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Research article

Validation for equation of state in wide regime: Copper as prototype

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Abstract

In this paper we introduce the wide regime equation of state (WEOS) developed in Institute of Applied Physics and Computational Mathematics (IAPCM). A semi-empirical model of the WEOS is given by a thermodynamically complete potential of the Helmholtz free energy which combines several theoretical models and has some adjustable parameters calibrated via some experimental and theoretical data. The validation methods of the equation of state in wide regime are presented using copper as a prototype. The results of the WEOS are well consistent with the available theoretical and experimental data, including ab initio cold curve under compression, isotherm, Hugoniot, off-Hugoniot and sound velocity data. It enhances our confidence in the accuracy of the WEOS, which is very important for the validation and verification of equation of state in high temperature and pressure technology.

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1. Introduction

The states and thermodynamic properties of matter are described by equation of state (EOS). EOS is of immediate interest in astrophysics, planetary physics, power engineering, controlled thermonuclear fusion, impulse technologies, engineering, and several special applications [1]. Numerous techniques and models have been developed for obtaining EOS of a variety of materials which are valid up to very extreme pressure (tens of Mbar) and temperature (several eV or even higher). The predominant methods to obtain EOS experimental data are through dynamic shock wave compression [2], static compression [3] and techniques that couple static and dynamic compression [4]. There are many models based on first-principle theories, such as Thomas-Fermi model [5] with various corrections [6,7], Hartree-Fock-Slater model [8], plasma [9] and liquid state models [10], models derived from Quantum Molecular Dynamic [11−14] and Quantum Monte Carlo [15−17] method. But until now none of them is universal in the wide regime and only applicable in a relatively limited regime. For this reason, the semi-empirical EOS models [1,18,19], where the functional form is motivated by sound theoretical results and the adjustable parameters are tuned to numerous experimental data at high pressure and temperature, have played a very significant role in numerous applications. Within the high-energy-density-physics community, multi-phase wide-range EOS [1], SESAME [18], and QEOS [19], which have been derived by scientists with the use of different physical assumptions and experiments, are widely referenced. In fact, the WEOS, which is accurate in wide regime, has been widely used in IAPCM for many years.

In this paper, we introduce the WEOS developed in IAPCM and take copper as an example to illustrate the performance of the WEOS.

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The theoretical model of WEOS is briefly described in Sec. 2. In Sec. 3 the validation of the EOS under extreme conditions of pressure and temperature is given, and the results for copper are presented. Finally, we summarize the state of the art of WEOS.

2. Theoretical model

Since some fundamental difficulties have not been overcome, a universal and rigorous theoretical model for describing the wide range thermodynamic properties of matter still does not exist. As we know, only very basic and limited results can be obtained using models based on simplified assumptions on the structure, energy spectrum, and the nature of the interaction between particles. Via the combination and modification of several existing models, similar to the case for the SESAME, we proposed a method to obtain the WEOS.

For a system at a given volume V and temperature T, the Helmholtz free energy can be written as trinomial form,

$$F(V,T) = F_c(V) + F_n(V,T) + F_e(V,T),$$

where $F_c(V)$ represents the 0 K energy, $F_n(V, T)$ is the vibrational free energy of lattice ions, and $F_e(V, T)$ is the free energy due to thermal excitation of electrons. Other thermodynamic quantities can be obtained through the corresponding relations with $F(V, T)$. For example, the pressure is obtained via $P = -(\partial F/\partial V)_T$, entropy is obtained via $S = -(\partial F/\partial T)_V$, and internal energy is obtained via $E = F + TS$.

The supporting equations for the free energy are verbose and well described in Refs. [1,20−23]. An outline of the modifications made in the WEOS model, compared with those traditional forms, is as below:

- The Born-Mayer (BM) potential combined with six order polynomial is used to express the cold curve. The BM potential is well suited for describing the cold curve in low compression range. However, beyond this range, six-order polynomial, obtained by fitting cold free energy evaluated from BM at low compression ratio and TF [5−7] models including TF, TFD (Thomas-Fermi-Dirac model only with exchange corrections) and TFC (Thomas-Fermi Kalitkin model with quantum and exchange corrections) at high compressions ratio, is more suitable and flexible. The pressure and its first volume derivative are continuous at the transition density. We give three sets of parameters, WEOS_TF, WEOS_TFD and WEOS_TFC, for one material, these parameters are kept the same below the transition density;
- The ionic term is expressed by the modified Debye model [20] where the high-temperature anharmonic effects are taken into accounted via an empirical interpolation [22] between a perfect solid under normal conditions and an ideal gas. After these modifications, the WEOS becomes suitable for correctly describing the solid, liquid and gas states;
- The electronic term is described by Formula [20,21,23] at low temperature (usually lower than 10 ev or even more lower), and EOS of electrons are calculated by Rational Function Method of Interpolation [24] from the theoretical database of TF models at high temperature.

There are about thirteen unknown parameters in the WEOS model and they are fitted using both theoretical and experimental data. The strategy of calibration of the WEOS model includes fitting experimental data on shock compression of solid density by least squares, optimizing two potential parameters of BM by the golden cross method until the least square deviation of the theoretical from experimental Hugoniot, determining the anharmonic factor and Grüneisen coefficient by comparing the Hugoniot of dense and porous density, obtaining six coefficients of polynomial by fitting cold curve from BM and TF models, interpolating electronic EOS from TF and TFC theoretical data, solving the volume of fusion and volume of gasification by the melting and boiling temperature at $P = 1$ atm. Finally, one must check the pressure, bulk modulus and Grüneisen coefficient at ambient condition.

In consideration of the accuracy of data and the range of pressure, we choose about 170 Hugoniot data from Refs. [25−28] and then fit them by polynomial regression. The shock velocity-particle velocity (D-u_P) relation of copper which is used in the calibration the WEOS model up to 990 GPa is $D = 3.899 + 1.52\ u_P - 0.009\ u_p{}^2$.

Until now we have studied nearly 40 elements which are marked by red color in period table in Fig. 1.

3. The validation formalism for the WEOS

Two key points here are the accuracy of the WEOS and the way to validate it. Due to the complicated physics and limitation of modern theoretical models of the thermodynamics of extreme states, only relatively limited phase states are accessible according to rigorous theoretical model. Therefore, the range of validity of the WEOS is restricted by the nature of the physical approximations. We focus our attention to the comparison with the available calculations by rigorous theoretical models and experimental data which have not been used in the procedure of calibration.

The thermodynamic consistency is always kept because all thermodynamic properties are derived from the free energy. The procedure of validation includes comparisons between the WEOS calculations and each one of the followings: the results of ab initio cold curve, the room-temperature isotherms from experiment, other semi-empirical models and electronic structure theories, experimental data on shock compression of dense and porous copper, off-Hugoniot information corresponding to the double shock in reflected shock wave and to adiabatic expansion of shock-compressed copper, measurements of the sound velocity in shock-compressed copper.

3.1. The ab initio cold curve

The density functional theory (DFT) [29,30] calculations are widely used in the high-pressure research. At room