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Molecular Dynamics Analysis of an Energetic System under Thermal and Shock Sollicitations

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We present in this paper molecular dynamics calculations concerning the decomposition of a simple system $A_2 \rightarrow 2A$ under thermal and shock sollicitations. For thermal decomposition, numerical results are consistent with the molecular collision theory. Arrhenius parameters are calculated. For shock decomposition, several regimes of propagation are observed depending upon the initial shock intensity. Analysis of chemical decomposition shows that kinetic parameters are strongly different from thermal decomposition.

I - INTRODUCTION.

The chemical process of decomposition in a reactive shock wave is far from being understood. Because both time and space scales of this phenomenon are very small, experiments must be performed at molecular level with a very high spatial and time resolution. Experiments are then extremely difficult to perform and interpret. Actually, molecular dynamics is the only one technique to provide information on atomic motions in a very small region during a very short time and some promising results are already published (ref. /1/-/6/ for example). In this paper we present first results using molecular dynamics obtained in our laboratory concerning energetic material in homogeneous phase.

The aim of this work is a numerical analysis by molecular dynamics of decomposition of a simple system : $A_2 \rightarrow 2A$ under static (thermal) and dynamic conditions (shock). In the first part, we describe the potential function of the system. In the second part, thermal decomposition is analysed for several initial temperatures. Results are interpreted with the classical molecular collision theory. In part III, decomposition under shock is studied for three shock intensities. As in the second part, kinetic parameters are estimated. Finally, results of thermal and shock decompositions are compared.

II - POTENTIAL FUNCTIONS.

By hypothesis, the potential function depends only upon interatomic distance r_{ij} between atoms i and j . It consists of two empirical functions ε_1 and ε_2 . The ε_1 function is a predissociative potential and describes interaction of atoms in a A_2 molecule, that is $r_{ij} < r_d$, where r_d is the dissociation length. For all other cases, we use the repulsive ε_2 function.

$$\varepsilon_1(r) = \sum_{k=0}^4 a_k \left(\frac{r_{ij}}{r_0} \right)^{k-n} \quad r_{ij} \leq r_d$$

$$\varepsilon_2(r) = \frac{\alpha}{\left(\frac{r_{ij}}{r_0} \right)^{\gamma}} + \beta, \quad r_{ij} \leq r_d$$

$$\varepsilon_2(r_{ij}) = \varepsilon_1(r_{ij}), \quad r_{ij} \geq r_d$$

Parameters a_k , α , β and γ are calculated with the following conditions :

$\varepsilon_1(r_{eq}) = \varepsilon_0$, $\varepsilon_1'(r_{eq}) = 0$, $\varepsilon_1(r_{act}) = e_{act}$, $\varepsilon_1'(r_{act}) = 0$, $\varepsilon_1(r_d) = 0$, $\varepsilon_2(r_d) = \varepsilon_1(r_d)$, $\varepsilon_2'(r_d) = \varepsilon_1'(r_d)$, $\varepsilon_2''(r_d) = \varepsilon_1''(r_d)$. r_{eq} is equilibrium distance of the A_2 molecule, r_{act} is the position of activation barrier. The parameters used in this work correspond to $r_0 = 1.10 \cdot 10^{-10} \text{m}$, $r_{eq} = 1.52 \cdot 10^{-10} \text{m}$, $r_0 = 1.71 \cdot 10^{-10} \text{m}$, $e_{act} = 2.73 \cdot 10^{-19} \text{J}$ and $\varepsilon_0 = 2.5 \cdot 10^{-19} \text{J}$ (figure 1). Note that because ε_2 is a repulsive function, any stable intermolecular regular structure exists at thermal equilibrium.

Fig.1. Potential functions ε_1 (—) and ε_2 (---) used in this work.

III - THERMAL DECOMPOSITION.

The overall system is composed of $8 \times 8 \times 8$ centred cubic unit cells (2048 atoms) with periodic boundaries on each face. Initial velocities are inferred from a Maxwell-Boltzmann distribution corresponding to a T_i temperature. Then, the evolution of the system is free and calculations are performed until all A_2 molecules are broken. Decomposition fractions are illustrated on figure 2 for five temperatures T_i .

Comparison between the numerical particle velocity distribution and Maxwell Boltzmann distribution calculated from average kinetic energy shows that thermodynamic equilibrium exists at any time; thus thermodynamic parameters are calculated with the usual statistical physics formulation. For example, temperature evolution is shown on figure 3.

Decomposition fraction versus time can be explained with the molecular collision theory. In this topic, two limit cases exist :

- for high temperatures, the decomposition mechanism is of first order : $A_2 \rightarrow 2A$.
- for lower temperatures, the decomposition mechanism is of second order : $2A_2 \rightarrow 2A + A_2$ or $A_2 + A \rightarrow 3A$.

The Arrhénius constant k is given by :

$$k(T(t)) = z \sqrt{T(t)} \exp\left(-\frac{e'_{act}}{k_b T(t)}\right)$$

where e'_{act} is an activation energy, z the frequency factor, T the temperature and k_b the Boltzmann's constant (noting that T is a function of time t). Numerical resolution of differential equations corresponding to different mechanisms shows that decomposition is of first order for the two higher initial temperatures (2121K and 1806K), and second order for the lower temperature (1023K). In the intermediate case, beginning of decomposition is of second order and of first order at the end of reaction. Calculated values of e'_{act} and z (table 1) are practically identical for all T_i ; this result confirms the choice of theoretical model to describe the numerical results on thermal decomposition.

Table 1. Kinetic parameters deduced from numerical calculations and molecular theory collision.

$T_i(K)$	$e'_{act}(J)$	$z(s^{-1}K^{-1/2})$
2121	$8 \cdot 10^{-20}$	$3 \cdot 10^{10}$
1806	$8 \cdot 10^{-20}$	$3 \cdot 10^{10}$
1508	$8 \cdot 10^{-20}$	$2,6 \cdot 10^{10}$
1274	$7,98 \cdot 10^{-20}$	$3,5 \cdot 10^{10}$
1023	$8,77 \cdot 10^{-20}$	$3,96 \cdot 10^{10}$

Fig.2. Decomposition fraction for various initial temperatures.

Fig.3. Temperature of system during decomposition.

IV - SHOCK DECOMPOSITION.

The system is made up by 60 unit cells in the x direction, and of 3 unit cells in the y and z directions (2160 atoms). The two faces perpendicular to the x-axis are mirrors, the other faces are periodic. After thermalisation, all particles move at time t_0 in the x direction with a velocity u_0 . So, a wave P is generated in the opposite direction. Three values of u_0 are used : 500m/s, 1500m/s and 2500m/s. The initial temperature is 251K.

For the lower u_0 (500m/s), any decomposition is observed during the calculation. The wave velocity is constant (1463m/s). For $u_0=2500$ m/s, decomposition occurs just on the compression front (figure 4). The wave velocity is constant (5115m/s). The last case ($u_0=1500$ m/s) is more complicated. We observe two regimes : the first one, between t_0 and $4 \cdot 10^{-12}$ s, corresponds to a wave velocity of 3097m/s. Reaction of decomposition occurs behind the compressive zone (figure 5). The wave P is thus an inert wave followed by a reactive wave. In the second regime, between $6 \cdot 10^{-12}$ s and the end of calculation, the compression zone is overtaken by

reaction zone and, as in the $u_0=2500\text{m/s}$ case, decomposition occurs on the compression front (figure 6). The wave velocity is 4479 m/s .

Behind the wave P, the thermodynamic equilibrium is rapidly achieved. Comparison between thermodynamic state behind P deduced from the wave velocity, the particle velocity and Hugoniot

relations and thermodynamic state deduced from statistical physics shows that P is a steady shock wave for $u_0=500\text{m/s}$ and $u_0=2500\text{m/s}$ (table 2 and 3). Shock wave is inert in the first case, and reactive in the second one. For $u_0=1500\text{m/s}$, the wave P is not a steady shock wave, because the reaction zone is (relatively) large and unstable in time.

Table 2. Average values for pressure P , density ρ , internal energy e and temperature T behind shock front deduced from statistical physics analysis.

$u_0\text{ (m/s)}$	$\langle P \rangle\text{ (Pa)}$	$\langle \rho \rangle\text{ (kg/m}^3\text{)}$	$\langle e \rangle\text{ (J/kg)}$	$\langle T \rangle\text{ (K)}$
500	$8,191\ 10^8$	1275	$2,793\ 10^6$	438
2500	$1,101\ 10^{10}$	1651	$5,788\ 10^6$	8669

Table 3. Pressure P_c , density ρ_c and internal energy e_c calculated from shock and particle velocities and Hugoniot relations.

$u_0\text{ (m/s)}$	$P_c\text{ (Pa)}$	$\rho_c\text{ (kg/m}^3\text{)}$	$e_c\text{ (J/kg)}$
500	$7,78\ 10^8$	1305	$2,800\ 10^6$
2500	$1,113\ 10^{10}$	1680	$5,824\ 10^6$

The decomposition under shock is a first order mechanism described in part III of this paper, because temperature behind the shock front is high. Kinetic parameters are not the same for the two cases (table 4). Increasing of e'_{act} is probably due to the growth of density with u_0 . Similarly, z must theoretically increase with temperature and density, and thus with u_0 .

Table 4. Kinetic parameters for shock decomposition.

$u_0\text{ (m/s)}$	$e'_{act}\text{ (J)}$	$z\text{ (s}^{-1}\text{K}^{-1/2}\text{)}$
1500m/s	$1,78\ 10^{-19}$	$1,9\ 10^{11}$
2500m/s	$1,85\ 10^{-18}$	$1,7\ 10^{17}$

Fig. 4. Average x component particle velocity (—) and fraction decomposition (---) for $u_0=2500\text{m/s}$ and $t=4.430 \cdot 10^{-12}\text{s}$. Velocities are divided by 1000.

Fig. 5. Average x component particle velocity (—) and fraction decomposition (---) for $u_0=1500\text{m/s}$ and $t=4.430 \cdot 10^{-12}\text{s}$. Velocities are divided by 1000.

Fig.6. Average x component particle velocity (—) and fraction decomposition (---) for $u_0=1500\text{m/s}$ and $t=7.833 \cdot 10^{-12}\text{s}$. Velocities are divided by 1000.

V - DISCUSSION.

Two main results of this work concern firstly the structure of the reactive shock wave, and secondly the decomposition kinetic under static and dynamic sollicitations. In homogeneous explosives shocked by a projectile, it is currently admitted that decomposition reactions begin at interface explosive/projectile with a significative delay. The reaction zone overtakes the inert shock wave propagating in explosive at rest. Thus, during a short time, the system is composed of explosive at rest, explosive shocked but not decomposed and a reaction zone behind the inert shock front. This structure is the same as the one observed in our molecular dynamics calculations.

Second point concerns the kinetic parameters for static and dynamic decompositions. Experimental works on PETN single crystal and liquid nitromethane [7-9] (that are homogeneous explosives) exhibit a strong decay of z and e'_{act} for shock decomposition versus thermal decomposition. Moreover, theoretical calculations show that activation energy of nitrogen monoxide is significantly lowered by intermolecular interaction. Our calculations do not reproduce these results because the potential function used here is too simple. Effect of molecular surrounding on energy activation cannot be taken into account with only a two particles potential function. Implementation in our code of more realistic potential functions is thus our first aim.

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