



Molecular Dynamics Study of Vibrational Nonequilibrium in Detonation of Polyatomic Liquids

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Abstract: Energy transfer mechanisms to internal molecular degrees of freedom in shock and detonation waves in polyatomic liquids are investigated. The proposed approach uses a new version of the method of nonequilibrium molecular dynamics based on the simplest model potential energy surfaces of reacting polyatomic molecules. The main feature is adaptation of some results and approaches of gas theory to liquids. It is shown that vibrational nonequilibrium is produced by shock compression and influences on chemical reactions. So, the structure of shock and detonation waves depends strongly on the peculiarities of vibrational spectra and the structure of normal modes of compounds. Numerical simulations have been carried out for steady state detonation waves and processes of initiation of detonation by shock waves or by local heating. The results demonstrate different shock wave chemistry for substances of almost identical behaviour at static conditions.

Keywords: molecular dynamics, detonation

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 vibrational energy transfer process is of great importance and can influence the structure of shock and detonation waves in such substances [1]. Available experimental data testify in favour of this opportunity [2]. 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.

Molecular Dynamics

Shock waves in liquids can be simulated by the method of nonequilibrium molecular dynamics based on numerical solution of equations of motion of a large number of atoms [3]. The direct way to account for 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 were carried out using simplified empirical PESs [4-6]. Dynamics of polyatomic molecules in small clusters or periodic cells was investigated by means of *ab initio* calculations [7, 8]. Such results involve many details specific to real molecular systems, but it is very difficult to extract any information about individual processes. The calculation of vibrational energy redistribution in the shock wave has been made only to diatomic molecules [9]. Besides, both simple *ab initio* and empirical PESs do not meet precision and reliability requirements. They are rather complicated and should be thoroughly examined before used.

In the present work, model PESs are constructed and used as in the previous study [10, 11]. They do not describe rigorously actual molecular systems. However, such PESs have a very simple adjustable structure. Their parameters can be estimated by *ab initio* calculations for several molecular configurations or can be taken from experiments performed at static conditions.

Vibrational Energy Transfer

Vibrational relaxation theory in gases is well developed at present. Numerical investigations include trajectory calculations on both empirical [12] and model [13] PESs. The latter allow some approximate analytical solutions.

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 a detailed dynamical description, i.e. without atomic trajectories based on all atom-atom interactions. The usual way is to put into the Hamiltonian only the terms responsible for the process under investigation.

SSH theory [14] operates with a small number of physically significant parameters of molecular systems. Its main result is that the relaxation of mean

vibrational energy to its equilibrium value is defined by the Landau-Teller equation

$$\frac{dE}{dt} = -\frac{E - E_0}{\tau}, \quad (1)$$

where the characteristic time is strongly dependent on temperature and vibrational frequency,

$$\frac{1}{\tau} \approx \left| \int f(t) \cdot \exp(i\omega t) dt \right|^2 \approx \lambda^2 \operatorname{sh}^{-2}(\pi \xi), \quad (2)$$

$\xi = \omega / \alpha v$ – adiabatic parameter, v – the velocity of molecular collision,

$$\alpha = -\frac{1}{V} \cdot \frac{\partial V}{\partial r} \text{ – hardness of intermolecular potential,}$$

$$f = -\frac{\partial V}{\partial x}, \quad \frac{\partial V}{\partial x} = \lambda \frac{\partial V}{\partial r}. \quad (3)$$

The parameters ξ and λ determine both rate and special features of vibrational-translational energy exchange in the case of diatomic molecules. These results have been generalized to the case of polyatomic molecules [14]. The parameters λ_k are defined mainly by a structure of normal modes (or by mass ratio in the case of diatomics). They can be determined from the Hessian eigenvectors in some assumptions, but they are treated as independently varying parameters in the current paper. Vibrational-translational exchange rate is proportional to λ at $\lambda \leq 1$. Some nonlinear effects can take place in the case of strong interactions, but they do not affect the dependence of the rate on vibrational excitation of molecules [13].

Some other results and approaches of gas theory have been used as well. Many assumptions are valid for liquids and easily fusible solids. The main difference between gas and liquid is the relative motion of molecules and is taken into account by the simplest variant of molecular dynamics for structureless particles [3].

Problem Statement

In the absence of chemical reactions, molecules have been simulated by multimode oscillators which interact with each other via isotropic intermolecular potential depending on vibrational coordinates [10].

The Hamiltonian of the system of N molecules:

$$H = \sum_i (\mathbf{p}_i^2 / 2m_i + H_{vib,i}) + \sum_{i,j \neq i} V_{ij}, \quad (4)$$

here indexes of molecules $i, j < N$, indexes of normal modes $k < K \leq K_m$, $K_m = 3 N_{at} - 6$, $N_{at} \sim 10$, and $N \sim 10^3 \div 10^6$.

The intermolecular potential is taken in the Lennard-Jones form,

$$V_0(r) = 4\varepsilon \cdot \left((r_0 / r)^{12} - (r_0 / r)^6 \right). \quad (5)$$

$$V_{ij} = V_0(|\mathbf{r}_i - \mathbf{r}_j|) \left(1 + \sum_k \lambda_{ik} \cdot x_{ik} + \sum_k \lambda_{jk} \cdot x_{jk} \right) \quad (6)$$

and corresponds to the model of “breathing spheres” [9].

The other way to introduce dependency on vibrational coordinates into a simple intermolecular potential is [10]

$$V_{ij} = V_0(|\mathbf{r}'_i - \mathbf{r}'_j|) \quad \mathbf{r}'_j = \mathbf{r}_j + \sum_k \lambda_{ik} \cdot x_{ik}. \quad (7)$$

This formula is more suitable to model chemical reactions due to unlimited vibrational motion. It accounts for a single atom-atom interaction from N_{at}^2 possible ones. Such interactions are almost equivalent from the viewpoint of energy exchange. Simplified forms of intermolecular potential may be used because our goal is not to calculate atomic trajectories.

Both techniques permit the splitting into translational and vibrational ones, that are independent on a time step. Thus, conventional monoatomic molecular dynamics is combined with the 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 from $\approx N^2 N_{at}^2$ to $\approx (N^2 + NK)$.

Internal Hamiltonian

The internal Hamiltonian corresponds to the sum of harmonic oscillators terms:

$$H_{vib} = (\mu / 2) \sum_k \dot{x}_{ik}^2 + U_a, \quad (8)$$

$$U_a = (\mu / 2) \sum_k \omega_k^2 x_{ik}^2. \quad (9)$$

To take into account unimolecular chemical reactions, the internal part of PES should be changed. In the space of vibrational coordinates of molecules, the simplest PES looks like two minima with smooth passage through a saddle-point between them. The usual practice is to build such PES from zeroth approximation terms U_a and U_b and interaction U_0 (term's splitting):

$$U = \frac{1}{2} \left((U_a + U_b) - \left((U_a - U_b)^2 + U_0^2 \right)^{1/2} \right), \quad (10)$$

$$U_b = -Q + (\mu / 2) \sum_k \omega_{bk}^2 (x_{ik} - x_{bk})^2. \quad (11)$$

The vibrational frequencies in the minima correspond to normal modes of initial and final molecular states (reagents and products), the level's difference gives a reaction heat effect Q , and the height of the barrier gives an activation energy E_A , that can be adjusted by changing x_{bk} .

RRKM theory [15] treats the unimolecular reaction mechanism as separated into two parts, the collisional activation and deactivation process and the microscopic reaction at constant energy.



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

Results

Numerical calculations have been carried out for different model systems. The cases of both narrow and wide spectra of low frequency vibrations (like benzene and hexane respectively) were considered carefully:

$$\omega_k = \{400, 100, 150, 200, 300\} \text{ cm}^{-1}, K=5, \quad (13)$$

$$\omega_k = \{400, 320, 340, 360, 380\} \text{ cm}^{-1}, K=5. \quad (14)$$

For example, *ab initio* MP2/sto-3g frequencies for some molecules of interest are

$$\text{Benzene } C_6H_6 \quad \omega_k = \{437, 437, 646, 646, \dots\}, K=30.$$

$$\text{Hexane } C_6H_{14} \quad \omega_k = \{46, 87, 182, 232, 244, 292, 363, 430, 529, \dots\}, K=54.$$

Pentane C_5H_{12} $\omega_k = \{102, 114, 190, 222, 259, 417, 419, \dots\}$, $K=45$.

Vibrational heat capacity tends to zero at low temperatures due to quantum effects:

$$C_{vib} \rightarrow 0 \text{ at } \theta = \frac{\hbar\omega}{k_B T} \geq 1. \quad (15)$$

So, some high frequency modes cannot be treated by classical mechanics and they should be excluded. Vibrations can absorb energy at $T < 1000$ K only if $\omega_k < 700 \text{ cm}^{-1}$, so that a very small number of modes should be taken into account in this molecules.

Different sets of λ were used in various combinations with vibrational spectra (13) and (14):

$$\lambda = \{0.1, 0.1, 0.1, 0.1, 0.1\}, \quad (16)$$

$$\lambda = \{0.5, 0.5, 0.5, 0.5, 0.5\}, \quad (17)$$

$$\lambda = \{0.5, 0.1, 0.1, 0.1, 0.1\}, \quad (18)$$

$$\lambda = \{0.5, 1.0, 1.0, 1.0, 1.0\}. \quad (19)$$

Other parameters are

$$M = \mu = 40 \text{ a.u.}, \varepsilon = 360 \text{ K}, r_0 = 0.34 \text{ nm}, U_0 = 10000 \text{ K}.$$

Shock Wave

The results of calculations display that shock wave in liquids starts with a relatively narrow zone of translational nonequilibrium (shock front). In the case of polyatomic molecules, the front is followed by a relaxation zone in which translational energy is transferred to internal degrees of freedom of the molecules. In the relaxation zone's head the total energy is allocated on translational, rotational and low frequency vibrational degrees of freedom, so that their mean energies exceed the equilibrium values defined by the temperature far behind the front. The case of wide vibrational spectrum (13) with λ - set (16) is presented in Figure 1.

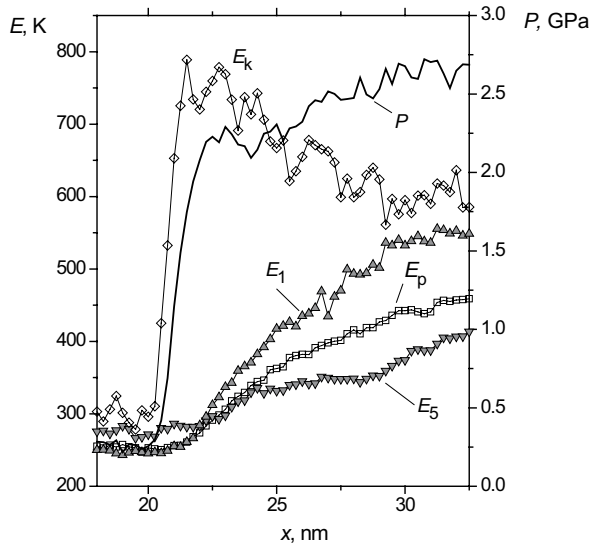


Figure 1. Pressure P and energies, kinetic E_k , vibrational E_1 and E_5 , and total vibrational potential energy E_p versus distance along shock wave propagation, x . System (13), (16).

Low frequency vibrations are overheated due to exponential term of eq. (2). In absence of low frequency vibrations (14) translational energy exceeds the equilibrium values for longer period. In the case of narrow spectrum the difference in λ_k can result in vibrational nonequilibrium. If a substance has a large vibrational heat capacity, the overheat can be quite significant and influence chemical reactions in the relaxation zone.

Detonation Wave

Numerical calculations performed out have shown some opportunity of simulating both steady state detonation waves and processes of initiation of detonation by shock waves or by local heating (Figure 2).

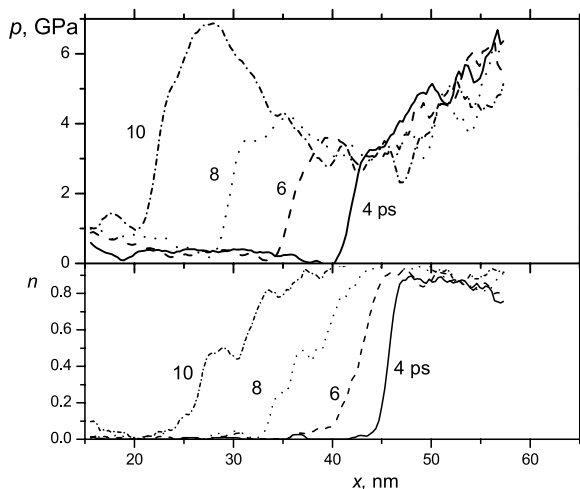


Figure 2. Local heating simulations. Pressure P and concentration of product molecules n versus distance along wave propagation x at various time moments t . Detonation wave initiation.

The typical structure of a detonation wave is presented in Figures 3-4. The molecule has a narrow spectrum (14), λ - (17), and permits a reaction with heat effect, $Q = 20000$ K, and activation energy, $E_A = 5000$ K along 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 performing out kinetic calculations.

Shock Wave Chemistry

Shock waves are usually simulated by molecular dynamics in very large systems with walls in x dimension and with periodic boundary conditions in y and z dimensions [3]. This is the technique used in current work. The main action of a shock wave is supposed to produce translational nonequilibrium. Some techniques were tested to simulate the shock action in small systems. The most suitable results have been achieved by changing the x size in time, while periodic boundaries in x direction have been used also to exclude near-wall effects. This method is used to compare static and shock wave chemistry in the case of slow reactions. Examples of such calculations are presented in Figure 4 and Figure 5.

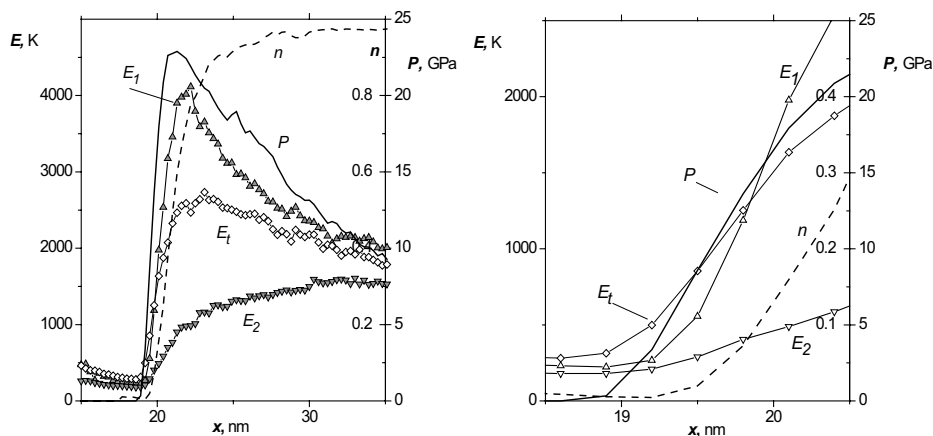


Figure 3. Pressure P , kinetic transversal energy E_t , vibrational energies E_1 and E_2 , and concentration of product molecules n versus distance along detonation wave propagation, x .

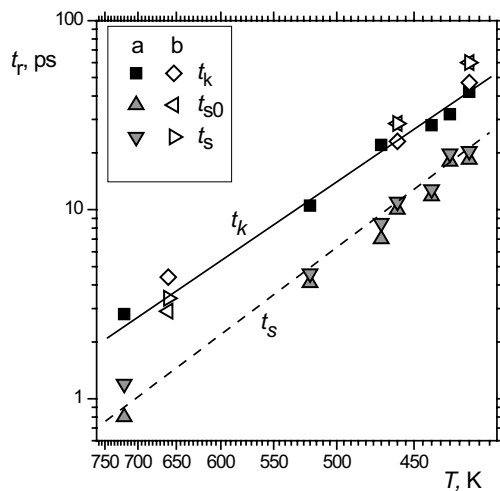


Figure 4. Chemical reaction time versus temperature. Systems (a) and (b) without heat release. Small volume shock compressed (t_s , t_{s0}) and preheated (t_k) in the same final volume.

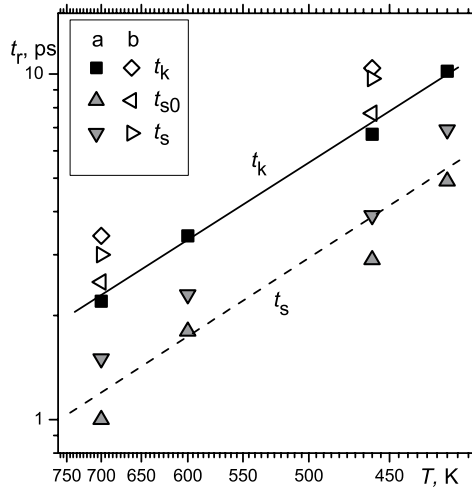


Figure 5. Chemical reaction time versus temperature. Systems (a) and (b) with heat release ($Q=10000$ K). Small volume shock compressed (t_s , t_{s0}) and preheated (t_k).

Values t_s and t_{s0} are measured from the start and finish of compression. Final volumes are the same for all data points. Compression rate is constant and varies from one point to another.

All systems have a narrow spectrum (14), and different sets of λ : (18) - system (a), (19) - system (b). Both systems presented in Figure 4 permit chemical reaction with an activation energy $E_A = 3000$ K and without heat effect, $Q = 0$.

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

The systems presented in Figure 5 permit chemical reaction with an activation energy $E_A = 4000$ K and with heat effect, $Q = 10000$ K. The results and explanation are similar to the previous case ($Q = 0$).

However, chemical kinetics in the exothermic case ($Q = 10000$ K) corresponds to a thermal explosion, i.e. the dependence of n on time has

accelerated growth, and the process has noticeable ignition delay. While there is decreasing growth without any delay in the isothermic case ($Q = 0$). So, these are quite different processes.

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 one to interpret various experimental data by means of a single set of rate constants [16].

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 vary 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 influences chemical reactions. So, the structure of shock and detonation waves depend strongly on the peculiarities of vibrational spectra and the structure of normal modes of compounds.

Acknowledgments

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