Wide-range equation of state for silver

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Abstract. Results of theoretical calculations and experimental measurements of the equation of state (EOS) are discussed and applied to silver. The thermodynamic properties of silver and its phase diagram are calculated with the use of multi-phase EOS model. Theoretical calculations of thermodynamic properties of the solid, liquid, and plasma phases, and of the critical point, are compared with results of experiments. The analysis deals with thermodynamic properties of solid silver at \( T = 0 \) and 298 K from different band-structure theories, static compression experiments in diamond anvil cells, and the information obtained in shock-wave experiments. Thermodynamic data in the liquid and plasma states, resulting from traditional thermophysical measurements, “exploding wire” experiments, evaluations of the critical point and measurements of the principal Hugoniot are presented. These data are analyzed in a self-consistent manner.

1. Introduction
Equation of state (EOS) describes fundamental thermophysical properties of matter. The EOS, governing the functional dependence among the parameters that characterize the state of a substance, is the main quantitative characteristic of a substance, which makes it possible to apply the general formal body of thermodynamics and dynamics of continuous media (mathematical physics) to describe different physical objects and processes [1–3]. The EOS information can only be obtained by using sophisticated theoretical models or from experiments [4–6]. The EOS is of considerable interest for basic research and has numerous important applications [7–11]. States of matter characterized by high-energy-density occupy a broad region of the phase diagram, for example, hot compressed matter, strongly coupled plasmas, hot expanded liquid and quasi-ideal plasmas. Our knowledge of these states is limited, because theoretical modeling is complicated and experiments are difficult to perform.

Silver is rather unreactive and malleable metal. It exhibits the highest electrical conductivity, thermal conductivity, and reflectivity of any metal. Silver and its alloys are of wide use in the manufacture of electric parts, batteries, contacts, telescopic mirrors, solar photovoltaic panels, control rods in pressurized water nuclear reactors. Its usage in parts of modern air and spacecrafts, pulsed power installations, nuclear reactors motivates developing of wide-range EOS.

2. EOS for silver
The multi-phase EOS model as well as the procedure of EOS construction is described in details for aluminum [12]. We present results of developing silver EOS below.
Figure 1. Pressure in silver at T=0 K: 1—this work; 2—[13]; 3—[14]; 4—[15].

Figure 2. Pressure in silver at T=298 K: 1—this work; 2—[16]; 3—[17]; 4—[18]; 5—[19]; 6—fit of the Vinet equation to data [19].

According to [25, 26], silver is in fcc-phase under normal conditions. The compressibility of silver at room temperature has been studied in diamond anvils to 30 [16], 40 [17], 150 [18] and 122 GPa [19]. According to the results of static studies we can conclude about the absence in silver of structural phase transformations in the range of pressures up to 150 GPa. The obtained for silver cold curve agrees with calculations on the base of Thomas–Fermi model with quantum and exchange corrections [15] to 100-fold compressions. It also provides for good agreement with results of early semiempirical models [13,14] to 40-fold compressions, see figure 1. The developed EOS describes with a good accuracy the static compression data at room temperature [16–19]
to pressure of 150 GPa. The comparison between calculated room-temperature isotherm and results of experiments is shown in figure 2. The melting curve of silver has been determined to \( \lesssim 8 \) GPa [27, 28]. The calculated by EOS melting curve is consistent with results of mentioned experiments.

The compressibility of silver in the shock wave has been studied to the pressure of \( \lesssim 200 \) GPa with the use of plain explosive generators [22–24]. The maximum shock pressure of 440 GPa accessed through the use of hemispherical explosive systems [20, 21]. The comparison of the calculated principal Hugoniot with the experimental data is given in figure 3. It proves the fact that developed EOS describes with high accuracy available shock-wave experimental data for silver.

Analogous to shock-wave data, there is a good correspondence for silver between all available experimental data and theoretical predictions in the region of lower densities and moderate temperatures, as it is demonstrated in figure 4. The silver EOS describes with very good accuracy results of measuring the density of liquid metal at \( P = 1 \) bar [29]. Calculated parameters of the critical point \( p_c = 1.06 \) GPa, \( T_c = 7053 \) K, \( V_c = 0.3059 \) cm\(^3\)/g and \( s_c = 1.118 \) J/gK are in agreement with available evaluations [2, 30, 31]. The value of evaporation temperature at normal pressure \( T_v = 2440 \) K coincides with the reference one [32]. Results of comparison with experiment on isochorically heated silver at density of 0.43 g/cc [33] and theoretical calculations with the use of quantum-molecular-dynamics method [33] are given in figure 4. According to chemical model of plasma [34], these points, like previously reported EOS for nickel [35], occupy a domain of non-ideal ionized plasma and are described with a high fidelity by developed multi-phase EOS for silver.

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**Figure 3.** Pressure-density phase diagram of silver at high pressure. Nomenclature: lines—EOS calculations; \( H \)—principal Hugoniot; \( M \)—melting region; \( T \)—isotherms; markers—experimental data (1—[20, 21]; 2—[22–24]).
Figure 4. Phase diagram of silver at lower densities. Nomenclature: lines—EOS calculations; \( R \)—evaporating region with the critical point (CP); \( M \)—melting region; \( P \)—isobars; \( L \)—density of liquid metal at room pressure [29]; markers—evaluations of CP (1—[30]; 2—[2]; 3—[31]; 4—this work).

Figure 5. EOS of silver in plasma region. Nomenclature: 1—multi-phase EOS isochore 0.43 g/cc; 2 and 3—experimental data and QMD calculations [33], correspondingly.
3. Conclusion
The developed EOS describes with high accuracy and reliability a broad range of the phase diagram, from the high-pressure shocked metal to regions of the phase diagram with much lower densities accessed in the process of the isochoric heating. The high accuracy suits this EOS to be applied in advanced numerical modeling for solving numerous problems in the physics of high energy densities.

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