

MOLECULAR DYNAMICS STUDY OF VIBRATIONAL - TRANSLATIONAL NONEQUILIBRIUM IN A LIQUID OF POLYATOMIC MOLECULES BEHIND THE SHOCK WAVE FRONT

A. L. Smirnov, S. P. Karkach, O. V. Skrebkov and A. N. Dremin

Institute of Problems of Chemical Physics of Russian Academy of Sciences, Chernogolovka, 142432, Russia
e-mail: asmir@icp.ac.ru

In the present work the shock wave in a liquid consisting of polyatomic molecules is simulated by the method of nonequilibrium molecular dynamics [1] based on numerical solution of motion equations of a large number of particles. To take into account internal degrees of freedom of molecules the motion of separate atoms on a total surface of a potential energy, including both intra- and intermolecular interactions is considered. Unfortunately, there is not enough information on such surfaces for polyatomic molecules, especially in configurations permitting rearrangement of atoms. Furthermore, these interactions should be constructed by reducing potential barriers on reaction paths and vibrational frequencies, to carry out calculations up to the equilibrium region for reasonable time. Alongside with such a conventional approach the present work implements also another way to take into account internal degrees of freedom. The molecules are simulated by multimode oscillators which interact with each other via the isotropic intermolecular potential depending on vibrational coordinates. Such a model of “breathing spheres” is popular in investigation of vibrational relaxation in gases, being a basis of the SSH theory [2]. The given method allows one to explore the processes of the energy redistribution in the shock wave by varying independently each of the following physically significant parameters of the system: small number of parameters of the intermolecular potential, the amount of vibrational degrees of freedom and their frequencies associated with normal modes of molecules.

The calculation results show that the shock wave in a liquid of polyatomic molecules consists of a relatively narrow zone of translational nonequilibrium (shock front) followed by relaxation zone, in which translational energy is transferred to internal degrees of freedom of molecules down to equilibrium defined by the temperature far behind the front. In the relaxation zone head the total energy is allocated on translational, rotational and low frequency vibrational degrees of freedom so that their mean energies exceed their equilibrium values. In the case of a large vibrational heat capacity of substance the overheat can be quite significant to influence chemical reactions in the relaxation zone.

It was found experimentally (see [3]) that under the shock wave conditions aromatic and aliphatic compounds behave differently. The shock destruction process for aromatic compounds differs from that observed in thermal equilibrium. This is in agreement with our calculations of the shock wave structure that strongly depends on the peculiarities of vibrational spectra and relaxation times of compounds.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant № 04-03-32676).

References

- [1] V.Y. Klimenko, A.N. Dremin. Structure of shock wave front in a liquid - In : Detonation, Chernogolovka, 1978, pp. 79-83.
- [2] Herzfeld K.F., Litovitz T.A. Absorption and dispersion of ultrasonic waves, N.Y.-Lond.: Acad.Press, 1959.
- [3] A.N. Dremin, L.V. Babare. The shock wave chemistry of organic substances – AIP Conference Proceedings “Shock Waves in Condensed Matter - 1981” (Menlo Park). N.Y., 1982, pp. 27-41.