Thermodynamic modeling of hydrogen fluid parameters at isentropic and shock wave compression

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Abstract. The thermophysical parameters of hydrogen were calculated based on the model of a theoretically substantiated wide-range equation of state constructed using the potentials of intermolecular interactions Exp-6 using perturbation theory and statistical mechanics relations. The calculation results are consistent with experimental data and calculations of other authors.

1. Introduction

Hydrogen is the most common element in the universe. Despite this, its properties are not yet fully understood, especially under conditions of high pressures and temperatures. Data on the states of hydrogen are needed in many fields of physics: thermonuclear fusion, astrophysics (when modeling the atmospheres and bowels of planets), in physics and chemistry of detonation and shock waves and etc.

Over the past decade, interest in studying the equation of state (EOS) of hydrogen has increased, primarily in connection with the study of its metallization. Experimental methods for determination of the thermodynamic properties of hydrogen at high pressures were improved significantly. New methods have emerged for laser initiation of powerful shock waves in liquid hydrogen and laser diagnostics for determining the thermophysical properties of hydrogen in megabar pressure ranges [1]. The rapidly developing methods of computer modeling of hydrogen state parameters based on chemical and physical models are often inconsistent with each other [2 - 5]. The number of publications devoted to the study of the properties and metallization of hydrogen increases annually.

The EOS was proposed on the basis of the “3+” chemical model in [4], in which a plasma consisting of atoms, electrons, and ions in a given volume and temperature is considered. The hydrogen EOS was developed in [5] taking into account dissociation and ionization. It is based on a modified model van der Waals (vdW).

The purpose of this work is to determine the range of pressures and temperatures in which a chemical model based on the pairwise interaction of particles (molecules and hydrogen atoms) reliably describes shock-wave and isentropic compression of hydrogen.

1.1. Method of calculation.

Equations of state (EOS), used to find the characteristic functions of thermodynamics, are needed for reliable prediction of the thermodynamic properties of the fluid phase of hydrogen (fluid is a gas with a liquid density). Then the thermodynamic properties of the system can be expressed in terms of partial derivatives of the characteristic functions of thermodynamics, determined using EOS.

In this paper, a model of theoretically justified wide-range EOS is used for hydrogen, constructed using the potentials of intermolecular interactions Exp-6 based on the theory of perturbations and relations of statistical mechanics [6].

1.2. Problem statement

We consider an ensemble of identical molecules with a pair of spherically symmetric potential for intermolecular interaction Exp-6 at a fixed temperature $T$, volume $V$ and number of particles $N$. Only
paired intermolecular interactions are taken into account. The Helmholtz energy (and, consequently, any other thermodynamic characteristic obtained by differentiating the Helmholtz energy) of an ensemble of molecules at given values of temperature $T$ and volume $V$ is the sum of three components:

$$
\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3
$$

The first term is the Helmholtz energy of an ideal gas at the same $T$ and $V$. The second term is an excess value due to the intermolecular interaction. The third term is a consequence of the correction of the distribution function of the Percus–Jevik solid spheres. The appearance of the summand $\Delta F_3$ in the expression for the Helmholtz energy is related to the correction of the Percus–Jevik distribution function of solid spheres made by Wehrle and Weiss. Since this correction is significant only at high densities, the contribution of $\Delta F_3$ to the total Helmholtz energy was greatest in the region of high densities and low $T$. It is similar to the contribution of dissociation and pressure ionization models.

The accuracy of the developed EOS model of a single-component fluid, determined from the average deviations of the calculated values of dimensionless pressure and internal energy from the Monte Carlo (MC) calculations (57 MC points) (40), was only $\delta Z = 0.60\%$ and $\delta U^* = 0.87\%$ ($Z$ is the ratio of pressure $P(T,V)$ to the pressure of the corresponding ideal gas at the same temperature $T$ and volume $V$; $U^* = \Delta U/Nk_BT$, $\Delta U$ is the change of internal energy, $k_B$ is the Boltzmann constant). The obtained results indicate a high accuracy of the KLRR-T theory, which deteriorates only at the values of the packing coefficient of solid spheres $\eta > 0.57$ due to an increase in the metastability of the effective solid-sphere fluid at a dimensionless density $\rho^* \sim 6$ ($\rho^* = r_m^2/N$, $r_m$ - is the distance between molecules, corresponding to the minimum potential energy $\varphi(r)$).

The IVTANTERMO database was used as a calorific EOS [7].

Hydrogen dissociates to form a mixture of atoms and molecules at high pressures and temperatures. The theory is extended for a multicomponent mixture (of different molecules) by applying the vdW effective potential model [8]. The potential parameters of the effective fluid are determined through the parameters of the intermolecular interaction potentials of individual molecules and atoms in the multicomponent mixture according to the formulas from [8].

$H_2$ and $H$ particles are ionized to form $H_2^+$, $H^+$ and electrons at an even higher temperature. To calculate the ionization of hydrogen, it is assumed that the ion density is small, the Coulomb interaction between the ions can be ignored, and the condition for preserving the electric charge in the system is fulfilled. The formation of ions and electrons was taken into account by setting the Coulomb potential energy.

The theoretical model EOS of multi-component gas described above was implemented in the TDS thermodynamic code [6] for practical equilibrium thermodynamic calculations of complex chemical systems containing a multi-component gas phase at high pressures.

The parameters of the intermolecular interaction potential of hydrogen atoms and molecules are borrowed from [6] and presented in table 1.

| Molecule | $a$ | $r_0$, Å | $\varepsilon/k_B$, K |
|----------|----|--------|-------------------|
| $H_2-H_2$ | 11.2 | 3.49 | 30.4 |
| H-H | 11 | 2.1 | 50 |
| $H_2-H$ | 11.1 | 2.795 | 38.99 |

Also, to verify the calculated data obtained using the TDS code, the MC simulation of the hydrogen states was carried out using the MCCCS Towhee package [9] with the intermolecular potential exp-6 with the parameters of the Table 1, as for the TDS code. There were considered systems consisting of 1000 particles for MC modeling. For the simulation, 100000 steps (configurations) were performed for each state of the system.

2. Results of calculations

The equilibrium thermodynamic parameters of the isentropy, shock adiabate, isotherm and the dependence of the speed of sound on the pressure of hydrogen are calculated in a wide range of pressures and temperatures from the ideal gas state to fluid up to 350 GPa.
The entropy value $S = 44.9 \text{ J/(g·K)}$ was taken from [5]. It can be seen from Figure 1 that the MC line and dotted line [5], obtained without taking ionization into account, are located below the TDS calculation (solid line) at $\rho \geq 0.6 \text{ g/cc}$ when noticeable hydrogen ionization begins.

It is possible that metastable states are realized in this region, in which dense heated hydrogen passes into a conducting state [1, 4].
The calculation results of Hugoniot adiabat of hydrogen are presented graphically in Figure 2 in the form of the dependence of pressure on compression ratio in comparison with experimental data [11, 12]: line 1 - thermodynamic calculations of TDS (with ionization); line 3 - Monte Carlo calculations (without ionization); symbols – experimental data [11, 12]; line 4 - calculations of Sesame [13]; line 5 – calculations of SAHA [14].

Calculations of Sesame [13] (Figure 2, line 4) and SAHA [14] (Figure 2, line 5) were performed for liquid deuterium. The initial states of deuterium in these calculations are as follows: [13] – $\rho_0 = 0.171$ g/cc; [14] – $\rho_0 = 0.130$ g/cc.

The calculation results of isentropic and shock-wave compression of hydrogen (with different values of the initial density of liquid hydrogen) are in satisfactory agreement with experimental data.

The modeling are presented graphically in Figure 3 and 4 in the form of the dependence of pressure on density along three isotherms (Figure 3) and the dependence of the sound velocity on the pressure along the isotherm $T = 300$ K (Figure 4) in comparison with reference data [5, 15, 16].
Figure 3. Dependence of pressure on density along isotherms: 1 - 1000 K; 2 - 600 K; 3 - 300 K. Solid lines - TDS calculations, dotted lines - calculations [5].

Figure 4. The dependence of the sound velocity on the pressure along the isotherm $T = 300$ K. Solid line – TDS calculations, dotted line – calculations from [5]; symbols – experimental data [15, 16].
The agreement of the MC calculations with the equilibrium thermodynamic calculations TDS and the available experimental data in Figures 1, 2 (without ionization) proves the correctness of the EOS obtained on the basis of the KLRR-T theory in the region $P \leq 60$ GPa.

The results of calculations of isentropic, isothermal, shock-wave compression and sound velocity of hydrogen (with different values of the initial density of liquid hydrogen) are in satisfactory agreement with experimental data and calculations by Medvedev [5].

3. Conclusion

Thus, a satisfactory agreement between the performed calculations of TDS and MC with experimental data proves the applicability of the EOS fluid model based on the KLRR-T theory and this technique for modeling hydrogen states up to $P = 60$ GPa and the possibility of their application for various scientific and technical problems.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment project No. 0723-2020-0036).

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