $v_{Ax}(x)$, where x —is an axis along detonation wave propagation. Using relation $t = -\int_{x_0}^x dx_1/v_{Ax}(x_1)$ we obtained the time it takes the Lagrangian particle move to the point x from x_0 —reference point.

The kinetic model parameters are used in approximation of self-sustained detonation wave. The model provides greater reaction zone than observed in MD with usage of reaction rates from fitting of thermal decomposition in samples with different densities (equation 8) and the same initial temperature T_0 . The Arrhenius reaction rate is used to approximate products in self-sustained detonation wave by integration of equation: $\dot{n}_f = k(0.5 - n_f)$, where k is defined in equation 10 and determined as described at figure 1. At the beginning of reactions, when the detonation front has just come and AB molecules dissociation is dominating, products are fitted most precisely with Arrhenius form of the kinetic coefficient.

5. Conclusions

A simple two component kinetic model of chemical reactions in AB model explosive is proposed for using in hydrodynamics simulation of detonation. The kinetic model correctly describes final chemical compound in burned AB explosive in self-sustained planar detonation (figure 2). Using of AB material in initial states close to the shock compression in the series of isochoric thermal decomposition with different densities provides more precise approximation (figure 3) of products in self-sustained detonation wave due to faster reactions for high densities of AB material (table 1) than obtained using of the same annealing temperature for different densities of energetic material [3]. An implementation of developed kinetics to hydrocode is a next step of consistent atomistic and hydrodynamic simulations. The hydro-simulation of detonation in AB explosive on proper for real explosives scales gives rise to such simulation in a porous PETN.

References

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