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Equation of state for hydrogen and helium in the chemical picture

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Abstract

Shock experiments have reached the megabar pressure range and temperatures typical in planets such as Jupiter. The equation of state and other material properties such as electrical conductivity are needed for hydrogen and helium in order to model such objects. We develop an equation of state that considers pressure dissociation and ionization. We make use of fluid variational theory and Padé approximations. A chemical picture is applied considering the species electrons, protons, atoms and molecules. Comparison with experimental equation of state data is presented.

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1. Fluid variational theory for the neutral fluid

Knowledge of the behaviour of hydrogen and helium at high pressures and temperatures is important for models of giant planets, such as Jupiter, or extrasolar planets detected recently. The megabar pressure range (1 Mbar = 100 GPa) is now accessible by shock wave experiments, and equation of state (EOS) data [1, 2] as well as electrical conductivities [3] have been measured. For instance, the nature of a nonmetal-to-metal transition and of an increased compressibility compared with standard EOS data, which were both observed at about 1 Mbar, are under intensive investigation.

We construct an EOS via the free energy $F[\rho, T]$ as a thermodynamic potential so that all other thermodynamic quantities can be derived [4, 5]. For an arbitrary set of species, the free energy reads

$$F[\rho, T] = \sum_x N_x f_x^{\mathrm{id}}[\rho, T] + \frac{1}{2} \sum_{x,y} N_x N_y f_{x-y}^{\mathrm{cor}}[\rho, T]. \tag{1}$$

N_x is the number of particles of species x, f_x^{id} is the respective ideal part of the free energy and f_{x-y}^{cor} the correlation part for the interactions between the species x and y.

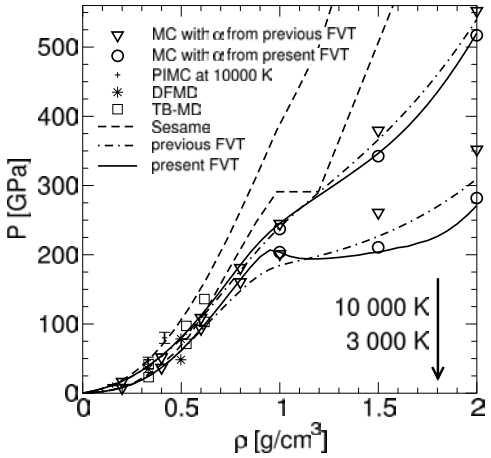

Figure 1. Isotherms of the pressure for the H–H_2 mixture as a function of the density: thick solid lines, present FVT [6]; dashed lines, previous evaluation [4]; triangles and circles, respective MC simulations at the same composition; plus signs with error bars, path integral Monte Carlo (PIMC) at 10 000 K [7]; stars, density functional molecular dynamics (DFMD) at 10 000 K and, in addition, at a hydrogen density of 0.5 g cm^{-3} for 3000 K [8]; boxes, tight binding molecular dynamics (TB-MD) [9]; thin solid lines, interpolated Sesame EOS isotherms [10].

We use fluid variational theory (FVT) to obtain the free energy of helium and an H–H_2 mixture from effective pair potentials $\phi_{xy}(r)$ which are chosen to be of the exp-6 form; for details, see [4, 6]. FVT is based on the Gibbs–Bogoliubov inequality

$$F \leqslant F_0 + \langle \phi - \phi_0 \rangle_0 \tag{2}$$

where a hard sphere system is used as reference system (index 0). For simplicity, here we give only the expression for the free energy of a one-component system which is applied for helium; the expressions for an H–H_2 mixture can be found in [4, 6]:

$$F^{\mathrm{FVT}}[\rho, T] \approx \min_{\eta} \left\{ F_{HS}[T, \eta] + 12N\eta \int_1^{\infty} y^2 \phi_{xx}[\mathrm{d}y] g[y, \eta] \, \mathrm{d}^3 y \right\}. \tag{3}$$

Minimization is performed with respect to the packing fraction η. F_{HS} is the free energy and $g[y, \eta]$ is the pair correlation function of the hard sphere reference system. V is the volume and $d = [6\eta V/(\pi N)]^{1/3}$ is the hard sphere diameter.

Recently, we have studied possible non-additivity effects and we have used the correct pair correlation function for the H–H_2 interaction in the hard sphere reference system within an advanced version of FVT [6]. In figure 1 we can see only small differences between the earlier FVT [4] and the present FVT with the accurate interaction terms in the region up to 0.6 g cm^{-3} for hydrogen, which is relevant for the shock experiments in deuterium in the neutral fluid domain. Monte Carlo (MC) simulations performed for the same dissociation degree α as derived from FVT show very good agreement. Other theoretical EOS data are also given.

2. Fully ionized plasma and the PACH model

The fully ionized plasma consisting of protons and electrons occurs in the limit of high temperatures. This region is treated by the Padé approximation (PA) which is constructed from known limiting cases such as, for example, the Debye–Hückel limiting law for low

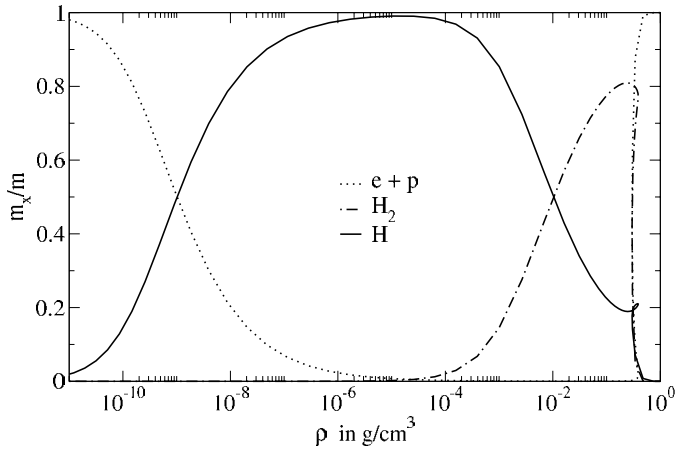

Figure 2. Mass fraction of the various species in dense hydrogen at 10 000 K.

densities and the Gell-Mann–Brueckner result for high densities. Simulation data for the intermediate region are used for a proper interpolation (for details, see [5]). The free energy F^{PA} for the plasma consists again of ideal parts f^{id}, correlation parts f^{cor}, and an exchange part f^{x}:

$$F^{\mathrm{PA}} = N_e f_e^{\mathrm{id}} + N_p f_p^{\mathrm{id}} + \tfrac{1}{2} N_e^2 \left(f_{ee}^{x} + f_{ee}^{\mathrm{cor}} \right) + \tfrac{1}{2} N_p^2 f_{pp}^{\mathrm{cor}} + N_p N_e f_{pe}^{\mathrm{cor}}. \tag{4}$$

Combining the EOS for the neutral fluid and the fully ionized plasma via equations (3) and (4), a partially ionized plasma (H_2, H, p, e) is described within the model of PAs in the chemical picture (PACH); see [11, 12]. A polarization correction F_e^{pol} for the interaction between electrons and neutral particles [13] is also considered. The total free energy then reads

$$F^{\mathrm{PACH}} = F^{\mathrm{FVT}} + F^{\mathrm{PA}} + F_e^{\mathrm{pol}}. \tag{5}$$

The respective composition which is needed, for example, for the calculation of the electrical conductivity [14] is derived from mass action laws which describe the chemical equilibrium between atoms and molecules (dissociation) as well as between atoms, electrons and protons (ionization). The resulting mass fraction is shown in figure 2 as a function of the mass density for a temperature of 10 000 K. A transition from a fully ionized state to an atomic phase and a subsequent formation of molecules is obtained with increasing density. Simultaneous pressure dissociation and ionization lead to a fully ionized plasma in the high-density limit. Whether or not this abrupt transition is accompanied by a phase instability, the plasma phase transition, is still an open question, see [12, 15].

3. Hugoniot curves for deuterium and helium

Shock experiments are characterized by the Hugoniot equation which relates the internal energy U, the pressure P, and the density ρ via

$$U[\rho, T] - U_0 = \frac{1}{2} \left(P[\rho, T] + P_0 \right) \left(\frac{1}{\rho_0} - \frac{1}{\rho} \right). \tag{6}$$

Quantities with index 0 represent the initial state before the shock while the other determines the compressed state.

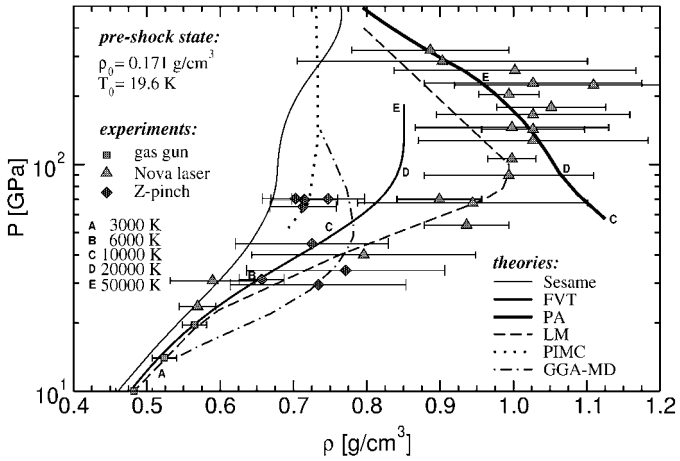

Figure 3. Hugoniot curve for deuterium plotted with Nova laser data [1], *Z*-pinch data [2], gas gun data [17], and the Sesame data base [10]: FVT, fluid variational theory [4]; PA, Padé approximation [5]; LM, linear mixing [20]; PIMC, path integral Monte Carlo [18]; GGA-MD, generalized gradient approximation molecular dynamics [19]. The characters A–E symbolize the increasing temperature along the FVT and PACH Hugoniots.

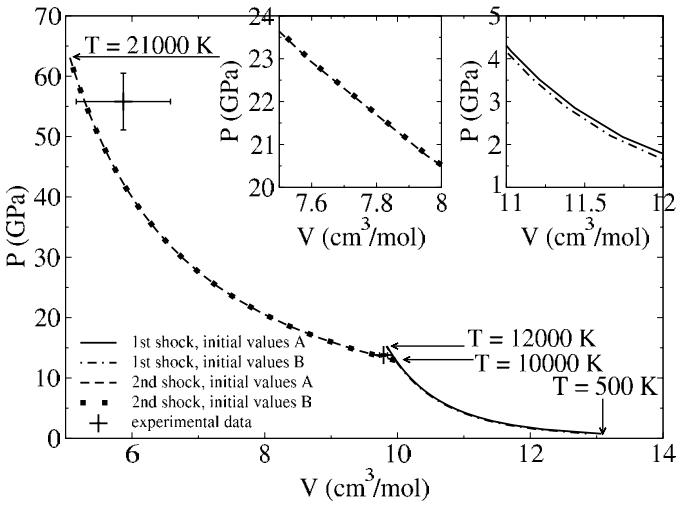

Figure 4. Hugoniot curve for helium calculated within the present FVT compared with double-shock experiments [22]. Initial conditions A are taken from [22], while B represents the values calculated using the present FVT. The insets zoom into regions of the first and second shocks.

The results of the PA and the FVT are compared for deuterium with other models and the experiments in figure 3; see also [16]. The PA is valid for the fully ionized plasma domain and shows good agreement with the Nova laser data [1] for high pressures above 100 GPa. The cusp-condition constraints approximation (CCA) applied in this region [21] gives results much closer to the PIMC Hugoniot. For pressures below 50 GPa, the FVT results are in reasonable agreement with the gas gun data [17] and the Nova laser data. The combined ionization–dissociation model is under construction for conditions along the Hugoniot curve. CCA would be an alternative for the fully ionized plasma instead of using PA. The resulting Hugoniot is

expected to show an increased compressibility compared with the Sesame data base [10] but not as much as the Nova laser data indicate. The new *Z*-pinch data [2] do not show such a feature and are in very good agreement with simulation results [18, 19]. The explanation of these discrepancies between both the existing experiments and the various theoretical EOS is an open problem of crucial importance in order to understand the behaviour of hydrogen at megabar pressures.

The FVT used so far for hydrogen and deuterium was also applied to determine the EOS of helium. We compare with double-shock experiments [22] in figure 4. Our results agree very well with an earlier calculation [23] and the experiments. Small differences occur in the low-density limit. Therefore, we applied the initial conditions given in [22] (A) as well as those calculated within the present FVT (B). The differences are small, especially for the second shock.

4. Summary

We have developed an EOS for hydrogen and helium within a chemical picture which is capable of treating dissociation and ionization processes. The neutral fluid domain at low temperatures and not too high pressures, as well as the fully ionized plasma at high temperatures and/or high pressures, are incorporated as limiting cases. We find reasonable agreement with existing experimental data for the Hugoniot curves of deuterium and helium. The behaviour of hydrogen at about 1 Mbar, especially the value and location of the maximum compression, is still an open problem. A combination of the EOS for both materials (H–He mixture) is planned in order to model the interiors of giant planets such as Jupiter similar to previous work [24].

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