

12. Е. Б. Смирнов, О. В. Костицын, и др.. Уравнение состояния 1,3,5 –триамино – 2,4,6 – тринитробензола на основе результатов статических экспериментов. XII Забабахинские научные чтения. 2014, Снежинск
13. В. М. Dobratz, Р. С. Crawford. Properties of Chemical Explosives and Explosive Simulants // Lawrence Livermore National Laboratory, 1985.- Report №UCRL-52997, Change.
14. E.V. Shorohov, B.V. Litvinov. Hugoniot adiabat of plasticized TATB-based explosive compositions // ShockWaves end Marseille III. Springer Verlag Berlin Heidelberg 1995.
15. E.B. Smirnov, A.N. Averin, B.G. Loboiko, O.V. Kostitsyn, Yu.A. Belenovskiy, A.V. Lebedev, V.N. Scherbakov, K.M. Prosvirnin, A.N. Kiselev, K.V. Eganov, V.M. Volkov, V.V. Kozel. Shock compressibility of low-sensitive he of different initial porosity // 15th International Detonation Symposium, July 13 – 18, 2014, San Francisco, CA.

EQUATION OF STATE OF CHON EXPLOSIVES

*M.F. Biriukova¹, D.V. Petrov¹, A.Yu. Garmashev¹, A.K. Muzyria¹, Yu.M. Kovalev²,
E.B. Smirnov^{1,2}, A.V. Stankevich¹, E.S. Shestakovskaya², L.H. Badretdinova³*

¹ RFNC-VNIITF, Snezhinsk, Russia

² South Ural State University (SRI), Chelyabinsk, Russia

³ Kazan National Research University of Technology, Kazan, Russia

Construction of equations of state (EOS) appears to be an essential element in mathematical modeling of nonstationary gasdynamic processes of impulse action on matter. Current EOS for explosives are oriented towards solution of such individual tasks as: isothermic compression, Hugoniot adiabats, and calculations of temperature dependencies of isobaric heat capacity. The approach described in the given paper would make it possible to solve all the above problems comprehensively.

Solid explosives EOS is most often based upon the two potentials: Gibbs potential $G(T,P)$ and Helmholtz potential $F(T,V)$ [1]. In the present paper when constructing physically correct equation of state of explosive it is the most convenient to reason from Helmholtz free energy. When constructing the function $F(V,T)$ analytic expression it is generally accepted to present it in the form of the sum of potential (elastic) and kinetic (heat) constituents:

$$F(V, T) = F_{\Pi}(V) + F_T(V, T), \quad (1)$$

where $F_{\Pi}(V)$, $F_T(V, T)$ is the potential (elastic, or cold) and heat parts of the free energy, respectively.

Quasiharmonic part of the free energy is determined by vibrational motion of molecules incorporated into crystal and could be presented by well-behaved various models [1-5]. In the given paper we describe explosives thermal characteristics in Debye and Einstein approximation and then obtain the thermal constituent if the form:

$$F_T = MRT(\ln(1 - \exp(-\frac{\theta_D(\delta)}{T})) - \frac{D(\theta_D/T)}{3}) + (3N - M)RT \ln(1 - \exp(-\frac{\theta_E}{T})), \quad (2)$$

where: $\delta = \rho/\rho_{ok} = V_{ok}/V$ - specific volume; ρ - current density; R - molar gas constant; N - number of atoms in a molecule; $(3N - M)$ - number of high-frequency oscillations; M - number of low-frequency oscillations; θ_E - Einstein characteristic temperature; $D(\theta_D/T)$ - Debye function; θ_D - Debye temperature. The pressure thermal constituent, according to equation (2), can be put as follows:

$$P_T(\delta) = MRTD(\frac{\theta_D}{T})\gamma(\delta)\rho_0 + \frac{(3N - M)R\theta_E\gamma(\delta)\rho_0}{\exp(\theta_E/T) - 1}, \quad (3)$$

The potential component form in equation (1) depends upon a solid body type. For solid bodies referring to molecular crystals the attractive forces are Van der Waals forces, while repulsive forces, as in

ionic crystals, are caused by electron shell overlapping [6]. Using examination of repulsive and attractive forces as the basis we choose the expression for EOS cold constituent with consideration of zero-point vibrations of the form:

$$F_{II} = \frac{3}{8} MR \rho_0 \gamma(\delta) \theta(\delta) + \frac{3C_{0k}^2}{bn(b-3n-1)} [3n \exp[b(1-\delta^{-1/3})] - b\delta^n], \quad (4)$$

where b, n - empirical constants; ρ_0 - density at $T=293K$; ρ_{0k} and C_{0k} - density of matter and velocity at $T=0 K$ and $P=0$ ГПа; $\gamma(\delta)$ - Grüneisen coefficient. Besides, it is recommended to present elastic potential and elastic pressure component of the form:

$$P_{II}(\delta) = \frac{3C_{0k}^2 \rho_{0k}}{(b-3n-1)} [\delta^{2/3} \exp(b(1-\delta^{-1/3})) - \delta^{(n+1)}], \quad (5)$$

$$E_{II}(\delta) = \frac{3}{\rho_0} \left[\frac{3\rho_{0k} C_{0k}^2}{b-3n-1} \exp(b(1-\delta^{-1/3})) - \frac{3\rho_{0k} C_{0k}^2}{b-3n-1} \delta^{1/3} \right] \quad (6)$$

Based on the examination of Grüneisen coefficient analytic representation, the Grüneisen coefficient volume dependence in Zubarev-Vaschenko form is chosen for constructing explosive EOS. With consideration of (5) we obtain the expression for Grüneisen coefficient in the form:

$$\gamma(\delta) = \gamma_0 \left(-\frac{1}{2} \delta \frac{\partial^2 (P_{II} / \delta^{4/3}) / \partial \delta^2}{\partial (P_{II} / \delta^{4/3}) / \partial \delta} \right), \quad (7)$$

According to equations $\theta(\rho) = \theta_0 \exp \int \frac{\gamma(\rho)}{\rho} d\rho$, and (7) for Debye temperature, we can put:

$$\theta_D(\delta) = \theta_0 \exp \left(\frac{1}{2} \gamma_0 \frac{\partial (P_{II} / \delta^{4/3}) / \partial \delta}{(P_{II} / \delta^{4/3})} \right), \quad (8)$$

where θ_0, γ_0 - Debye temperature and Grüneisen coefficient at $\rho = \rho_{0k}$, respectively.

The obtained phase-unchanged semi-empirical EOS based on Helmholtz free energy is used for determining CHON explosives EOS. We use pentaerythrite tetranitrate ($C_5H_8N_4O_{12}$), cyclo-trimethylenetrinitramine ($C_3H_6N_6O_6$), and triamino-trinitrobenzene ($C_6H_6N_6O_6$) as representatives of the given chemical composition.

Isothermic compression curve of triamino-trinitrobenzene down to pressures $\sim 6,5$ GPa at temperature $T_0=293 K$ is obtained at accelerator facilities at INP SB RAS using powder diffraction technique at triamino-trinitrobenzene compression in diamond anvil cell. Isothermic compression of pentaerythrite tetranitrate down to pressures 10 GPa is obtained by pressing [7]. Data on pentaerythrite tetranitrate is borrowed from paper [8].

The interrelation between explosive pressure $P(\delta)$ and volume fraction (triamino-trinitrobenzene, pentaerythrite tetranitrate, cyclo-trimethylenetrinitramine) is presented in Figures 1-3.

$$P(\delta) = P_{II}(\delta) + P_T(\delta), \quad (9)$$

Data on triamino-trinitrobenzene isothermic compression [12] is approximated by equation (9) obtained on the hypothesis that pressure is composed of potential and thermal constituents in combination with data from paper [9]. Data [9] is used with a view to extend the calculated relationship validity range up to 14 GPa. Data from papers [10] and [11] is neglected at approximation, they are presented for comparison purposes. The calculated curve deviation $P(\delta)$ from the experimental data (Figures 1b, 2b, 3b) does not exceed this data error and levels 2-3%.

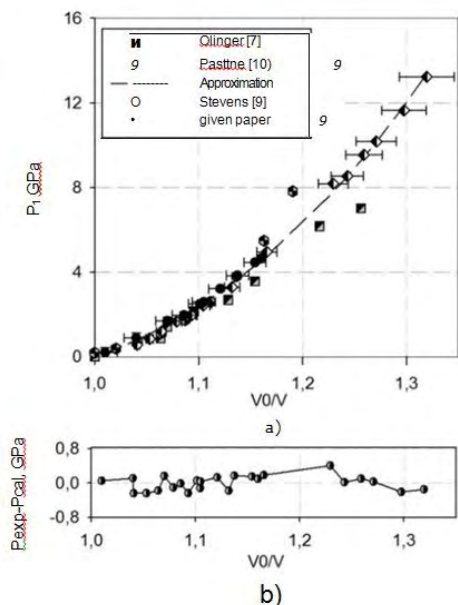


Figure 1. Triamino-trinitrobenzene isotherm at $T=\text{const}$

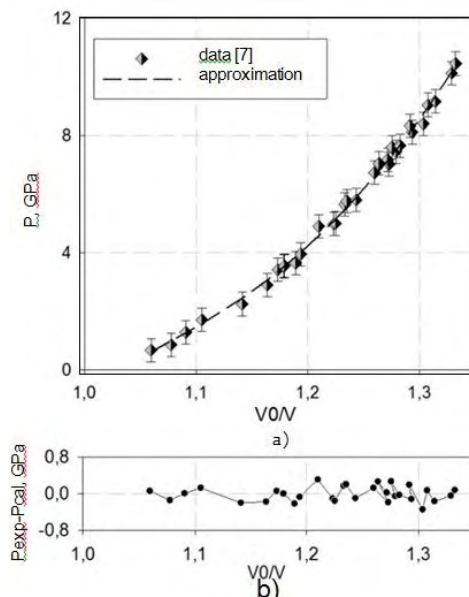


Figure 2. Cyclo-trimethylenetrinitramine isotherm at $T=\text{const}$

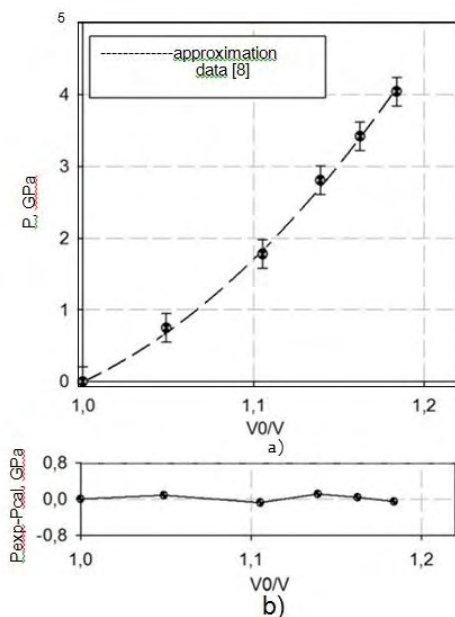


Figure 3. Pentaerythrite tetranitrate isotherm at $T=\text{const}$

For an update on EOS thermal constituent we conducted experiments on explosive constant-pressure heating and cooling processes at pressure 0.1 MPa with diffractometric approach within the temperature range from 150 K to 370...500 K (depending on explosive type). The conducted X-ray structure analysis allows us to construct isobars.

Explosive isobars from Figure 4 are calculated on the basis of the expression: $V = \frac{V_{0k}}{1 + V_{0k} K_{\alpha} D(\theta_D/T)}$,

where V_{0k} – volume at $T=0K$; K_{α} – parameter to be fit; $D(\theta_D/T)$ – Debye function.

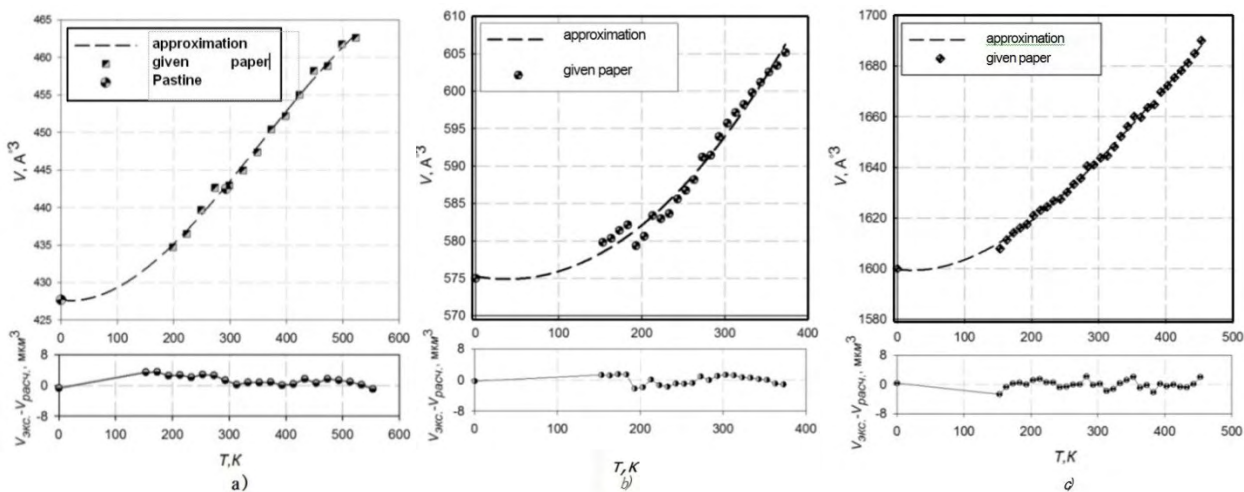


Figure 4. Triamino-trinitrobenzene (a), pentaerythrite tetranitrate (b), cyclotrimethylenetrinitramine (c) isobars at pressure $P=10^5$ Pa within temperature range from 150 K to 370...550 K (depending on explosive type)

Explosive EOS correctness is verified by description of experiments with powdered samples of triamino-trinitrobenzene explosive under investigation. For that purpose we use data for isobaric heat capacity $C_P(T)$ obtained with calorimetric technique.

For heat capacity $C_P(T)$ the following expression is valid:

$$C_p = MR(4D(\frac{\theta_D}{T}) - \frac{3\theta_D}{T}) + (3N - M)R(\frac{\theta_E}{T})^2 \frac{\exp(\frac{\theta_E}{T})}{(\exp(\frac{\theta_E}{T}) - 1)^2} (1 + \alpha\gamma(\delta)T) \quad (10)$$

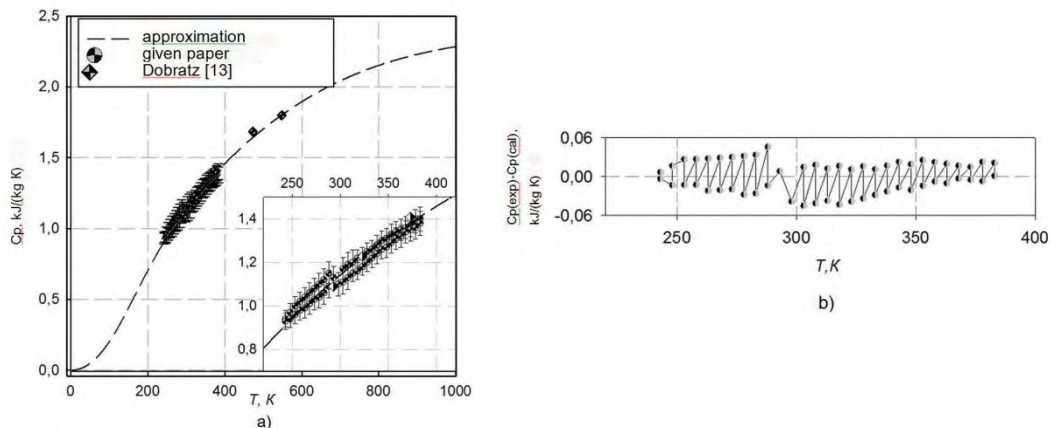


Figure 5. Triamino-trinitrobenzene heat capacity at constant pressure C_p

Heat capacity at constant pressure $C_P(T)$ calculated according to expression (10) is presented in Figure 5a. By comparing values calculated according to formula (10) with experimental data we obtain good agreement within empirical data error. Figure 5a presents experimental data from the American researchers' paper [13], which are in good agreement between each other and the data in the given paper.

Figure 5b presents the approximation quality in the form of difference between experimental and calculated values, which does not exceed 6%.

Correctness of triamino-trinitrobenzene explosive EOS was verified by description of shock compression experiments. Hugoniot adiabat P_r presenting dependence of shock pressure on compressed matter specific volume has the form:

$$P_r = \frac{P_{II}(\delta) + \frac{\rho_0 \gamma(\delta)}{\delta} [E_0 - E_{II}(\delta)]}{1 - \frac{\gamma(\delta)(1-\delta)}{2\delta}}, \quad (11)$$

where P_{II} – potential pressure (6), $a E_{II}$ – elastic potential (6) and E_0 have the form:

$$E_0 = E_{II}(1) + \frac{R}{\mu} \left[\frac{9}{8} \theta_0 + 3TD \left(\frac{\theta_0}{T} \right) \right].$$

Figure 6a together with experimental data of papers [14, 15] presents a calculated isotherm of triamino-trinitrobenzene explosive and triamino-trinitrobenzene Hugoniot adiabat calculated on the basis of equation (11).

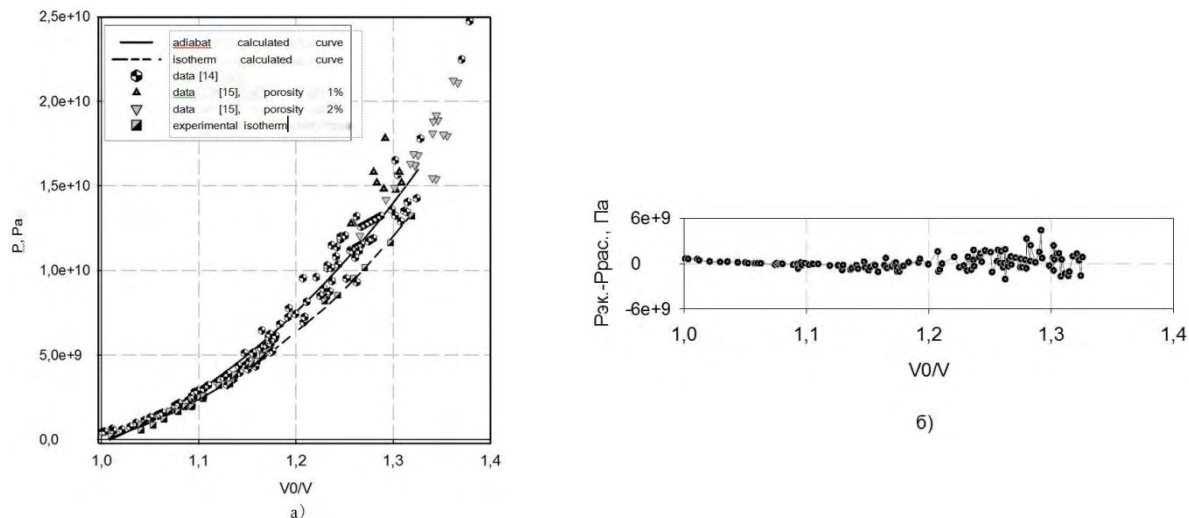


Figure 6. Hugoniot adiabat and triamino-trinitrobenzene isotherm

Relative positions of the isotherm and the adiabat are in agreement with physical interpretation of isothermic and adiabatic compression of materials.

We obtain semi-empirical equation of state of crystal explosive (triamino-trinitrobenzene, pentaerythrite tetranitrate, cyclo-trimethylenetrinitramine), which thoroughly describes static experiments on isothermal compression and constant-pressure cooling and heating. EOS validity is verified by good description of experiments on shock compression and heat capacity determination for powdered explosives.

It may be expected that application of the proposed EOS would make it possible to enhance precision of description of unfissioned explosive thermodynamic parameters at numerical simulation of shock-wave and detonation processes.

References

1. V. N. Zharkov, V. A. Kalinin. Equation of State of Solid Bodies under High Pressures and Temperatures // M.: Nauka, 1968, 311 pp.
2. A. T. Sapozhnikov, A. V. Pershina. Semi-empirical Equation of Metal State within Pressures and Temperatures Wide Range. VANT. Techniques and Codes for Numerical Solution of Mathematical Physics Problems. 1979. Vol. 4(6). 47-55.
3. P. I. Dorogokupets. Equation of State of Minerals Based on Potential Method in Bose-Einstein Approximation. Vestnik OGGGN RAS, 2000, № 5 V, 1(15).
4. Yu. M. Kovalev, A. V. Belik. Determination of thermal Constituent of Molecular Crystals Equation of State. Bulletin of South Ural State University. 2013, № 9 (300). Physics. Volume 16. Pp. 5–10.
5. Yu. M. Kovalev. Grüneisen Coefficient Form Determination for Molecular Crystals. Academy of Sciences Reports. 2005, V. 403, N 4, pp. 475-477

6. A. I. Kitaigorodsky. *Molecular Crystals*//M.: Nauka, 1971. - 424 p.
7. B. Olinger, P.M. Halleck, and H.H. Cady, The Isothermal Linear and Volume Compression of Pentaerythritol Tetranitrate to 10GPa and the Calculated Shock Compression, *Jour. Chem. Phys.*, Vol. 62, pp. 4480-4483, 1975.
8. E. F. C. Byrd, B. M. Rice, Ab Initio Study of Compressed 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, Cyclo-trimethylenetrinitramine, 2,4,6,8,10,12-Hexanitrohex-aazaisowurzitane, 2,4,6-Trinitro-1,3,5-benzenetria-mine, and Pentaerythritol Tetranitrate, *J. Phys. Chem. C* 2007, 111, 2787.
9. L. L. Stevens, N. Velisavljevic, D. E. Hooks, D.M. Dattelbaum. Hydrostatic Compression Curve for Triamino-Trinitrobenzene Determined to 13.0 GPa with Powder X-Ray Diffraction. *Propellants, Explosives, Pyrotechnics* 33, No. 4, 2008.
10. D. J. Pastine, R. R. Bernecker. P,V,E,T Equation of State for 1,3,5-Triamino-2,4,6-Trinitrobenzene, *J. Appl. Phys.* 1974, 45.
11. B. Olinger, H. Cady. The Hydrostatic Compression of Explosives and Detonation Products to 10 GPa and Their Calculated Shock Compression: Results for PETN, TATB, CO₂ and H₂O, 6th Symposium (International) on Detonation, Coronado, California, USA, 1976.
12. E. B. Smirnov, O. V. Kostitsyn et al., Equation of State of 1,3,5-triamino-2,4,6-trinitrobenzol Based on Static Experiments Results. XII Zababakhin Scientific Talks. 2014, Snezhinsk
13. B. M. Dobratz, P. C. Crawford. Properties of Chemical Explosives and Explosive Simulants // Lawrence Livermore National Laboratory, 1985.- Report №UCRL-52997, Change.
14. E.V. Shorohov, B.V. Litvinov. Hugoniot adiabat of plasticized TATB-based explosive compositions // *ShockWaves* end Marseille III. Springer Verlag Berlin Heidelberg 1995.
15. E.B. Smirnov, A.N. Averin, B.G. Loboiko, O.V. Kostitsyn, Yu.A. Belenovsky, A.V. Lebedev, V.N. Scherbakov, K.M. Prosvirnin, A.N. Kiselev, K.V. Eganov, V.M. Volkov, V.V. Kozel. Shock compressibility of low-sensitive he of different initial porosity // 15th International Detonation Symposium, July 13 – 18, 2014, San Francisco, CA.

EXPERIMENTAL STUDY OF THE RESIDUAL STRONG NUCLEAR INTERACTION VIA RENORMALIZATION OF THE ELEMENTARY EXCITATIONS ENERGY OF SOLIDS

V.G. Plekhanov

Fonoriton Sci. Lab., Garon Ltd., Lasnamae 22 - 3, Tallinn 11413, Estonia

Keywords: strong interaction, quarks, gluons, excitons, phonons, quantum chromodynamics and electrostatics.

Abstract. Artificial activation of the strong interaction by adding of one neutron to the nucleus causes the global reconstruction of the macroscopic characteristics of solids. The experimental evidence of macroscopic manifestation of the strong interaction in optical spectra of solids which are differ by term of one neutron from each other (using LiD crystals instead LiH) has been presented. This evidence is directly seen from luminescence and scattering spectra. As far as the gravitation, electromagnetic and weak interactions are the same in both of kind crystals, it only changes the strong interaction. Therefore a sole conclusion is made that the renormalization of the energy of electromagnetic excitations (electrons, excitons, phonons) is carried out by the strong nuclear interaction. The necessity to take into account the more close relation between quantum chromodynamics and quantum electrostatics is underlined. In the first step the quantum electrostatics should be taken into account the strong interaction at the description of elementary excitations (electrons, excitons, phonons) dynamics in solids.