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Equations of state of H₂ and D₂

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Abstract

The equations of state of hydrogen and deuterium are studied using the ideal mixing model. An effective potential with many-body effects has been taken into account. The Helmholtz free energy of a molecule is calculated by employing pure fluid perturbation theory, and the expression for the free energy of an atom is modelled following a similar formula in liquid metal perturbation theory. The Helmholtz free energy for a system with dissociation is given by combining the molecular free energy and atomic free energy. The equation of state obtained this way is in good agreement with experiment.

1. Introduction

Hydrogen is the most abundant element in the universe. Its electronic structure is the simplest, but the properties under extreme conditions are so complicated that they stimulated the theoretical work on the metal transition. With the advent of high-powered lasers, shock Hugoniot data for deuterium in regimes of extremely high pressure have been obtained [1]. The difference between the experimental data and Sesame Hugoniot stimulated ones results from the equation of state (EOS) used. We studied the EOSs of hydrogen and deuterium using the ideal mixing model. An effective potential with many-body interactions has been taken into account.

2. The method used to calculate the EOSs

Under high pressure, molecular hydrogen and deuterium are complicated mixtures of H₂, H, H⁺, e⁻ and D₂, D, D⁺, e⁻ respectively. We neglect H⁺, e⁻ and D⁺, e⁻, and only consider systems including H₂ and H or D₂ and D. Using the ideal mixing model [2], we express the thermodynamic properties of dissociating fluid hydrogen as averages of those from pure molecular and monatomic hydrogen EOSs. We write the Helmholtz free energy for a system of N molecules as

$$F(V, T, x) = (1 - x)F_{\text{H}_2}(V, T, x = 0) + xF_{\text{H-H}}(V, T, x = 1) - TS_{\text{mix}} + (1 - x)D^0 \quad (1)$$

where T is the temperature, V is the volume, x (which is determined by minimizing F) is the fraction of dissociated molecules. The mixing entropy of one particle is S_{mix} :

$$S_{\text{mix}} = -k \left[(1-x) \ln \frac{1-x}{1+x} + 2x \ln \frac{2x}{1+x} \right] \quad (2)$$

where k is the Boltzmann constant, F_{H_2} is the free energy of the pure molecule. The latter can be given as [3]

$$F_{\text{H}_2} = F_{\text{H}_2}^0 + F_{\text{H}_2\text{int}}^0 + F_{\text{H}_2\text{conf}} \quad (3)$$

where $F_{\text{H}_2}^0$ is the translational free energy, $F_{\text{H}_2\text{int}}^0$ is the contribution from the rotational and vibrational degrees of freedom, $F_{\text{H}_2\text{conf}}$ is the configuration free energy. The three terms can be expressed as follows:

$$\begin{aligned} F_{\text{H}_2}^0 &= 2.5NkT \\ F_{\text{H}_2\text{int}}^0 &= N \left\{ \frac{1}{2} \hbar \nu + kT \ln[1 - \exp(-\beta \hbar \nu)] \right\} + NkT \ln \rho \\ F_{\text{H}_2\text{conf}} &= F_{\text{HS}}(\eta) + F(\eta)NkT + \frac{\rho N}{2} \int d^3r \phi(r) g_{\text{HS}}(r, \eta) \end{aligned} \quad (4)$$

where $\beta = 1/\kappa T$ and $\eta = \pi \rho d^3/6$, ρ is the numerical density, d is the hard-sphere diameter. $F_{\text{HS}}(\eta) = \frac{4\eta - 3\eta^2}{(1-\eta)^2} NkT$ is the hard-sphere excess free energy. The factor $F(\eta) = -(\frac{\eta^4}{2} + \eta^2 + \frac{\eta}{2})$ adds the hard-sphere entropy. $\phi(r)$ is the pair potential, which may be an *ab initio* potential, the Silvera–Goldman (SG) potential, the SW potential, the Yang–Ross (YR) potential, etc. $g_{\text{HS}}(r, \eta)$ is the hard-sphere radial distribution function. $F_{\text{H-H}}$ is the monatomic free energy, which is modelled following that of liquid metal perturbation theory, and given by [2]

$$F_{\text{H-H}} = 2[F_{\text{H-H}}^0 + F_{\text{EG}}(V) + f_{\text{LDA}} + F_{0\text{ep}}(V, T)]. \quad (5)$$

The calculation of the four terms in equation (5) has been described in detail in [2].

Substituting equations (4) and (5) into (1), we get the Helmholtz free energy for the mixture. Using the mass action law

$$\left(\frac{dF}{dx_j} \right)_{T, V, x_j} = 0, \quad (6)$$

the equilibrium value of x is given by

$$x^2 = \frac{q}{4+q} \quad (7)$$

where $q \equiv \exp[-(F_{\text{H-H}} - F_{\text{H}_2} + D^0)/kT]$.

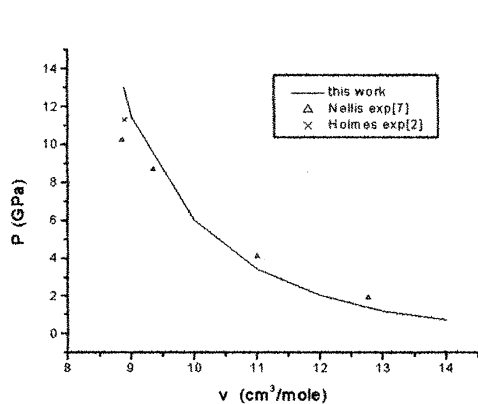
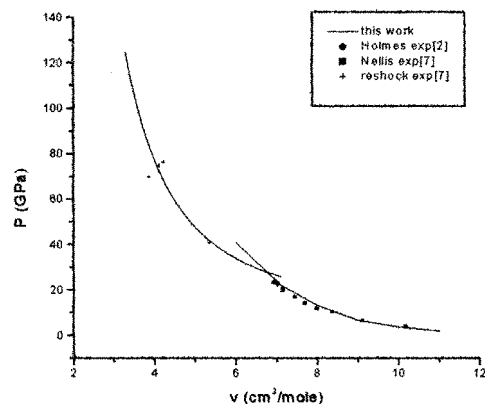
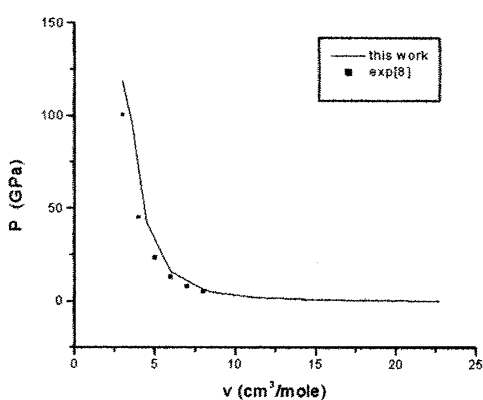
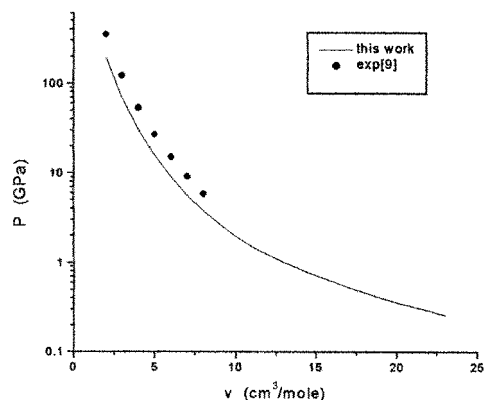
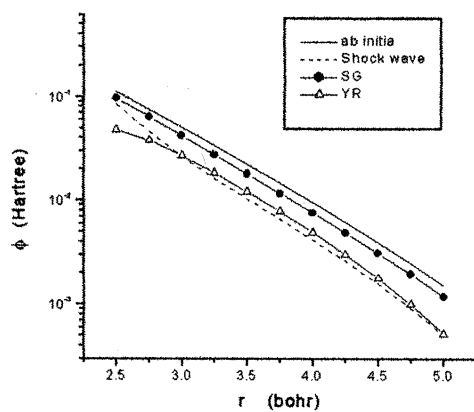
The pressure (P) and the internal energy (E) are calculated by taking the appropriate derivatives of equation (1) numerically, i.e.

$$\begin{aligned} P &= -\frac{\partial F}{\partial V} \\ E &= \frac{\partial(\beta F)}{\partial \beta}. \end{aligned} \quad (8)$$

The Hugoniot were calculated by using one of the Rankine–Hugoniot relations:

$$E - E_0 = (P + P_0)(V_0 - V)/2 \quad (9)$$

which connects the thermodynamic state (P, E, V) behind the shock front with the initial state (P_0, E_0, V_0) ahead of the shock front. We solve equation (9) for (P, E) at fixed temperature by varying V . The initial state [3] for hydrogen is $(V_0, T_0) = (28.422 \text{ cm}^3 \text{ mol}^{-1}, 20.35 \text{ K})$; that for deuterium is $(V_0, T_0) = (23.64 \text{ cm}^3 \text{ mol}^{-1}, 20.38 \text{ K})$.

Figure 1. The Hugoniot of liquid H₂.Figure 2. The Hugoniot of liquid D₂.Figure 3. The $T = 300$ K isotherm of H₂.Figure 4. The $T = 300$ K isotherm of D₂.Figure 5. The repulsive region of Ree's *ab initia* potential, the SG potential, the SW potential, and the YR potential.

3. Results and discussion

We try Ree's *ab initia* potential [4], the SG potential [5], the SW potential [6], and the YR potential [3]. The YR potential is the best; its use leads to reproduction of most of the

experimental results. In figure 1 we compare the experimental H₂ single-shock data of Nellis and Mitchell [7] and Holmes *et al* [2] with our theoretical Hugoniot based on ϕ_{YR} . In figure 2 we compare the experimental D₂ single- and double-shock data of Nellis and Mitchell [7] and Holmes *et al* [2] with our theoretical Hugoniot based on ϕ_{YR} . In figures 3 and 4 we give the 300 K isotherms including the experimental [8, 9] and theoretical results for H₂ and D₂, respectively. Obviously the calculations are in agreement with experiment data both for the Hugoniot and for the isotherm. These results show that the ideal mixing model is valid for shock-compressed liquid hydrogen and deuterium. The temperature that we calculated is near the experiment result of Holmes *et al*. The x -value for our range of pressure (showing the fraction of dissociated molecules) changes from 0.0011 to 0.2. The differences between Ree's *ab initio* potential, the SG potential, the SW potential, and the YR potential are studied. If the *ab initio* potential is the true two-body interaction, all of the others are effective potentials, with many-body effects, which can reproduce the experimental data in the appropriate range of temperature and pressure, and these potentials are not valid outside of these regions. Electrons in hydrogen molecules are loosely bound to nuclei and easily change their charge density when a second or third molecule is placed nearby; hence the many-bond effects are important. The repulsive regions for Ree's *ab initio* potential, the SG potential, the SW potential, and the YR potential are shown in figure 5. The *ab initio* potential is stiffer than the SG, SW, and YR potentials. The difference between the former and latter represents a real many-body contribution in the effective pair potential.

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