

# Molecular Dynamics Study Of Vibrational Nonequilibrium In Detonation Of Polyatomic Liquids.

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## 1 Introduction

Most liquid explosives consist of polyatomic molecules of complicated structure (ten or more atoms and various bond types). They have high vibrational heat capacity, so that vibrational energy transfer process is of great importance and can influence on the structure of shock and detonation wave in such substances. Available experimental data testify in favour of this opportunity [1]. For example, under shock wave conditions aromatic and aliphatic compounds behave differently, the shock destruction process for aromatic compounds differing from that observed in thermal equilibrium. This was supposed to be connected with the difference in vibrational relaxation times of that compounds.

Shock waves in liquids can be simulated by the method of nonequilibrium molecular dynamics [2] based on numerical solution of equations of motion of a large number of atoms. The direct way to account internal degrees of freedom of molecules is to consider the motion of separate atoms on a total potential energy surface (PES). Numerical simulations of steady state detonation waves are carried out usually on empirical PESs. Dynamics of small groups of molecules can be investigated by means of *ab initio* calculations. Such results involve many details specific to real molecular systems, but it is very difficult to extract any information about individual processes. Besides, both simple *ab initio* and empirical PESs do not meet precision and reliability requirements. Moreover, they are rather complicated and should be thoroughly examined before used.

## 2 Problem Statement

In the present work, model PESs are constructed and used as in previous study [3,4]. They do not describe rigorously actual molecular systems. However, such PESs have very simple adjustable structure.

Our starting point is vibrational relaxation theory in gases which is well developed at present [5]. The theory is based on the following assumptions. Intramolecular interactions are much stronger than intermolecular ones. So that, corresponding motions are separated in zeroth approximation. Energy exchange processes can be modelled without detailed dynamical description, i.e. without atom's trajectories based on all atom-atom interactions. Usual way is to put into Hamiltonian only the terms responsible for the process under investigation.

Some other results and approaches of gas theory have been used as well. Many assumptions are valid also to liquids and easily fusible solids. The main difference between gas and liquid is relative motion of molecules, and it is taken into account by the simplest variant of molecular dynamics for structureless particles [2].

In absence of chemical reactions, molecules have been simulated by multimode oscillators which interact with each other via isotropic intermolecular potential depending on vibrational coordinates [3]. This corresponds to the model of "breathing spheres" [5].

The other way to introduce dependency on vibrational coordinates into a simple intermolecular potential is more suitable to model chemical reactions due to unlimited vibrational motion [4]. It accounts a single atom-atom interaction from  $N_{at}^2$  possible ones. Such interactions are almost equivalent from viewpoint of energy

exchange. Simplified forms of intermolecular potential may be used because our goal is not to calculate atom's trajectories.

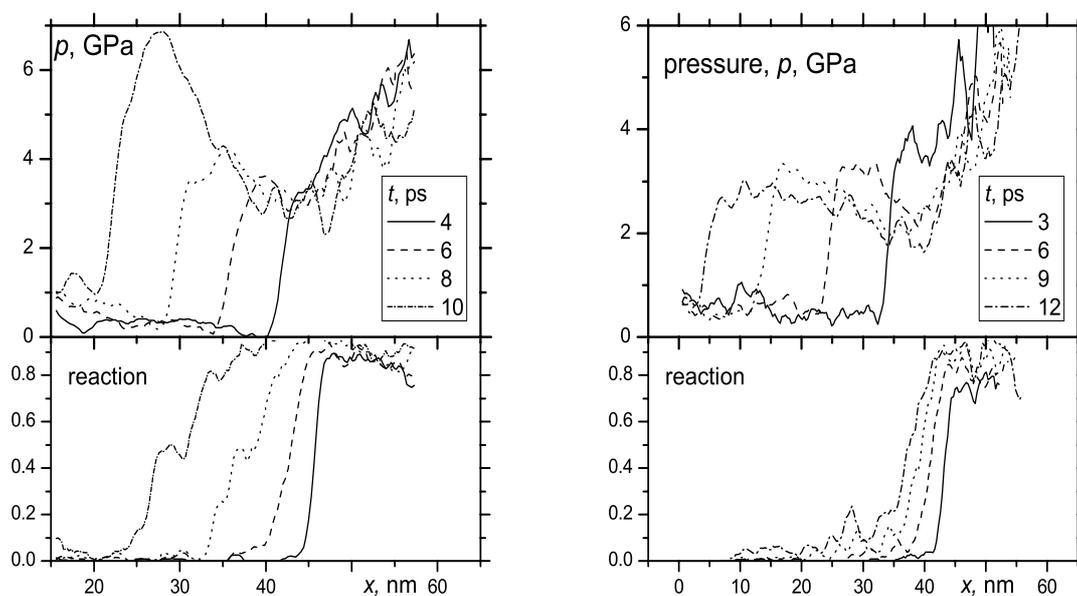
Both ways permit the problem's splitting into translational and vibrational ones, that are independent on a time step. Thus, conventional monoatomic molecular dynamics is combined with complicated internal part via a single parameter per each molecule. Pairs of molecules are looked over instead of pairs of atoms, that reduces dramatically calculation expenses.

To take into account unimolecular chemical reactions, internal part of PES should be changed [4]. In the space of vibrational coordinates of molecules, the simplest PES looks like two minimums with smooth passage through a saddle-point between them. The vibrational frequencies in the minimums correspond to normal modes of initial and final molecular states (reagents and products), the level's difference gives reaction heat effect  $Q$ , and the height of the barrier gives activation energy  $E_A$ .

It should be noted that the above information about the PES used here is sufficient to define chemical system evolution in frames of conventional transition state theory for the case of thermal equilibrium.

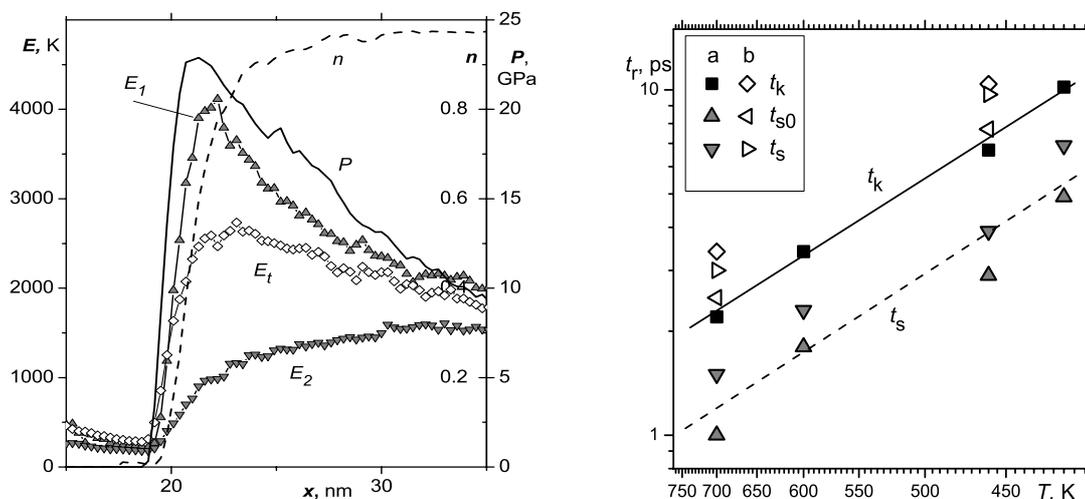
### 3 Results

Numerical calculations have been carried out to different model systems. They have shown some opportunity of simulating both steady state detonation wave and processes of initiation of detonation by shock wave or by local heating (fig.1-2).



**Fig 1.** Local heating simulations. Pressure  $P$  and concentration of product molecules  $n$  versus distance along wave propagation  $x$  at various time moments  $t$ . Detonation wave initiation in the case of fast reaction (a).

**Fig 2.** Shock wave decay and combustion wave propagation in the case of slow reaction (b).



**Fig 3.** Pressure  $P$ , kinetic transversal energy  $E_t$ , vibrational energies  $E_1$  and  $E_2$ , and concentration of product molecules  $n$  versus distance along detonation wave propagation,  $x$ .

**Fig 4.** Chemical reaction time versus temperature. Systems (a) and (b) with heat release ( $Q=10000$  K). Small volume shock compressed ( $t_s$ ,  $t_{s0}$ ) and preheated ( $t_k$ ).

The typical structure of detonation wave is presented on fig.3. The molecule permits a reaction with heat effect,  $Q = 20000$  K, and activation energy,  $E_A = 5000$  K along vibrational coordinate  $x_1$ .

There are two zones of vibrational relaxation. First, vibrational excitation of reagents takes place and it boosts chemical reaction. Explosive's chemical energy is released as an internal vibrational energy of products, and then it transfers during a relaxation to translational degrees of freedom and further to mechanical energy of a stream. In contrast to the case of shock wave, vibrational nonequilibrium of products is very large due to the heat release. This should be taken into account in carrying out kinetic calculations.

The main action of shock wave is supposed to produce translational nonequilibrium. It is possible to simulate the shock action in small systems with periodic boundaries to exclude near-wall effects [4]. This method is used to compare static and shock wave chemistry in the case of slow reactions. Examples of such calculations are presented on fig.4. Values  $t_s$ , and  $t_{s0}$  are measured from start and from finish of compression. Final volumes are the same to all data points. Compression rate is constant and varies from one point to another.

Both molecular systems (a) and (b) presented on fig.4 permit chemical reaction with activation energy  $E_A=4000$  K and with heat effect,  $Q=10000$  K. They have narrow vibrational spectrum, almost equal total relaxation times but different structure of normal modes.

Reaction mode ( $k=1$ ) of system (a) relaxes faster than other modes (2-5) due to this difference, so that it takes more energy than in equilibrium. Reaction rate depends mainly on mean vibrational energy of reaction mode and raises compared to thermal conditions. In the case of system (b), passive modes (2-5) relaxes slightly faster than active one. The reaction rate tends to equilibrium value. Straight line  $t_k$  approximates reaction time in system (a) at thermal conditions. It corresponds roughly both thermal ( $t_k$ ) and shock compressed ( $t_s$ ) data to system (b) also.

These results demonstrate different shock wave chemistry for substances of almost identical behaviour at static conditions.

The effect of vibrational nonequilibrium on chemical process is similar to that observed in gas mixtures behind shock waves. The account of it within the frames of kinetic description allows to interpret various experimental data by means of a single set of rate constants.

## 4 Conclusions

The advantages of the model proposed are the following: (i) low calculation expenses, (ii) the simplest way to exclude high frequency vibrations, and (iii) small number of physically significant parameters, that can be varying independently. Its basic application seems to estimate some fast transient effects in polyatomic liquids, and also to produce input data for problems formulated within the framework of kinetic or phenomenological approaches.

The calculations have shown that vibrational nonequilibrium is produced by shock compression and then influences on chemical reactions. So, the structure of shock and detonation waves depends strongly on the peculiarities of vibrational spectra and normal modes' structure of compounds.

## References

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