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A model for the equation of state of warm dense hydrogen

V K Gryaznov[1] **and I L Iosilevskiy**[2]

[1] Institute of Problems of Chemical Physics RAS, Chernogolovka, 142432, Russia
[2] Moscow Institute of Physics and Technology, Dolgoprudnyi, 141700, Russia

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Abstract
A model in the framework of a chemical picture for the equation of state of warm dense hydrogen (SAHA-D) is presented. An intense short-range repulsion of neutral particles is described in a simplified form (the soft sphere model). Coulomb corrections are used via a modified pseudopotential model. The results of calculations of principal Hugoniots, double shock and isoenrope are compared with experiment and first principle calculations.

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1. Introduction

In the past 10 years great interest has been paid to the equation of state (EOS) of dense hydrogen and its isotopes. Now there are a number of experiments in which megabar pressures are generated by powerful lasers [1], magnetically launched flyers [2] and high explosives [3, 4]. Together with single-shock, results for double-shock [5–7] were obtained. Last year results of the experiment in Sarov on isoentropic compression of liquid deuterium up to 300 GPa were published [8], which indicate a possibility of phase transition in warm dense deuterium at densities from 1.4 to 1.8 g cm^{-3}. The existence of phase transition in high-density hydrogen has been under discussion for the past several years [9–11]. Interest in this phenomenon is associated first of all with the realization of the so-called plasma phase transition [12, 13]. In the present work, a thermodynamic model for warm dense hydrogen based on a chemical picture is proposed and applied for calculations of principal Hugoniots, reverberated shock and isoentrope of liquid deuterium.

2. The thermodynamic model

The SAHA-D EOS is based on the chemical picture of plasma [14, 15] which represents plasma as a mixture of interacting electrons, ions, atoms and molecules. The component

composition of hydrogen includes e^-, H, H^+, H_2 and H_2^+. For this case, the Helmholtz free energy reads

$$F(\{N_i\}, V, T) = \sum_i F_i^{(\mathrm{id})} + F_e^{(\mathrm{id})} + \Delta F_{ii,ee,ie}^{(\mathrm{int})}(\{N_i\}, V, T). \tag{1}$$

The first term of the Helmholtz free energy (1) is the contribution of the ideal gas of 'heavy' particles, atoms, ions and molecules. The contribution of the electronic ideal gas to the Helmholtz free energy expression (1) is represented by the second term $F_e^{(\mathrm{id})}$. The ideal gas of free electrons is considered as a partially degenerate Fermi gas [16].

The third term of the Helmholtz free energy (1) is responsible for the inter-particle interaction. In this work, the main inter-particle interaction is the Coulomb interaction between charged particles in the framework of a pseudopotential model, generalized for the case of multi-stage ionization [15, 17]. In this model, the depth of electron–ion pseudopotential of each electron–ion pair is strongly correlated with boundary-separating free and bound states that are taken into account when the partition function is calculated. Simultaneously, the parameters of correlation functions expressed via pseudopotentials are calculated from general equations applicable to any values of the Coulomb coupling parameter.

For the very important at high densities short-range repulsion of heavy particles in $\left(\mathrm{H}, \mathrm{H}^2, \mathrm{H}_2^+\right)$, the soft spheres approximation of Young [18] is modified for the *mixture* of soft spheres of *different radii*. The packing factor Y is calculated over individual radii r_j of particles as

$$Y = \frac{\pi\sigma_c^3}{6} = \frac{4\pi r_c^3}{3}, \qquad r_c = \left[\frac{\sum n_j r_j^3}{\sum n_j}\right]^{1/3}, \tag{2}$$

where σ_c is the average diameter in soft sphere potential $V(r) = \varepsilon_{SS}\,(r/\sigma_c)^{-s}$.

We must note that the contribution from inter-molecular H_2–H_2 (D_2–D_2) repulsion dominates in EOS of dense hydrogen (deuterium) in a wide range of low-temperature conditions. Parameters of soft sphere H_2–H_2 potential $V(r) = \varepsilon_{SS}\,(r/\sigma_c)^{-s}$ have been chosen according to the spherically symmetrical part of the non-empirical 'atom–atom approximation' of Yakub [19]. For deuterium, these parameters are as follows:

	S	ε_{SS}	r_{molecule}	Q
D_2	6	0.138 eV	$2.0a_0$	1

Atom–atomic (D–D) and atom–molecular (D–D_2) repulsion becomes dominating in hydrogen (deuterium) thermodynamics at a high temperature and compression. The critical value is the ratio of atom and molecule diameters, $R(1{:}2) \equiv \sigma(\mathrm{H})/\sigma(\mathrm{H}_2)$. From the non-empirical 'atom–atom approximation', $R(1{:}2) \approx 0.8$ [20]. Note that for the atom–atom potential of Ross *et al* [21] $R(1{:}2) \approx 0.4$.

3. Results and discussion

Using the SAHA-D model, computations of composition and thermodynamic properties of warm dense deuterium have been carried out. The comparison of our calculation results for principal Hugoniot of several deuterium initial densities with the experiment and first principle calculations is represented in figure 1.

One can see that SAHA-D data are in good agreement with the experimental results for all four initial densities of deuterium over the whole pressure range. Note that the discrepancies

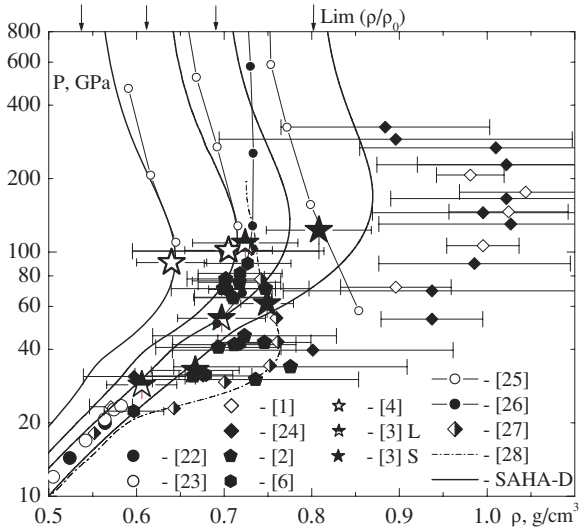

Figure 1. Shock compressed deuterium (single shock). Experiment: Nellis *et al* [22], Holmes *et al* [23], Da Silva *et al* [1], Collins *et al* [24], Anderson *et al* [2], Knudson *et al* [6]; pre-compressed gaseous D_2—Grishechkin *et al* [4] ($\rho_0^1 = 0.1335$ g cm^{-3} and $\rho_0^2 = 0.153$ g cm^{-3}); liquid D_2—Boriskov *et al* [3] *L* ($\rho_0^L = 0.171$ g cm^{-3}); solid D_2—Boriskov *et al* [3] *S* ($\rho_0 = 0.199$ g cm^{-3}); ab initio calculations: DPIMC—Levashov *et al* [25] (for initial densities, ρ_0^1, ρ_0^2 and ρ_0^L), RPIMC—Militzer and Ceperley [26], DFT/MD—Desjarlais [27], Holst *et al* [28]; SAHA-D calculations: Grishechkin *et al* [4] (for initial densities, ρ_0^1, ρ_0^2, ρ_0^L and ρ_0^S). Arrows on the upper side correspond to the ideal-gas compression limit for initial densities ρ_0^1, ρ_0^2, ρ_0^L and ρ_0^S correspondingly.

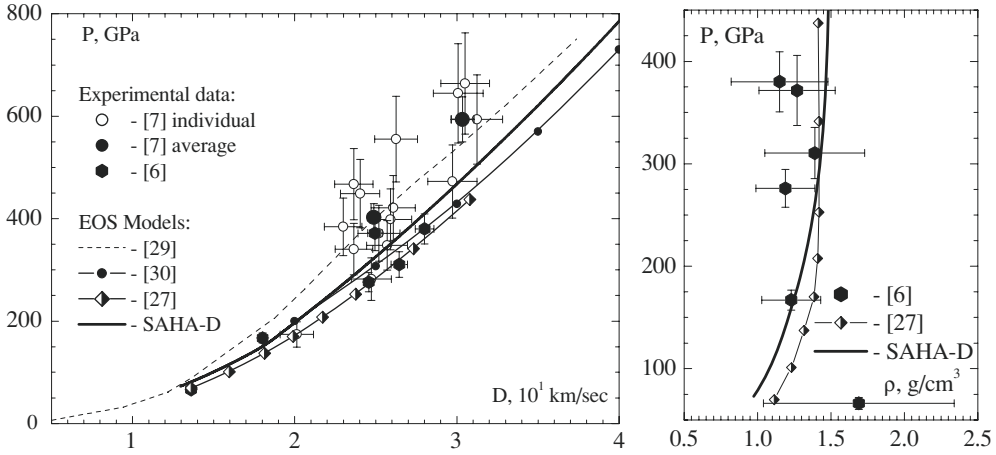

Figure 2. Deuterium double shock: Mostovych *et al* [7], Knudson *et al* [6], Ross [29], Militzer *et al* [30], Desjarlais [27]; SAHA-D—current work.

between SAHA-D data, PIMC [25, 26] and DFT/MD [27, 28] results are of the same order of magnitude as the uncertainty in these first principle calculation data. The results of calculation for deuterium double shock are represented in figures 2 and 3.

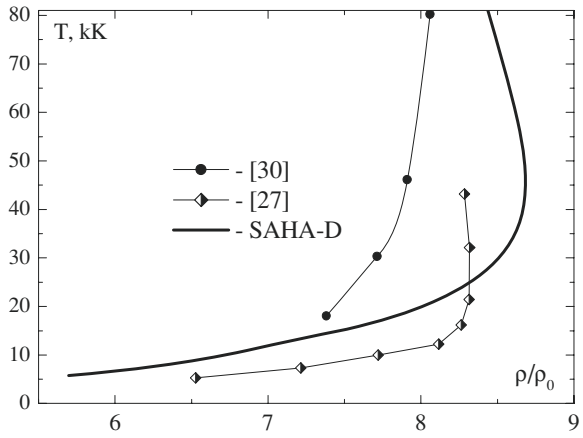

Figure 3. Temperature in deuterium double shock. Theoretical results: Militzer *et al* [30], Desjarlais [27]; SAHA-D—current work.

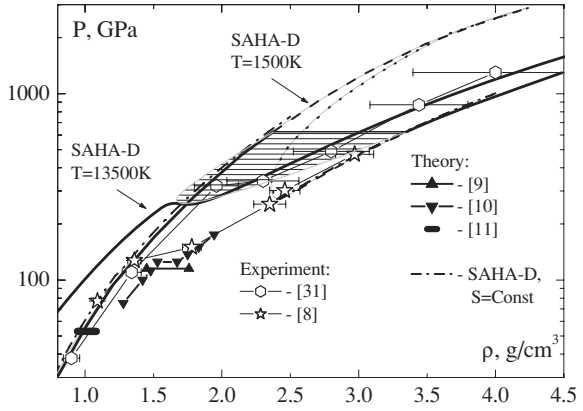

Figure 4. Isentropic compression of deuterium. Comparison of experimental data and theoretical results. *Experiment*: Grigog'ev *et al* [31], Fortov *et al* [8]; *theory*: plasma phase transition at $T =$ 4000 K—Beule *et al* [9]; dissociative phase transition at $T = 1500$ K DFT/MD-–Scandolo [10]; phase transition-like discontinuity in $P(T)_{\rho\,=\,\mathrm{const}}$ at $T = 3000$ K—Bonev *et al* [11]; SAHA-D: isotherm $T = 1500$ K, isotherm $T = 13\,500$ K, isoentrope $S =$ const; shaded area—estimation of phase transition with component composition jump.

Using the SAHA-D model with a modified ratio of atom and molecule diameters (in this case $R(1{:}2) = 0.6$) the isoentrope of liquid deuterium was calculated. Calculation of isotherms was also carried out. The results of calculations are represented in figure 4, where the predictions of different kinds of hypothetical phase transitions are demonstrated as well. It should be noted that two branches of the isoentrope calculated with the SAHA-D model are in good agreement with the experiment. At the same time, the SAHA-D model demonstrates a discontinuity in isoentropic compression. This discontinuity is followed by a sharp change in dissociation degree and can be associated with the phase transition connected with the jump of component composition. In figure 4 two boundary isotherms $T = 1500$ K and $T =$ 13 500 K of this hypothetic phase transition are presented. The shadowed area is the estimation of the two-phase region of this phase transition.

For example, at the left branch of the isoentrope at pressure 250 GPa the dissociation degree is less than 3%, while at the right branch this value is more than 98%. This jump of dissociation degree is followed by the jump of the Debye coupling parameter, and the electron degeneracy parameter as well.

4. Conclusions

In this work, we have proposed a SAHA-D model for the description of EOS of warm dense deuterium. This model provides a good description of all available shock wave (for single- and double-shock) experiments. The SAHA-D model with a modified repulsion parameter gives a satisfactory description of the experiment on isoentropic compression as well. Jump-like density discontinuity is followed by a phase transition with a sharp change in component composition.

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