

# MOLECULAR-DYNAMICS SIMULATION OF PROCESSES IN 3-D SOLID EXPLOSIVES

Andrey V. Utkin

Igor F. Golovnev

Vasily M. Fomin

utkin@itam.nsc.ru

## 1 Introduction

An important fundamental problem is the study of processes in reacting condensed media and, in particular, the study of detonation phenomena in solid explosives. Experimental studies of chemical reactions and the structure of detonation and shock waves (including that at the micro- and mesoscale) face significant difficulties caused, first, by high intensity of these waves and, second, by the scales of these phenomena in time (nanoseconds) and space (from 10 to 100 Å). At the moment, there is no rigorous kinetic theory of phenomena in solid explosives in the presence of chemical reactions. In this connection, the molecular-dynamics method remains the only adequate research tool that allows one to resolve the fine spatial structure of wave phenomena in such systems and provides the most exhaustive information about them (a set of generalized coordinates and momenta of all atoms). These data, if adequately averaged over mesoscale volumes in which local thermodynamic equilibrium is assumed, should yield continuum-approach parameters. This offers a means for verification of the applicability of main conservation equations, written either in the most general integral form or in the stationary form for the entire computation domain (including the undisturbed region of the crystal, the reacting zone, and the detonation products), to detonating solid explosives [1]. Also of considerable interest is comparison of molecular-dynamics data with the predictions of the continuum theory of detonation, including verification of the Chapman-Jouguet condition. It is the detailed examination of this point that the present work is aimed at.

As the physical system, we consider a three-dimensional hypothetical molecular crystal in which exothermic reactions are possible. The reaction was initiated by an impulse of an external force applied to the left side of the crystal and acting on it during a certain time interval,  $\tau_c = 2 \cdot 10^{-13}$  s. In the numerical experiment, the crystal was placed in an adiabatic shell that restricted the dispersion of detonation products in the plane normal to the propagation direction of the detonation wave. This variant is of interest because it makes it possible to reduce the three-dimensional problem in its present formulation to a one-dimensional problem of the continuum theory of detonation.

A detailed description of the intermolecular potential and mathematical model was reported elsewhere [1].

## 2 Results

### 2.1 Initiation and development of the detonation

In the numerical experiments, we studied the processes that occurred in the crystal under the action of the impulse of the external force  $F_0$ . The value of  $F_0$  was  $13 \cdot 10^{-11}$  N, the duration of the force impulse was  $\tau_c = 2 \cdot 10^{-13}$  s, and the initial temperature of the crystal was  $T = 0$  K.

The force  $F_0 = 13 \cdot 10^{-11}$  N gave rise to self-sustained detonation wave that propagated across the crystal at a velocity greater than the speed of sound. As an example, we show here the dynamic sweep of detonation in the crystal placed in an adiabatic shell (Fig. 1). In this case, the detonation velocity is  $D = 10.928$  km/s. Figure 2 illustrates the time variation of the detonation wave front position; these data prove that the wave propagates in the crystal at a constant velocity.

To investigate into the state of the molecular crystal prior to arrival of the detonation wave, we used the following procedure. A control mesocell (a mesocell in which the time variation of energy and

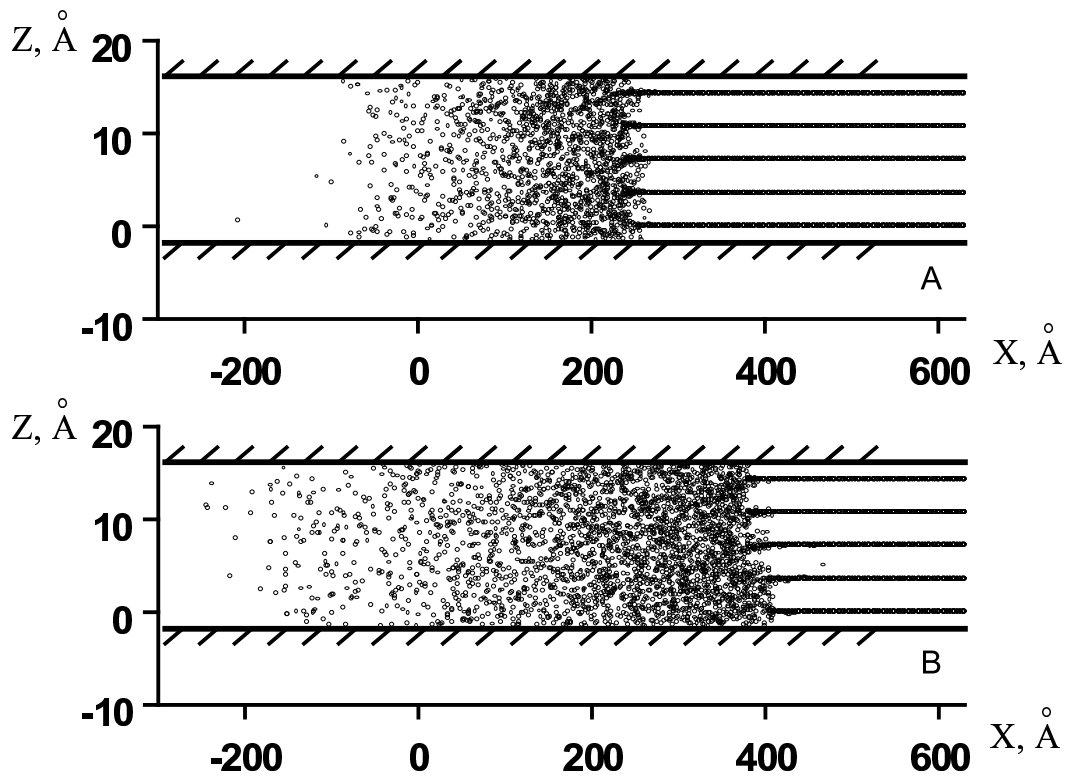


Figure 1: Evolution of the detonation in the crystal placed in an adiabatic shell (side view in the XZ plane) for two times: A –  $t = 30 \cdot 10^{-13} \text{ s}$ ; B –  $t = 42.5 \cdot 10^{-13} \text{ s}$ . The force  $F_0 = 13 \cdot 10^{-11} \text{ N}$  was terminated at the time  $t = 2 \cdot 10^{-13} \text{ s}$ .

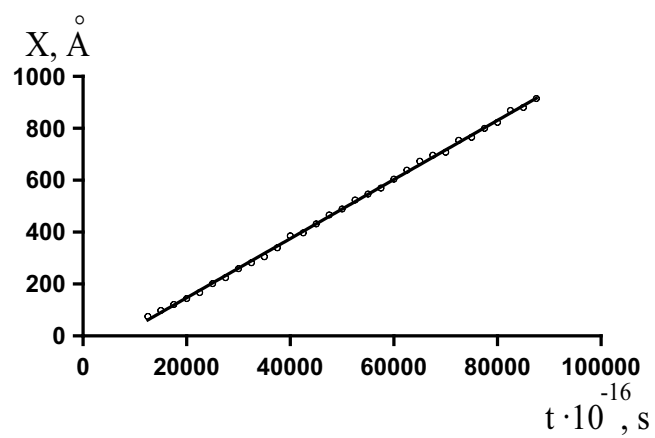


Figure 2: Detonation wave front position versus time.

structure parameters was monitored) was placed at a certain distance from the left side of the crystal ( $460.12 \text{ \AA}$ ). As is seen from Fig. 3, the intramolecular energy  $E_{MOL}$  (the vibrational energy of the molecules), the rotational energy  $E_{ROT}$ , and the kinetic energy  $E_K$  of molecules in this mesocell all display a sharp rise over times of the order of  $10^{-14} \text{ s}$ , with no chemical reaction having yet emerged. It should be emphasized that, during these short time intervals, crystal molecules acquire considerable rotational energy. This process, however, develops so rapidly that atoms in the crystal have no enough time to change their position by the moment at which the chemical reaction begins, and, till the very onset of the reaction, the structural factor remains practically unchanged.

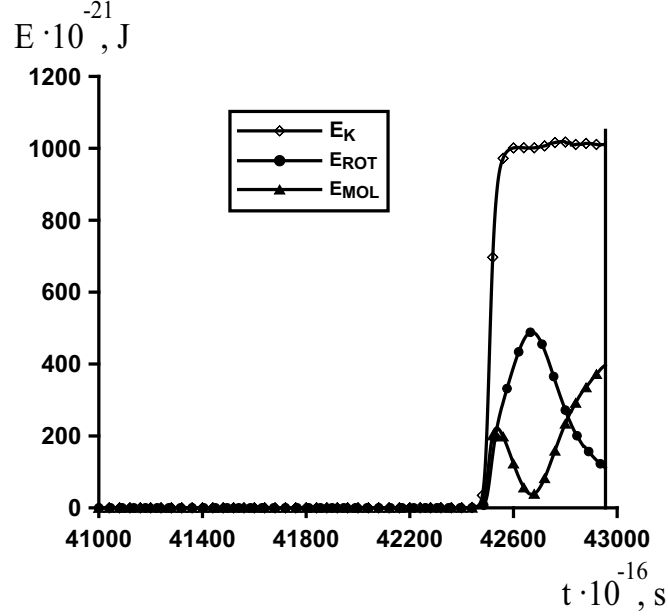


Figure 3: Variation of energy microparameters of the control mesocell in time. The chemical reaction emerges at the moment  $t = 42.955 \cdot 10^{-13} \text{ s}$  (vertical straight line).

## 2.2 Comparison with the continuum theory of detonation

As it is known, the equations of mass, momentum and energy conservation in their stationary one-dimensional form (Hugoniot relations),

$$\rho_0 D = \rho (D - u), \quad (1)$$

$$P_0 + \rho_0 D^2 = P + \rho (D - u)^2, \quad (2)$$

$$\varepsilon_0 + \frac{P_0}{\rho_0} + \frac{D^2}{2} = \varepsilon + \frac{P}{\rho} + \frac{(D - u)^2}{2}, \quad (3)$$

do not allow one to uniquely determine the detonation-wave velocity and, in the framework of continuum mechanics, it is required to invoke an additional selection condition for velocities (Chapman-Jouguet condition). In this connection, of considerable interest are:

Comparison of molecular-dynamics data with the predictions of the continuum theory of detonation.

Checking of automatic fulfillment of the Chapman-Jouguet condition in modeling detonation at the microscale using only the second Newton law for moving atoms.

In continuum mechanics, the procedure for determining the detonation velocity is as follows. Using the equation of mass conservation (1) and the equation of momentum conservation (2), we eliminate the detonation velocity  $D$  and the velocity  $u$  of the reaction products behind the detonation front from the energy equation (3). Then, we obtain the following expression for the Hugoniot function (detonation adiabat):

$$h(T, \tilde{V}) = \varepsilon - \varepsilon_0 - \frac{1}{2} (P + P_0) (\tilde{V}_0 - \tilde{V}), \quad (4)$$

where  $\tilde{V}_0$  is the specific volume of the undisturbed crystal and  $\tilde{V}$  is the specific volume of the substance behind the shock front. The set of parameters  $(T_H, \tilde{V}_H)$  for which  $h(T, \tilde{V})$  turns into zero defines the Hugoniot detonation adiabat. Eliminating the velocity  $u$  from equations (1) and (2), we obtain the equation for the Rayleigh line (Michelson line):

$$\rho_0^2 D^2 = (P - P_0) / (\tilde{V}_0 - \tilde{V}). \quad (5)$$

The intersection of this line with the detonation adiabat yields a set of detonation velocities; yet, according to the Chapman-Jouguet condition, the minimum velocity from this set corresponds to normal detonation.

To find the thermodynamic parameters at the Chapman-Jouguet point, the equation of state for detonation products is necessary; in the present work, this equation was obtained as follows. Since, in the present numerical experiment, the detonation product is a monoatomic gas, to construct the required equation of state, we used the following physical system.

A total of 5000 atoms were placed in a cubic reservoir of size  $d_{ES}$  whose walls were modeled by the repulsive branch of the Lennard-Jones potential. To set the momenta of the atoms in the system at the initial time, the Monte-Carlo method at the temperature  $T_{ES}$  was used, and then the system was allowed to relax to its equilibrium state during a time interval of  $10^{-11}$  s. The size  $d_{ES}$  of the reservoir was varied in the range from  $65 \text{ \AA}$  to  $100 \text{ \AA}$ , which corresponded to a density variation of  $0.116 \cdot 10^3 \text{ kg/m}^3$  to  $0.423 \cdot 10^3 \text{ kg/m}^3$  (for the atomic mass  $m_{at} = 23.253 \cdot 10^{-27} \text{ kg}$ ); the temperature was varied in the interval from  $20000 \text{ K}$  to  $50000 \text{ K}$ . This choice of the thermodynamic values was made taking into account results of preliminary physical experiments on detonation-wave propagation in the crystal.

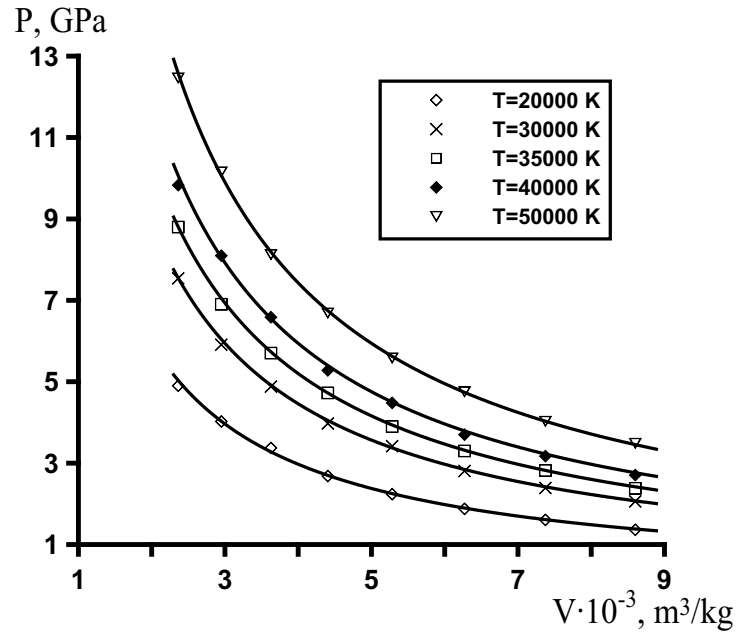


Figure 4: Time-averaged total pressure versus specific volume. The sets of points were obtained from numerical experiments performed for various temperatures; the curves drawn through the points were calculated using the equation of state for a perfect gas.

The data gained allowed us to plot a series of points for different temperatures (see Fig. 4). It follows from the data that the numerical data can be well fitted with the equation of state for a perfect gas,

$$P_{id} \tilde{V} = \frac{k_B}{m_{at}} T.$$

The latter can be attributed to the fact that the gas temperature is high and, in spite of the high density, the kinetic energy of atoms is far in excess of their potential energy, i.e., the thermal part far exceeds the potential part of the pressure.

Applying the equation of state of a perfect gas to finding the pressure in the detonation products and assuming that the specific internal energy is given by the relation  $\varepsilon = \frac{3}{2} \frac{k_B}{m_{at}} T$ , we can calculate the

Hugoniot detonation adiabat (see Fig. 5).

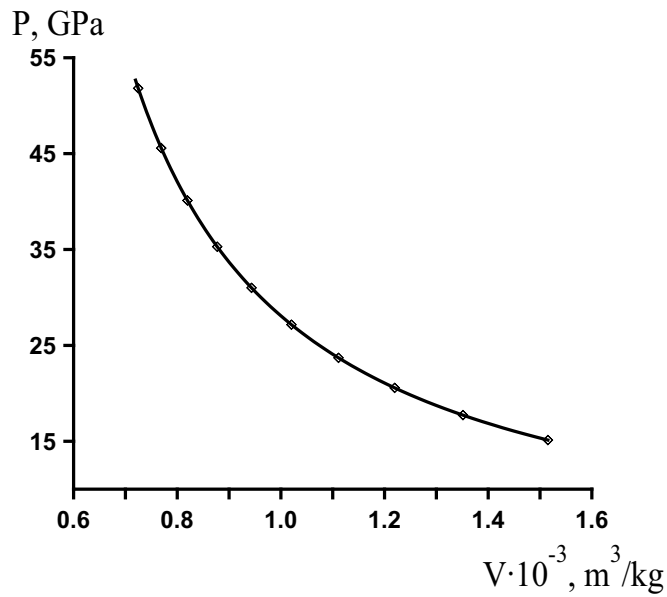


Figure 5: Hugoniot pressure versus specific volume.

With known specific volumes and Hugoniot pressures, we could use relation (5) to calculate the set of detonation velocities  $D$  as a function of specific volume (Fig. 6).

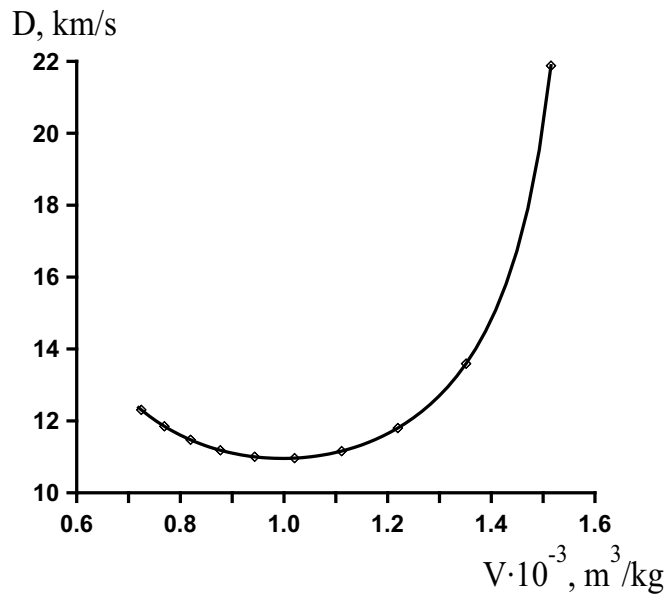


Figure 6: Detonation velocity versus specific pressure.

The Chapman-Jouguet velocity, i.e., the minimum detonation velocity for the set of pressures and specific Hugoniot volumes, was found to equal  $D_{CJ} = 10.955 \text{ km/s}$  [2]. The pressure, the specific volume (or density), and the mass velocity for this point are  $P_{CJ} = 28.079 \text{ GPa}$ ,  $\tilde{V}_{CJ} = 10^{-3} m^3/kg$  ( $\rho_{CJ} = 10^3 \text{ kg/m}^3$ ), and  $u_{CJ} = 4.089 \text{ km/s}$ .

The detonation velocity obtained in the numerical experiment on detonation-wave propagation in the crystal placed in an adiabatic shell is  $D = 10.928 \text{ km/s}$ . Thus, the Chapman-Jouguet detonation velocity obtained from the continuum theory and the detonation velocity obtained in the numerical experiments agree within 1%.

By definition, all chemical reactions must be over at the Chapman-Jouguet point [2,3]. To find the position of this point in the crystal, we used the following procedure. At a time interval equal to 50 time

steps, we performed mesoanalysis over the whole calculation domain; from the chemical composition gained, the first cell behind the reacting zone with completely dissociated molecules was found.

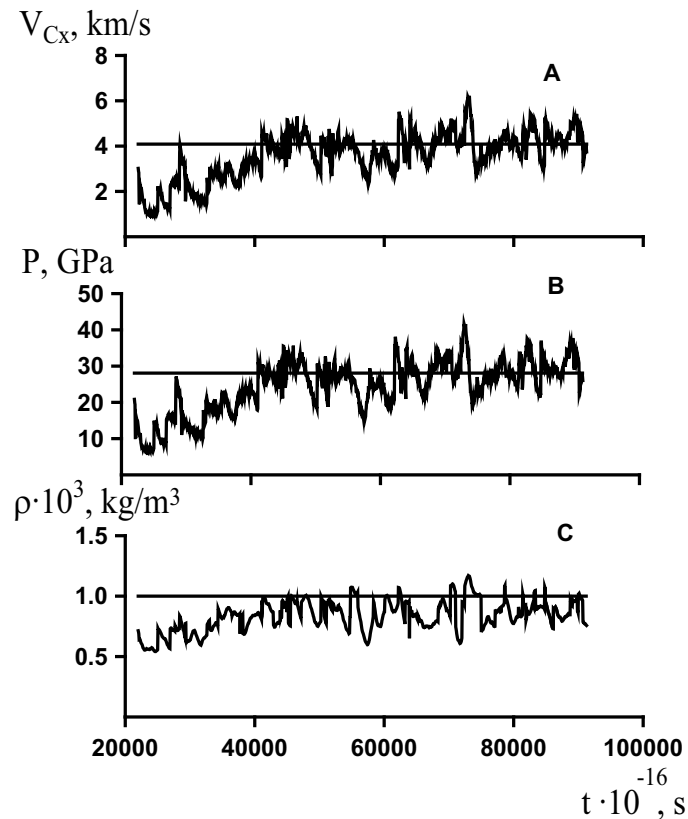


Figure 7: Time dependences of the mass velocity along the  $x$ -axis (A), pressure (B), and density (C) at the Chapman-Jouguet point. The horizontal straight line indicates the theoretical values of the Chapman-Jouguet parameters.

In this mesocell, the following parameters were found: mass velocity, pressure, and density. The values obtained were compared with the predictions of the continuum theory of detonation. It is seen from Fig. 7 that a certain time after the onset of the chemical reaction is required (about  $30 \cdot 10^{-13} \text{ s}$ ) until the thermodynamic characteristics come (with the accuracy to fluctuations) to their constant asymptotic values. After the coming to the asymptotics, the values fluctuate around their mean values. For the time interval from  $40 \cdot 10^{-13} \text{ s}$  to  $92 \cdot 10^{-13} \text{ s}$ , the following values for the mean velocity, mean pressure, and mean density were obtained:  $\bar{V}_{Cx} = 4.062 \text{ km/s}$ ,  $\bar{P} = 27.964 \text{ GPa}$ , and  $\bar{\rho} = 0.89 \cdot 10^3 \text{ kg/m}^3$ .

## 2.3 Conclusions

**The main conclusions of the present work can be summarized as follows:**

Results of the present molecular-dynamic modeling were compared with the predictions of the continuum theory of detonation. A good agreement between the detonation velocities and between the values of thermodynamic parameters at the Chapman-Jouguet point was obtained.

The Chapman-Jouguet condition is proved to be automatically fulfilled if the second Newton law was used in modeling the detonation.

## References

- [1] V.M. Fomin, I.F. Golovnev, and A.V. Utkin, Relation between the atomistic picture and continuum mechanics description of detonating solid-state explosives // *Shock Waves*. – 2003. V.13. 2. – P. 155-165

[2] Ya.B. Zel'dovich and A.S. Kompaneets, Theory of Detonation, Nauka. Moscow, 1955, 268 p.

[3] K.P. Stanyukovich, Explosion Physics, Nauka, Moscow, 1975. 703 p.