The Hugoniot adiabat of crystalline copper based on molecular dynamics simulation and semiempirical equation of state

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Abstract. The molecular dynamics (MD) method was used for prediction of properties of copper under shock-wave compression and clarification of the melting region of crystal copper. The embedded atom potential was used for the interatomic interaction. Parameters of Hugoniot adiabats of solid and liquid phases of copper calculated by the semiempirical Grüneisen equation of state are consistent with the results of MD simulations and experimental data. MD simulation allows to visualize the structure of cooper on the atomistic level. The analysis of the radial distribution function and the standard deviation by MD modeling allows to predict the melting area behind the shock wave front. These MD simulation data are required to verify the wide-range equation of state of metals. The melting parameters of copper based on MD simulations and semiempirical equations of state are consistent with experimental and theoretical data, including the region of the melting point of copper.

1. Introduction
The research of phase and polymorphic transitions of matter under intense pulsed impact are needed for obtaining new knowledge about physical processes and properties of materials at high pressures, densities and temperatures. These data constitute the scientific basis of promising energy projects such as the controlled thermonuclear fusion with inertial confinement of hot plasma, the space nuclear installations, and numerous applied problems of explosion physics [1]. The obtained data are necessary for understanding of the processes occurring in the detonation waves of heterogeneous energy-intensive substances with particles of metals and materials used as shell charges.

Behavior of substances in a wide range of pressure and temperature, including high pressures and temperatures, can be predicted on the basis of semiempirical equation of state (EOS) [2–4] and molecular dynamics (MD) simulation. Quant-molecular dynamics and molecular dynamics simulations [5–13] give the opportunity to visualize the internal structure of the substance for determining and prediction of structural and phase transformations in the substance under shock compression. Models of wide-range semiempirical EOS of different phases of the substance are required for gasdynamic and thermodynamic calculations at high pressures and temperatures. Models and coefficients of semiempirical EOS substances are usually based on data of comprehensive isotropic compression. Therefore such EOSs forecast the phase transformation parameters insufficiently correctly due ignoring the anisotropy of the structure
of the material, which manifests itself in different compressibility along various crystallographic directions. This can reduce the reliability of gasdynamic and thermodynamic calculations based on semiempirical EOS models.

The structure anisotropy and phase transformations of the substance under shock wave can be taken into account by MD modeling. This allows us to compare the Hugoniot parameters obtained by MD simulations with calculated according to semiempirical EOS. Such comparison lets to estimate the range of superheating or supercooling of substance due to anisotropy. Structure disorder and melting of crystal behind the shock wave begins in various crystallographic directions at different pressure and temperature [9–13], which impedes to accurately determine parameters of the beginning and total melting of the substance.

Thus, the aim is to determine the region in which the anisotropy can lead to significant differences in deformation along various crystallographic directions of the example of well-studied copper based on MD simulation and to assess the effect of this phenomenon on the accuracy of semiempirical EOSs that don’t take into account the anisotropy of the crystal.

2. Equation of state

Experimental shock Hugoniot get the data for finding the thermodynamic properties of matter in a wide range of pressures and temperatures. It is necessary to know EOS to calculate the state parameters of shock-compressed matter. EOS models are based traditionally on experimental data on shock compressibility of materials. Usually, to describe the state of matter in shock waves using semiempirical wide-range analytic EOS as $P = P(V, E)$ ($P$ is the pressure, $V$ is the specific volume) in the form of Mie–Grüneisen: $PV = P_0 V + \Gamma E$, where $P_0$ is the pressure at temperature $T = 0$ K, $\Gamma$ is Grüneisen constant, $E$ is the thermal energy of the crystal lattice. The value of $P_0$ is determined by the structure of the lattice and the interaction potential of the particles. The first term in this equation describes the energy of elastic interaction of atoms and the second—thermal energy of interaction of atoms of the crystal lattice [14].

The EOS is possible to obtain as the isochoric-isothermal potential of the matter. The first and second isochoric-isothermal potential partial derivatives give values of thermodynamic and thermo-physical and elastic-mechanical properties of substances in the investigated interval of pressures and temperatures. Thus, the EOS is necessary not only for calculating gasdynamic processes and the thermodynamic parameters of shock-compressed matter, but also to predict whole line of properties of this substance at high pressures and temperatures. EOS materials are also required for computer calculations of thermophysical properties at high pressure and temperatures. The wide-range semiempirical EOSs based on experimental data of compressibility are often unable to correctly predict the phase transformations of matter in shock and detonation waves. The parameters of phase transitions are found from the equality of chemical potentials of phases but at the same time the chemical potentials are determined from semiempirical EOS of the phases and depend on accuracy of semiempirical EOS. To correct EOS it is important to get accurate experimental date of the density change in shock waves. However, the currently used traditional experimental methods do not allow to directly measure the density and temperature in shock waves.

The atomic structure of crystalline substances is compressed and is changed as a result of structural and polymorphic phase transformations under compression of substances in shock wave. However the obtaining of information on polymorphic and phase transformations at high pressures and temperatures using experimental Hugoniot data is problematic. Structural and polymorphic transformations of matter are displayed on the shock Hugoniot as small tilts or the curve bends. These small deviations are uniquely difficult to predict and interpret the changes in the internal structure of the material compressed in the shock wave. The application of semiempirical EOS also has difficulties to uniquely identify structural and phase changes especially nonequilibrium transformations.
3. MD simulation

MD simulation allows to calculate the changes of atomic structure and accurately find the parameters of the initial melting point of the substance in the shock wave.

Implemented in SageMD code [15] Hugoniotstat method [16] has been used for MD simulations of shock compression of a copper crystal. The computational MD supercell is constructed from unit cells in each direction and consisted of 13500 atoms of cooper. In carrying out MD simulations in all three spatial directions used periodic boundary conditions. The embedded atom method potential [15] was used for the interatomic interaction in solid and liquid phases in contrast to semiempirical EOS obtained for each phase of cooper. After the formation of the computational cell the temperature was determined from the Rankine—Hugoniot relationship for fixed pressure. For set pressure $P$ and obtained temperature $T$ the thermophysical and thermodynamic properties of cooper behind the shock front were determined. Figure 1 presents the calculated Hugoniot adiabates based on semiempirical EOS and MD simulation versus experimental data [17–19].

The visualization tools allow to track the atomic structure, the distribution of atoms in a microvolume and to determine the phase state of matter. The change of the atoms location in the computational cell during melting clearly indicates the loss of near and long-range order. The use of the radial distribution function (RDF) of atoms in the MD modeling allows to analyze the transformation of condensed matter and fix the melting behind the shock wave front.

As shown in figure 2 there are three peaks of RDF at pressure $P = 180$ GPa, the first two are most pronounced. The RDF peaks shift to the left with increasing pressure and the second and third maxima degrade, that is clearly seen at $P = 260$ GPa and $P = 280$ GPa, respectively. The radial distribution function of the atoms at higher pressure $P > 220$ GPa indicates the disappearance of long-range order in the crystal lattice, it is possible that at these parameters begins melting of cooper crystal. The melting region of copper crystal under shock compression...
Figure 2. The dependence of RDF on distance at shock-wave compression up to pressure 180, 220, 260, 280 GPa.

is located in the range of pressure of 220–280 GPa and a temperature of 5560–6700 K.

The figure 3 shows the dependence of the deformation of copper along various crystallographic directions on the pressure behind the shock wave. The existence of a strong dependence on the orientation of a copper crystal in a shock wave, as shown in MD simulations [9–13], was experimentally verified in [20]. According to experimental results [20] that this phenomenon is not visibly observed. Real crystal defects and structural imperfection negate the differences in deformation in various directions. However, the absence of a dependence of the compression on the orientation of the copper crystal can be due to the low degrees of compression of copper in the shock wave in experimental studies [20]. The visible difference in deformation of the crystal along the directions occurs at pressures above 100 GPa. The greatest deviation in deformation along the directions starts near the melting range of copper in a shock wave at a pressure above 200 GPa.

Most of the experimental techniques don’t allow to obtain direct information on the density and microstructure of substance during the dynamic experiment. The radiographic study with the usage of high-energy beams of charged particles (including protons) provide such opportunities [1, 21]. Direct measurement of density in shock compressed sample copper have been performed at the Los Alamos Neutron Science Center (USA) in 2008. Method of proton-radiographic allows to measure with high precision the density of the copper compressed by the shock waves. The pressure and density values obtained by this method are shown in figure 3 by the round marker.

The differences in the deformation of a copper crystal along various crystallographic directions (if they exist in a real crystal) can lead to difficulties in accurately experimentally determination of the beginning and finishing of melting. Our MD simulation shows that the two-phase starts from \( P = 220 \) GPa, \( T = 5560 \) K and the total melting occurs at \( P = 280 \) GPa, \( T = 6700 \) K. This range is slightly wider than the experimentally determined mixed phase pressure from 232 to 265 GPa [22]. The orientation dependence of copper compression along the crystallographic
directions leads to the expansion of the two-phase region into lower pressures and temperatures. In this case, melting begins as a result of overheating in one crystallographic direction (100) as in [11]. If we neglect the differences in the deformation along the crystallographic directions, the melting range will decrease. The consideration of anisotropy does not give significant advantages for the prediction of the properties of substances up to the melting region.

4. Conclusion
The new unique experimental data obtained by proton radiography make possible to develop the physical and mathematical models of EOS with high reliability and good predictive qualities. Such EOS will form the basis of computer modeling of the behavior of substances and materials under extreme conditions. The accuracy of modeling forecast depends on the fundamental models, the depth of understanding of the physical processes, reliability of description materials properties at high pressures and temperatures.

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