OBTAINING OF ISOTHERMAL CHARACTERISTICS AND EQUATION OF STATE PARAMETERS FOR PETN BY THE METHODS OF REACTION MOLECULAR DYNAMICS AND THEMODYNAMICS

S. A. Gubin[1], S. A. Kozlova[1,2], and I. V. Maklashova[1]

[1]National Research Nuclear University MEPhI, 31 Kashirskoe Sh., Moscow 115409, Russian Federation
[2]National Research Center "Kurchatov Institute," 1 Kurchatov Sq., Moscow 123098, Russian Federation

Abstract: The isothermal compression of an unreacting pentaerythritol tetranitrate (PETN) single crystal has been investigated using molecular dynamics (MD) method in the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software package with the reactive force field (ReaxFF) in the pressure range up to 30 GPa. The values of the compression modulus coefficient $K_0 = 9.6$ GPa and the derivative of the compression modulus K_0 with respect to pressure $K_0' = 8.0$ were obtained based on MD simulation. These values can be used as parameters of the 3rd order Birch–Murnaghan thermal equation. The coefficients of the equation of state (EoS) in the Mie–Grüneisen form were fitted based on the obtained isotherms and experimental data. The authors used the method for determination the isochoric-isothermal potential of solids in the form of Einstein's quasi-harmonic approximation. The obtained EoS can be used to simulate the thermophysical properties of matter including those under static and shock-wave compression. Verification of the results showed good agreement with the experimental data in a wide range of pressure and temperature changes including at the shock Hugoniot.

Keywords: molecular dynamics; particle ensemble evolution; molecular crystals; dissociation; extreme impacts; equilibrium and nonequilibrium states; shock Hugoniot; equation of state

DOI: 10.30826/CE22150212 **EDN:** YGVWGB

Figure Captions

Figure 1 Individual molecule of PETN (*a*); and frontal view of the calculated super-cell of a PETN single crystal (3132 atoms) (*b*)

Figure 2 Dependence of the pressure during isothermal compression on the compression ratio of the PETN single crystal: *1* — MD, 300 K, this work; *2* — MD, 413 K, this work; *3* — MD (RealFF-lg) [7]; *4* — experiments [9]; and *5* — experiments [11]

Figure 3 Dependence of the pressure behind the shock front on density: *1* — the present authors' thermodynamic calculation using the obtained EoS in the Mie–Grüneisen form; and *2* — experimental data [18]

Table Caption

Table 1 Properties of solid PETN at normal conditions

Table 2 Equation of state coefficients for PETN

Acknowledgments

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Government Order Project No. 07232020-0036).

References

1. The classical molecular dynamics package LAMMPS. 2004. Available at: http://lammps.sandia.gov (accessed May 22, 2022).
2. Van Duin, A. Department of Mechanical Engineering. Available at: http://www.engr.psu.edu/adri/Home.aspx (accessed May 22, 2022).
3. Budzien, J., A. P. Thompson, and S. V. Zybin. 2009. Reactive molecular dynamics simulations of shock through a single crystal of pentaerythritol tetranitrate. *J. Phys. Chem. B* 113(40):13142–13151. doi: 10.1021/jp9016695.
4. Zybin, S. V., W. I. Goddard, P. Xu, A. V. Duin, *et al.* 2010. Physical mechanism of anisotropic sensitivity in pentaerythritol tetranitrate from compressive-shear reaction dynamics simulations. *Appl. Phys. Lett.* 96(8):081918. 3 p. doi: 10.1063/1.3323103.
5. Landerville, A. C., I. I. Oleynik, and C. T. White. 2009. Reactive molecular dynamics of hypervelocity collisions of PETN molecules. *J. Phys. Chem.* 113:12094–12104. doi: 10.1021/jp905969y.

6. Shan, T. R., and A. P. Thompson. 2014. Shock-induced hotspot formation and chemical reaction initiation in PETN containing a spherical void. *J. Phys. Conf. Ser.* 500(17):172009. doi: 10.1088/1742-6596/500/17/172009.
7. Liu, L., Y. Liu, S. V. Zybin, H. Sun, and W. A. Goddard. 2011. Correction of the ReaxFF reactive force field for London dispersion, with applications to the equations of state for energetic materials. *J. Phys. Chem.* 115(40):11016–11022. doi: 10.1021/jp201599t.
8. Strachan, A., A. C. T. van Duin, D. Chakraborty, S. Dasgupta, and W. A. Goddard. 2003. Shock waves in high-energy materials: The initial chemical events in nitramine RDX. *Phys. Rev.* 91:098301-1–098301-4. doi: 10.1103/PhysRevLett.91.098301.
9. Olinger, B., P. M. Halleck, and H. H. Cady. 1975. The isothermal linear and volume compression of pentaerythritol tetranitrate (PETN) to 10 GPa (100 kbar) and the calculated shock compression. *J. Chem. Phys.* 62(11):4480–4483.
10. The Cambridge Crystallographic Data Centre (CCDC). Available at: https://www.ccdc.cam.ac.uk (accessed May 22, 2022).
11. Yoo, C., H. Choong-Shik, W. M. Howard, and N. Holmes. 1998. Equations of state of unreacted high explosives at high pressures. *11th Detonation Symposium (International) Proceedings*. Aspen, CO. 951–957.
12. Zharkov, V. N., and V. A. Kalinin. 1968. *Uravneniya sostoyaniya tverdykh tel pri vysokikh davleniyakh i temperaturakh* [Equations of state of solids at high pressures and temperatures]. Moscow: Nauka. 312 p.
13. Molodets, A. M., M. A. Molodets, and S. S. Nabatov. 2000. Thermodynamic potentials of carbon. *Combust. Explo. Shock Waves* 36(2):240–245.
14. Burcat, A., and B. Ruscic. 2005. *Third millennium ideal gas and condensed phase thermochemical database for combustion with updates from active thermochemical tables*. Argonne National Laboratory by The University of Chicago.
15. Fan, J., F. Yan, Z. Zhaoyang, and J. Zhao. 2021. Thermal properties of energetic materials from quasi-harmonic first-principles calculations. *J. Phys. — Condens. Mat.* 33(27):275702. doi: 10.1088/1361-648X/abfc11.
16. Gonzalez, J. M., A. C. Landerville, and I. I. Oleynik. 2017. Vibrational and thermophysical properties of PETN from first principles. *AIP Conf. Proc.* 1793:070009. doi: 10.1063/1.4971597.
17. Dobratz, B. M. 1976. *Properties of chemical explosives and explosives stimulants*. Livermore, CA: LLNL.
18. Marsh, S. P. 1980. *LASL shock Hugoniot data*. Los Angeles, CA: University of California Press. 674 p.

Received February 21, 2022

Contributors

Gubin Sergey A. (b. 1945) — Doctor of Science in physics and mathematics, professor, head of department, National Research Nuclear University MEPhI, 31 Kashirskoe Sh., Moscow 115409, Russian Federation; gubin_sa@mail.ru

Kozlova Sandra A. (b. 1992) — engineer, National Research Center "Kurchatov Institute," 1 Kurchatov Sq., Moscow 123098, Russian Federation; engineer, National Research Nuclear University MEPhI, 31 Kashirskoe Sh., Moscow 115409, Russian Federation; sandra969@yandex.ru

Maklashova Irina V. (b. 1975) — senior lecturer, National Research Nuclear University MEPhI, 31 Kashirskoe Sh., Moscow 115409, Russian Federation; ivmaklashova@mephi.ru