Interpretation of experiments on shock compression and isentropic expansion of uranium by quantum molecular dynamics simulations

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Abstract. In this work, results of quantum molecular dynamics calculations of thermodynamical properties of uranium are presented. The experiments on shock compression and subsequent isentropic expansion of porous samples of uranium are well described. Our first-principle calculations of the shock Hugoniot and release isentropes of uranium demonstrate good agreement with experimental measurements. In addition, unique information of temperature along experimental curves was obtained including supposed entries of isentropes into the two-phase liquid–gas region according to the hypothetical kinks on the experimental isentropes.

1. Introduction

The equation of state (EOS) of uranium is essential for the analysis of nuclear safety of existing nuclear reactors or planned for future operation, including numerical modeling of hypothetical conditions that could lead to severe accidents [1].

Dynamic experiments are the basis for the construction of wide-range semiempirical EOS models. In this regard data on shock compression of porous samples significantly expand the investigated region of the phase diagram [2]. Moreover traditional data on release expansion of shocked solid and porous samples in the form of pressure–expansion velocity dependence may also include indirect information on evaporation. However, qualitative analysis of evaporation region is hampered because of lack of temperature information in shock-wave experiments. Therefore additional available information is required like isobaric expansion data and estimations of the critical point [3].

The development of computational methods and supercomputers made it possible to obtain reliable information on the thermodynamic properties of substances as a result of \textit{ab initio} calculations. During the last two decades the quantum molecular dynamics (QMD) method became very popular. It is based upon the density functional theory (DFT), but also takes into account the movement of ions. This approach does not use any empirical data except for fundamental physical constants, so it can serve as a kind of a reference method for the analysis of available experimental data. Currently up to 1000 and more atoms can be used in calculations [4–7], this allows one to study unordered systems and even phase transitions [8]. This makes
QMD a promising method for the description of thermophysical properties of matter in a wide range of parameters. Indeed, in our previous works we demonstrated high accuracy of QMD-computations for Al [9] and Cu [10] and more complicated metals like W [11] and Mo [12]. In this work we apply QMD to reproduce the Hugoniot and release isentropes of porous uranium samples using the method of re-shock Hugoniots and obtain valuable temperature information on experimental curves.

2. Method of calculation

In the work, the Hugoniot and release isentropes of porous uranium samples corresponding to the experiment [13] is reproduced. Calculations of the Hugoniot are performed by numerical solving the Rankine–Hugoniot relation, which connects thermodynamic quantities after and before the shock wave:

\[ H(P, V, E) = E - E_0 + \frac{1}{2}(V - V_0)(P + P_0) = 0, \]

(1)

where \( E \) is the specific internal energy, \( P \) is the pressure, and \( V \) is the specific volume [14]. The initial state parameters are denoted by subscript 0. In case of the Hugoniot calculation of a porous sample the initial specific volume \( V_0 \) is assumed to be the initial specific volume of the porous sample \( V_{00} = 1/\rho_{00} = m/\rho_0 \), where \( \rho_{00} \) is the initial density of porous sample, \( m \) is the porosity, and \( \rho_0 \) is the reference density of solid uranium at ambient conditions. According to this model, a heated solid sample is compressed by a shock wave after the instant collapse of the pores at the initial pressure [14]. To obtain a point on the Hugoniot, we make a series of calculations and use the bisection method to get parameters for which the function \( H(P, V, E) \) vanishes with a desired accuracy.

As a result, our simulation provides the internal energy and pressure on the Hugoniot (1) at given density. The velocity of the shock front (\( u_s \)) and particle velocity behind the shock (\( u_p \)) can be easily restored using the laws of conservation of mass and momentum [15]:

\[ u_s = u_{p0} + V_0 \sqrt{(P - P_0)/(V_0 - V)}, \]

(2)

\[ u_p = u_{p0} + \sqrt{(P - P_0)(V_0 - V)}, \]

(3)

where \( u_{p0} \) is a particle velocity ahead of the shock front. In case of the Hugoniot calculation for initially undisturbed solid and porous samples \( u_{p0} = 0 \); again, for a porous sample \( V_0 \) is assumed to be the initial specific volume of the porous sample \( V_{00} = 1/\rho_{00} = m/\rho_0 \). In case of the calculation of a re-shock Hugoniot the substance ahead of the shock front is accelerated by a previous shock wave, \( u_{p0} > 0 \), and we assume that the shock has velocity \( u_s - u_{p0} > 0 \) with respect to the material ahead of it.

A key feature of the QMD analysis of shock wave experiments is the restoration of temperature information along experimental curves [9, 16]. Current experiments with independent temperature measurements demonstrate very good agreement with QMD calculations [17, 18], confirming predictive power of the method.

In this work, release isentropes are restored by the method of re-shock Hugoniots, which is based on the feature of the second-order contact of a Hugoniot and isentrope at the same initial point [14]. Each successive point on the calculated curve is related to the previous one by the Hugoniot equation (1), where the previous state parameters are denoted by index 0. In turn, the particle velocity on the calculated isentrope can be obtained using equation (3). Earlier it was shown, that an isentrope can be described very well with just several re-shock steps [19, 20].
3. Simulation parameters

We use the method of quantum molecular dynamics using the theory of the density functional with finite temperature (FT-DFT) [21] to obtain the thermophysical properties of uranium. For QMD simulations we use the plane-wave pseudopotential code VASP [22–25] and a projector-augmented wave (PAW) [26] potential with 14 valence electrons for uranium. It should be noted that the applicability of the chosen pseudopotential should be accurately checked for a given range of thermodynamic parameters through the comparison of results of calculations with more accurate pseudopotentials or all-electron approach [27–29]. The detailed analysis for the chosen pseudopotential was presented previously [30]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [31,32] corrections for the exchange-correlation functional is used. The Fermi smearing for electron occupancies is applied. All QMD simulations are made in the canonical ensemble (NVT), so the density of matter $\rho$ is defined by the lattice parameter and remains constant during the simulation process. We use the Nozé–Hoover thermostat to maintain a given temperature. The dynamics of U atoms was simulated within no less than 4 ps with 2 fs time step. The Baldereschi mean-value [33] $k$-point \{1/4, 1/4, 1/4\} is used for sampling the Brillouin zone. Thermodynamic parameters of the system are found by averaging of the corresponding values at the equilibrium stage of the simulation, the estimated statistical error is less than 1%. In this work, QMD simulations are performed for 54 and 128 atoms of U in the range of temperatures from 3 to 56 kK and densities from 6 to 22 g/cm$^3$. The plane-wave cutoff energy is fixed at 500 eV.

4. Results

Calculated Hugoniot of uranium with a porosity $m = 2.45$ together with two release isentropes (denoted as $S_1$ and $S_2$) which correspond to the experiment by Zhernokletov [13] are presented in figure 1 in the pressure–particle velocity plane. The initial densities of porous samples in the experiment were slightly different: $\rho_{00} = 7.50$ g/cm$^3$ for $S_1$ and 7.80 g/cm$^3$ for $S_2$. The reference density of solid uranium is $\rho_0 = 19.1$ g/cm$^3$ [34]. The initial points of the isentropes $S_1$ and $S_2$ correspond to the shock states with experimental particle velocities $u_{pH} \approx 2.94$ and 5.12 km/s, respectively. Other parameters obtained by QMD are as follows: densities are $\rho_H \approx 19.3$ and 22 g/cm$^3$, temperatures are $T_H \approx 22$ and 56 kK, and pressures are $P_H \approx 120$ and 330 GPa, correspondingly. Thus, pressure obtained in the QMD calculation is consistent with experimental data. Two different step sizes on density are used for the release isentrope reconstruction, 4 and 2 g/cm$^3$. A smaller step should provide more accurate result. Nevertheless, 4 g/cm$^3$ density step is also good at describing experimental points as can be seen in figure 1. The obtained points are in excellent agreement with the experimental data from the work by Zhernokletov [13]. In figure 1 we also show EOS by Bushman [35] from the same work.

As can be seen in figure 1, there is a change in the slope on experimental pressure dependences. It is clearly seen for the isentrope $S_1$ and not so evident for $S_2$. The kinks are often used for the calibration of semiempirical EOSs, because they may be treated as entry points of isentropes into the two-phase liquid–gas domain [36]. The presented EOS predicts the entry into the two-phase domain only for the experimental isentrope $S_1$. However it provides lower expansion velocities at low pressures than detected in the experiment. As can be seen in figure 1, low pressure experimental points at the isentrope $S_2$ are also systematically located to the right of the EOS curve. It should be noted, that some theoretical models predict relatively high critical pressure and temperature of uranium [1,37]. So the probability for low-pressure points of isentrope $S_2$ to be located in the two-phase region can not be dismissed. We indicate the supposed kinks on the experimental pressure dependences in figure 1 by arrows. The kinks correspond to pressures of $P = 0.24$ and 0.78 GPa for the isentropes $S_1$ and $S_2$, correspondingly. In this work, we tried to determine temperatures corresponding to hypothetical points of change in the slope of experimental release isentropes of uranium.
Figure 1. The Hugoniot of samples with initial porosity $m = 2.45$ and isentropic expansion curves corresponding to the experiment by Zhernokletov [13] in the $P–u_p$ plane for U. The experimental Hugoniot and isentropic data are solid and open circles, correspondingly; dotted line is interpolation curve. Dashed line is EOS by Bushman [35]. Red stars are the Hugoniot points obtained from QMD; blue stars (open and solid) are release isentropes obtained from QMD by the method of re-shock Hugoniots with the step on density $\Delta \rho = 2$ and $4 \text{ g/cm}^3$, correspondingly; black arrows indicate hypothetical points of change in the slope of experimental release isentropes.

Figure 2 demonstrates the QMD results as well as experimental and theoretical data upon shock compression of solid [38–44] and porous samples of uranium [13] in the pressure–density plane. Our calculation for the principal Hugoniot is consistent with experiment as well as QMD calculation by Yanilkin [44]. Our calculated density on the Hugoniot of porous uranium samples $m = 2.45$ is higher than presented by Zhernokletov [13] at the same pressure. The QMD-calculated isentropes have been interpolated by cubic polynomials. The extrapolation of the isentropes made it possible to estimate densities corresponding to the states where experimental release isentropes change their slopes in $P–u_p$ dependences.

Finally, we have calculated temperature along the isentropes that is shown in figure 3. QMD points for the isentrope $S_1$ are approximated by a linear fit and for $S_2$ by a quadratic polynomial. Using the extrapolation of the QMD calculated points the temperatures corresponding to the kinks on isentropes are estimated as $T = 7.77 \text{ and } 11.2 \text{ kK}$ for the isentropes $S_1$ and $S_2$, respectively. We also show the reconstruction of the coexistence curve by different models.
Figure 2. The principal Hugoniot and the Hugoniot of samples with $m = 2.45$ and isentropic expansion curves corresponding to the experiment by Zhernokletov [13] in the $P–\rho$ plane for U. Red stars are Hugoniot points obtained from QMD; blue stars (open and solid) are release isentropes obtained from QMD by the method of re-shock Hugoniots with step on density $\Delta \rho = 2$ and $4 \text{ g/cm}^3$, correspondingly. Isentropes are interpolated by cubic polynomials. The experimental Hugoniot data by Zhernokletov [13] are solid circles; other experimental data [38–42] are shown as open symbols. The EOS by Crockett et al [43] is dashed line. QMD results for the principal Hugoniot by Yanilkin [44] are right orange triangles. Black arrows indicate hypothetical points of change in the slope of experimental release isentropes in figure 1.

previously presented by Iosilevskiy and Gryaznov [1]. As can be seen in figure 3, our calculations of the entry of experimental isentropes into the two-phase liquid–gas domain according to the kinks on the experimental isentropes do not correspond to the binodal reconstruction based on thermal EOS [45]. On the other hand, our results do not agree with a caloric EOS (code SAHA-U($H$) [1]) either. It is especially obvious for the isentrope $S_1$ where the kink on the experimental dependence is clearly seen. However, estimates of the critical point made according to the Likalter’s similarity relation [46] or so-called “plasma hypothesis” [1] and by the EOS by Lomonosov et al [3] are situated in the intermediate area. Thus, we can say that our rough estimation of the location of the two-phase domain is in satisfactory agreement with these works. It is obvious that the issue of the uranium coexistence curve location requires further experimental and theoretical efforts.
Figure 3. The Hugoniot of samples with porosity $m = 2.45$ and isentropic expansion curves derived from first-principle calculations in the $T$–$\rho$ plane for U. Red stars are the Hugoniot points obtained from QMD; blue stars with lines are release isentropes obtained from QMD. Dashed lines are coexistence curves according to different models presented by Iosilevskiy and Gryaznov [1]: the green one is reconstruction based on caloric EOS (code SAHA-U(H)), the critical point is a green circle; the purple line is based on thermal EOS [45], the corresponding critical point is a purple circle. Some other estimations of the critical point are also shown: black diamond, Likalter [46]; black circle, Lomonosov et al [3]. Black arrows indicate hypothetical points of change in the slope of experimental release isentropes in figure 1.

5. Conclusion
The QMD method was used to reconstruct the Hugoniot of porous samples of uranium with a porosity 2.45 in the pressure range from 30 to 330 GPa and isentropic expansion curves with initial mass velocities 2.94 and 5.12 km/s, corresponding to experiment [13]. First-principle calculations are in agreement with experimental points on shock compression of porous samples and subsequent isentropic expansion. The QMD method allowed us to obtain unique temperature information along release isentropes, so it made it possible to estimate both density and temperature of the supposed entries of the experimental isentropes into the two-phase liquid–gas domain according to the hypothetical kinks on the experimental isentropes.

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