Extinction and growth of cylindrical hotspots in AB model explosive: molecular dynamics studies

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Extinction and growth of cylindrical hotspots in AB model explosive: molecular dynamics studies

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Abstract. Atomistic simulations of a sample with AB model explosive heated quickly up within a small central cylinder were performed with the goal of finding a critical radius of such hotspot. The heating time was chosen to be much shorter than an acoustic time required for rarefaction wave for arriving to the center of hotspot. An isochoric thermal decomposition of AB material evolves inside the hotspot before the arrival of rarefaction wave. We found that the critical radius of such hotspots is determined by the equality of the acoustic time and a characteristic time of isochoric thermal decomposition controlled by initial hotspot temperature. For supercritical hotspots the decomposition of AB material leads to deflagration. The earlier arrival of rarefaction wave extinguishes the chemical reactions in hotspots with the subcritical radius.

1. Introduction

The difference between scales of processes involved in simulation of hotspots (HS) in condensed phase explosives [1] makes a challenge to the modern computational facilities [2–4]. A characteristic time of reaction in PETN [5] or AB [6] energetic material are within picosecond timescale in molecular dynamics (MD) simulation. At the same time, experimental data provides several microsecond timescale for the detonation initiation and associated characteristic reaction times. The macroscopic kinetic models [7] are usually calibrated by experiments, then may be used in the hydrodynamic simulation. Run-distance to detonation [8] data is widely used in the calibration of such macroscopic kinetics. Another kind of models [9] are based on chemical principals and include information from the experiments, where the reaction time is about 1-100 seconds, for example, adiabatic explosion and one dimensional time to explosion.

The difference of “fast” and “slow” heating is in different characteristic times - the reaction time in AB material $t_{\text{react}}$ (time to the acceleration of exothermal reactions), acoustic time of rarefaction immediately created HS $t_a$, duration of heating pulse $t_T$ to create a local high-temperature domain (time of HS creation). “Fast” heating is characterized by almost instant thermal energy deposition into the media. After that, reactions may be occurred and dumping of pressure in the high temperature region due to thermal expansion. In this situation the parameter of pulse duration formally excluded. The simplified model of hotspot provides an understanding of critical size and presented in this paper. “Slow” heating is associated with a mechanical equilibrium of hotspot and surrounding media. In that case, hot gas is trapped within a sample and the absence of pressure gradient leads to the thermal diffusion mechanisms.
of hotspot growth. Also difference between chemical and heating time should be taken into account. There are two limit cases associated with the completed reactions in the end of heating or, if induction time is long enough, the reaction will start after the heating.

2. Timescale characterization of hotspot

An isochoric thermal decomposition time defines critical radius of the hotspots introduced in section 4. There is a possible analysis is presented based on characteristic times contributed to the different processes during extinction or growth of isolated HS.

Let’s assume the heating duration is \( t_T \). This time recognizes that hotspot created by a contact with warm piston or by a short laser pulse. Two other timescales are a characteristic time of exothermal chemical reactions \( t_{react} \) (time to acceleration) and an acoustic (hydrodynamic) time \( t_a \). The acoustic time links the size of HS and velocity of perturbation propagation, which is equal to the sound in heated media for weak perturbations. Formal permutation of these time parameters provides \( 3! = 6 \) relations:

1) a) \( t_T < t_a < t_{react} \), b) \( t_T < t_{react} < t_a \);
2) c) \( t_a < t_{react} < t_T \), d) \( t_{react} < t_a < t_T \);
3) e) \( t_a < t_T < t_{react} \), f) \( t_{react} < t_T < t_a \).

The variants in 1) associated with HS created by “fast” heating and described in the next chapter.

Another widely studied limit case is thermal hotspot. As it is mentioned in previous chapter, this HS is in mechanical equilibrium with surrounding cold media, therefore \( t_T \) is the biggest time. Diffusion processes, thermal conductivity and energy release of high-temperature media from the HS defines a characteristic time to explosion. It should be noted, the mechanical equilibrium blocks deflagration wave propagation (a pressure jump is needed), therefore an additional energy would be deposited to form the front. Variants of point 2) are associated to the thermal hotspots. Last cases in 3) are intermediate ones. If the least time is acoustic e), then a mechanical equilibrium will be observed after heating and hot unreacted material will be in low-density state, the reaction should start later. If the chemical time is shorter than both else as in f), hot products at high pressure will form a shock wave. This case is associated with hydrodynamic calculation without explicit reaction zone. Another specific case of HS is a dynamically formed during the collapse of pore or gas bubble [1,2].

3. Simulation techniques

Simulated samples are melted a priori at density 1.18 g/cm\(^3\) and temperature \( T \approx 77 \) K with the Langevin thermostat. After that a cylindrical hotspot is created within samples. Plane disk has a radius \( L_r = 120 \) nm and width of 16 nm. Periodic boundary conditions are imposed in Z dimension. The creation of HS involves several steps:

(i) The Langevin thermostat equilibrate the sample at \( T = 77 \) K to melt initially and relax pressure to zero,

(ii) An additional Langevin thermostat in the central cylinder with radius of a specific HS,

(iii) Damping thermostat of waves coming to the free surface of the sample is realized by another Langevin thermostat with increasing rigidity as the free surface becomes closer and a target temperature \( T = 77 \) K. This thermostat acts only at \( \phi \) and Z components of atoms velocity, which are perpendicular to the radial motion of the media (\( \phi \) is a polar coordinates angle).

The time of the HS boundary arrival to the domain of damping thermostat defines an available molecular-dynamics simulation time.
4. Simulation results and discussion

An initial perturbation of atoms’ velocity vector isotropically in a space with Maxwellian
distribution equals to the target temperature of Langevin thermostat. The thermostat is turned
on at the next integration step of MD simulation inside given cylinder of HS’s radius. The
time of heating is $t_T = 0.2$ ps and the target temperature is $T = 2400$ K. Characteristic
time of thermostat is two times greater $t_T$. The temperature of HS is approximately 1950 K. Both
temperature and pressure profiles have a “jump” on the boundary of heated and cold material
(Figure 1) while density profile is plain.

The main requirement to preparation is absence of products molecules $A_2, B_2$ at the end
of HS creating. Also an acoustic time $t_a$ should be much larger then the time of heating $t_T$:
$t_T << t_a$, where definitely $t_a$ is a time of the first arrival of rarefaction wave into the center
of HS. Target temperature of the thermostat is limited by fast dissociation of $AB$ molecules.
The last is motivated by the velocity perturbation independently to the whole molecules in the
initial molecular crystal of $AB$. Therefore, a situation of relatively “too high” velocity of atoms
inside one molecule would greatly overstep initial temperature and corresponded to the initial
velocity permutation of atoms.

Different radii of HS provides different time of rarefaction wave arrival. In the center of
sample, an isochoric thermal decomposition is observed before the arrival. We simulate initiation
of reactions in case of HS with different radii $R_{HS} = 20, 23, 25$ nm, and on the figure 3, a products
curve and density in the center of HS is shown, which is taken from fixed cylinder of 3 nm radius.
It is observed, the HS with $R_{HS} = 20$ nm attenuates and the reactions of decomposition stop
at times greater than $t \gtrsim 80$ ps after the start of simulation. In case of HS $R_{HS} = 23$ nm
a slow production of $A_2, B_2$ molecules is observed before the rarefaction wave reflection from
the center of cylinder and after beginning of expansion in the center. This reflection induces
additional increase of density and temperature in the center, therefore reactions accelerate and
formation of deflagration front is observed. An additional maximum of density dependence in
time is shown on the figure 3. In HS with $R_{HS} = 25$ nm, the reactions accelerate and form
additional expansion of the gases outside heated hotspot with rise of the temperature and fall
of the density in the center.

On the figure 2, an initial stage of products curves and associated temperature dependencies
from figure 3 are shown. Dashed lines show temperature dependence and has a decrease after
rarefaction wave arrival. However, before the arrival, this dependences of products mass fraction
and temperature are similar to those in isochoric thermal decomposition simulation. The
**Figure 2.** Temperature (dashed lines) and mass fraction of products (circles) in a small 3 nm central cylinder inside HS as functions of time are similar to ones (black lines) observed in the isochoric thermal decomposition, before the arrival of rarefaction wave. The next Figure 3 shows corresponding evolution of density at the center of HS.

**Figure 3.** Density is shown by dashed lines and mass fraction of products by circles. Blue, red and green colored curves are associated to the HS of 20, 23, 25 nm, while black curves - to isochoric thermal decomposition. Black lines show a slope change when the reaction acceleration is observed in case of critical HS radius.

Isochoric thermal decomposition simulation employs periodic boundary conditions in the box of $16 \times 16 \times 16$ nm$^3$. About 195 thousands of atoms in this box are simulated. It is shown, the fluctuation according to the induction time and local start of exothermic reactions is negligible. A distribution of the local reaction start may be assumed uniform relatively to the boundary of HS and cold media.

In that way, in the simulation of HS the sample width in $Z$ direction should be equal to $L_z = 16$ nm. In case of system with $L_z = 8$ nm non-uniformity of reaction start inside cylindrical hotspot provides artificial uncertainty of critical hotspot.

Series of simulation with described “fast” heating in HS of cylindrical form provides condition...
for the critical radius.

The key characteristics of the “fast” HS are the size of HS and thermodynamic state of the explosive (temperature and density). A critical hotspot size is defined for given density and temperature. If radius of HS is less than the critical, exothermal reactions in the center are similar to the isochoric thermal decomposition, but the reactions decay and stop after rarefaction wave arrival. The rarefaction wave decreases temperature and density inside HS, slows energy release. After reflection of the rarefaction wave from the center, atoms move into the center again and additional spike of density and temperature should be observed. The condition of following HS’s growth is transition to intensive energy release after the reflection of radial rarefaction wave. Otherwise, the HS should decay. In case of HS greater than critical, product molecules formation and expansion out of the center is observed, but the acceleration of reactions happens before the reflection of the rarefaction wave.

5. Conclusion
In this research we suggested a classification of hotspots according relations between the characteristic times of three main processes – chemical decomposition, material motion, and a time of hotspot formation. Molecular dynamic simulation of hotspots produced by the isochoric heating for a time much shorter than any processes involved in AB material evolution were performed with the aim to find a critical size of such hotspots. We determined the critical condition between extinction and growth of those hotspots as a simple equality of the rarefaction time and characteristic times of chemical decomposition, which is controlled by the initial radius, density and temperature of such hotspots.

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