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Self-consistent fluid variational theory for the equation of state and dissociation of dense hydrogen and nitrogen

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Abstract

The self-consistent fluid variational theory (SFVT) is used to calculate the pressure dissociation of dense hydrogen and nitrogen at high temperatures. The accurate high-pressure and high-temperature effective pair potentials are adopted to describe the intermolecular interactions, which are made to consider molecular dissociation. This paper focuses on a mixture of atoms and molecules and is devoted to the study of the phenomenon of pressure dissociation at finite temperature. The equation of state and dissociation degree are calculated from the free energy functions in the temperature range 4000–15 000 K and density range 0.1–3.2 g cm⁻³ for dense nitrogen and in the temperature range 2000–10 000 K and density range 0.02–1.0 g cm⁻³ for dense hydrogen, which can be compared with other approaches and experiments. The pressure dissociation is found to occur in the higher density range, while temperature dissociation is a more gradual effect.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Knowledge of the equation of state (EOS) for dense hydrogen and nitrogen is of central importance for astrophysics as well as for the general understanding of the behavior of matter at extreme conditions [1]. Pressure dissociation has been found to become important in dense molecular fluids. The effective one-component model has been used to calculate the EOS of fluid He + H₂ mixtures [2]. The effects of dissociation on the EOS have been treated by using the dissociation model [3]. Various models have also been applied to study the behavior of hydrogen at ultrahigh pressure. For instance, the linear-mixing model of Ross [4], path-integral Monte Carlo (PIMC) method [5], wavepacket molecular dynamics (WPMD) [6] and quantum molecular dynamics (both density-functional (DF) [7] and tight-binding (TB) [8] approaches)

have been performed for conditions reached in shock wave experiments. Furthermore, various simulation methods have proven the importance of this effect by inspecting the variation of the pair distribution function with density [9]. In particular, assuming that effective pair potentials are valid for the interactions in a partially dissociated fluid, standard fluid variational theory (FVT) has been applied to a system with the dissociation reaction [10].

Developments in shock wave experimental techniques have been able to reach pressures to be probed beyond 100 GPa in hydrogen and nitrogen [11, 12]. The principal Hugoniot was determined up to 300 GPa in recently reported single shock wave laser driven experiments [13]. It has been shown that dissociation of hydrogen and nitrogen molecules becomes operative under such ultrahigh pressures. The multiple-shock Hugoniots of liquid nitrogen have been calculated by Mazevet *et al* using a finite-temperature density-functional theory (DFT) at the generalized gradient approximation (GGA) level [14, 15]. In this paper, we generalize standard fluid variational theory to a two-component system with a dissociative reaction for pressure dissociation in dense hydrogen and nitrogen. The dissociation equilibrium $A_2 \rightleftharpoons 2A$ ($A = H, \text{ or } N$) reflects the very subtle changes in the electronic and structural properties at high pressures via correlation contributions which are consistent with the equation of state. The composition is determined self-consistently taking into account all correlations, especially the $A-A_2$ interaction, when fulfilling the condition of chemical equilibrium, $\mu_{A_2} = 2\mu_A$, for the corresponding reaction $A_2 \rightleftharpoons A + A$.

2. Theoretical model

At sufficiently high temperatures and pressures, molecular A_2 will dissociate into atoms. It is adequately described as a mixture of A atoms and A_2 molecules. The chemical equilibrium between atoms and molecules $A_2 \rightleftharpoons A + A$ is considered to calculate the dissociation degree of the fluid.

Supposing that the dense fluid hydrogen/nitrogen consists of atoms and molecules which interact via the effective pair potentials described in the three-parameter potential of the exponential-6 form [16], we introduce the expression for the free energy of a two-component system with a reaction and give the other thermodynamic quantities. Considering in the following the dense hydrogen/nitrogen fluid at a fixed temperature T , and particle density n , we study the dissociation processes



In order to define the thermodynamics of the system, we introduce the free energy per particle $f^{\text{tot}} = F^{\text{tot}}/N$ and the degree of dissociation $\alpha = N_1/N$; $N = N_1 + N_2$ is the total number of particles. The free energy is given as a sum of the ideal contributions of the pure components f_i^{id} (with $i = 1, 2, 1 = A, 2 = A_2$) and a term for the correlations among all particles f_{ij}^c ,

$$f^{\text{tot}} = \sum_{ij} (f_i^{\text{id}} + f_{ij}^c). \quad (2)$$

The correlation part is determined variationally using the Gibbs–Bogolyubov inequality. In particular, one obtains in the case of a hard-sphere (HS) reference system

$$f^{\text{cor}} = \sum_{ij} f_{ij}^c \approx \min_{\eta_1, \eta_2} \{ f_{\text{HS}}[T, \alpha, \eta_1, \eta_2] + \alpha f_{11}[\alpha n, \eta_1] + 2\alpha(1 - \alpha) f_{12}[n, \eta_1, \eta_2] + (1 - \alpha) f_{22}[(1 - \alpha)n, \eta_2] \}. \quad (3)$$

The correlation contributions f_{ij} are given by integrals over the effective pair potential $\phi_{ij}(r)$ and the respective pair distribution functions $g_{ij}(r)$ which are approximated by those of the

hard-sphere reference system.

$$f_{ij} = 12\eta \int_1^\infty x^2 \phi_{ij}(d_i x) g_{ij}(\alpha_i, x, \eta_i, \eta_j) dx, \quad (4)$$

where $x = r/d$, and $d_i = [6\eta_i/(\pi\alpha_i n)]^{1/3}$. The free energy of a binary hard-sphere reference system f_{HS} is taken from [17]. The pair distribution functions of the hard-sphere reference system use the Percus–Yevick approximation. The total free energy of mixtures of hydrogen/nitrogen atoms and molecules is given by

$$f^{\text{tot}}(n, T, \alpha) = \alpha f_1^{\text{id}}(\alpha n, T) + (1 - \alpha) f_2^{\text{id}}[(1 - \alpha)n, T] + f^{\text{cor}}(n, T, \alpha). \quad (5)$$

The minimization of the correlation free energy f^{cor} in equation (3) is with respect to the packing fractions η_i , which is equivalent to minimizing with respect to the hard-sphere diameters d_i , and can be performed by the downhill simplex method in multi-dimension.

Pressure dissociation occurs in dense hydrogen/nitrogen as the temperature and pressure are increased. The fraction α of dissociation molecules is determined by the correlation contributions to the chemical potential according to

$$n_{\text{A}_2} = \frac{n_{\text{A}}^2 \Lambda_{\text{A}}^3}{\sqrt{2}} \sigma^{\text{int}} \exp(D_0 - \mu_2^{\text{cor}} + 2\mu_1^{\text{cor}}), \quad (6)$$

where D_0 is the dissociation energy of isolated A_2 molecules and Λ_{A} the thermal wavelength of A atoms. σ^{int} denotes the internal partition function of vibrational, rotational, and electronic states. Thus we see from equation (6) that the dissociation energy is effectively lowered by the introduction of μ_2^{cor} and μ_1^{cor} . Therefore, the modification of the binding energy of hydrogen/nitrogen molecules is according to follow formula:

$$\Delta\mu^{\text{cor}} = \mu_2^{\text{cor}} - 2\mu_1^{\text{cor}}. \quad (7)$$

Let us define an effective dissociation energy D_{eff} as

$$D_{\text{eff}} = D_0 - \Delta\mu^{\text{cor}} = D_0 - \mu_2^{\text{cor}} + 2\mu_1^{\text{cor}}. \quad (8)$$

The condition of chemical equilibrium $\mu_2 = 2\mu_1$ for the reaction equation (1) has to be fulfilled self-consistently within the free energy minimization as the above description by taking into account the correlation contributions to the chemical potentials. Then the pressure (P) and the internal energy (E) of the system can be calculated from the total free energy equation (5) by derivatives.

3. Results and discussion

A reliable performance of self-consistent fluid variational theory has been verified via calculating the Hugoniot of liquid nitrogen and deuterium. Comparisons with available experimental results [18–20] demonstrate that the SFVT calculations can reasonably reproduce the major trends in the basic nitrogen and hydrogen properties along the principal Hugoniot.

Figure 1 shows the surface of the dissociation degree of fluid hydrogen as a function of density and temperature in the ranges $0.02\text{--}1.0 \text{ g cm}^{-3}$ and $4000\text{--}10\,000 \text{ K}$. It can be noted that there is a minimum in each of the dissociation curves ($\alpha\text{--}\rho$ plane) from 4000 to 10 000 K. Depending on the values of temperature and density we find different locations of the minimum. The position of the minimum is shifted towards an elevated density with increase of temperature. The pressure dissociation increases strongly at densities above 0.5 g cm^{-3} , while temperature dissociation is a more gradual effect.

In figure 2, the pressure is shown as a function of temperature for a constant volume of $V = 6.0 \text{ cm}^3 \text{ mol}^{-1}$ ($r_s = 2$, where $r_s = d/a_{\text{B}}$ is the mean distance d between the

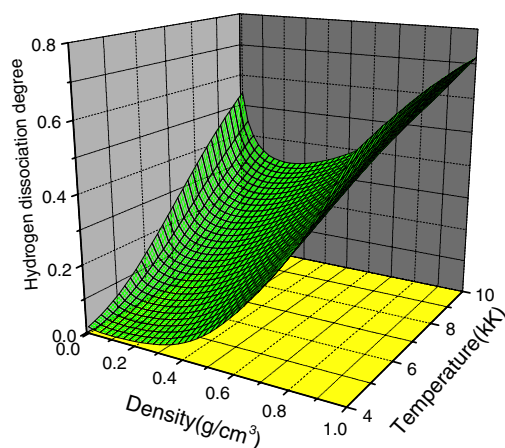


Figure 1. The surface of the dissociation degree of fluid hydrogen as a function of density and temperature.

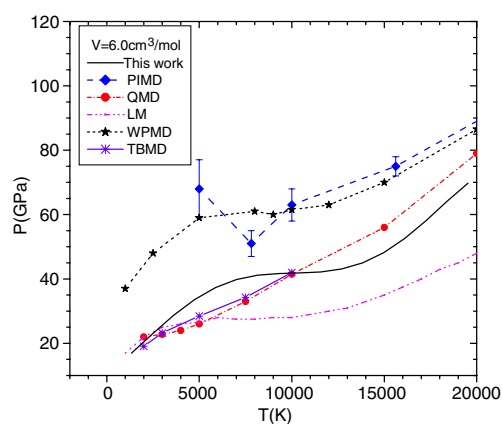


Figure 2. Pressure as a function of temperature for a constant specific volume $V = 6 \text{ cm}^3 \text{ mol}^{-1}$.

electrons in units of the Bohr radius a_B). The present SFVT is compared with path-integral Monte Carlo (PIMC) method [21, 22], quantum molecular dynamics (QMD) [7] simulations based on a tight-binding electronic structure calculation, tight-binding molecular dynamics (TBMD) [23], wavepacket molecular dynamics (WPMD) [24] simulations, and the linear-mixing (LM) model [25]. The present results lie between WPMD and the LM model in the entire temperature range. The pressure increases very slowly with increasing temperature between 5000 and 14000 K, which indicates where the dissociation occurs. The pressure–temperature curves from WPMD and the LM model show a similar behavior of the pressure but at values higher and lower than the present absolute values, respectively. The deviations of the present calculations from the WPMD and the LM method are because the dissociation reaction has been not included in the WPMD and the LM method. The present SFVT and WPMD calculations show an increase of pressure with increasing temperature up to about 5000 K. Further increase in temperature causes the dissociation of the molecules to atoms, which leads to a decrease of the thermal pressure. This effect nearly cancels the increase of the kinetic energy with temperature, so we observe a region with $(\partial p / \partial T)_n \approx 0$ between 5000

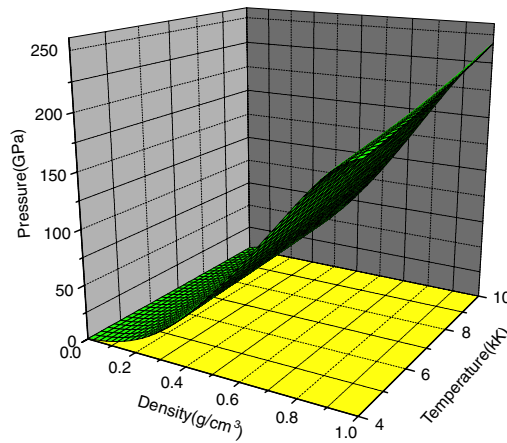


Figure 3. The surface of the pressure of H-H₂ mixtures as a function of density and temperature.

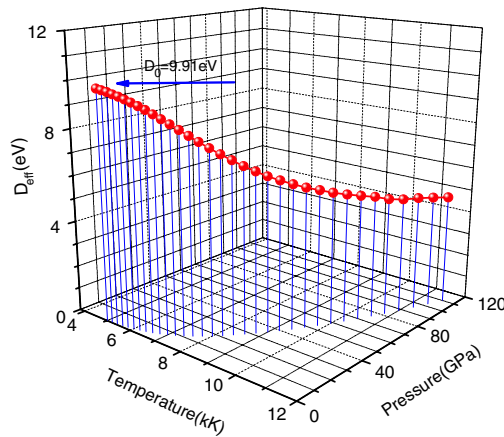


Figure 4. Effective dissociation energy of nitrogen as a function of temperature and pressure.

and 12 000 K. PIMD seems to overestimate the effect of dissociation below 10 000 K, so a region with $(\partial p/\partial T)_n < 0$ occurs. The additional considerations of ionization in our model would lead to lower pressure at higher temperatures. Therefore, the present SFVT is applicable to calculate the EOS of dense hydrogen in the temperatures range 2000–10 000 K and density range 0.02–1.0 g cm⁻³.

The equations of state of the fluid H-H₂ mixtures in the temperature range 4000–10 000 K and density range 0.02–1.0 g cm⁻³ have been predicted. The surface of the pressure of fluid hydrogen as a function of density and temperature is shown in figure 3. As can be seen, the pressure at low densities strongly depends on temperature, while in the intermediate-density region the pressure of fluid hydrogen increases with increasing density and temperature. At even higher densities, the pressure is a strong function of density for the fluid hydrogen.

Figure 4 shows a trajectory of the effective dissociation energy of dense fluid nitrogen as a function of temperature and pressure. It can be seen that D_{eff} will approach the dissociation energy ($D_0 = 9.91$ eV) of isolated N₂ molecules at pressure $P \rightarrow 0$, and it decreases with increase of pressure and temperature, whereas Ross' effective dissociation energy [19],

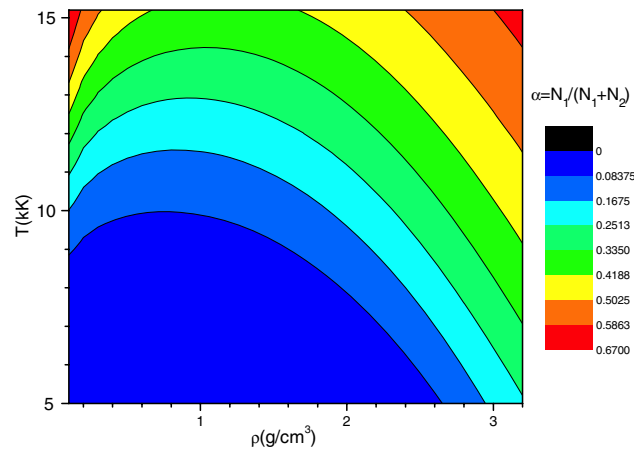


Figure 5. Contour of dissociation degree of fluid nitrogen as a function of density and temperature.

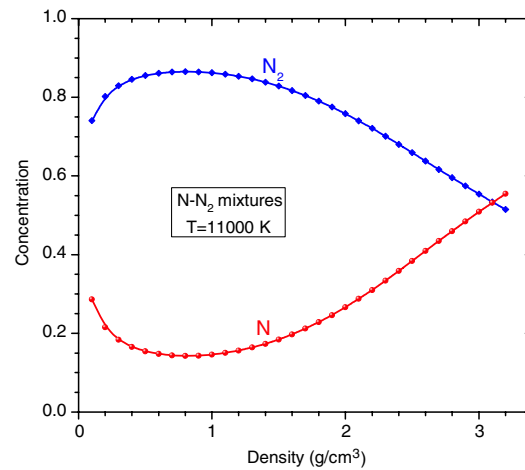


Figure 6. Concentration of atomic and molecular nitrogen as a function of density.

$D = D_0 - A(V_0 - V)^2$, depends on the parameters A , V_0 , and specific volume V . The correlation contribution in equation (6) yields a lowering of dissociation energy, so pressure dissociation becomes operative already in the neutral fluid. Neglecting these terms, almost no dissociation would occur at these conditions.

Figure 5 shows the contour of dissociation degree of fluid nitrogen as a function of density and temperature in the ranges $0.01\text{--}3.2\text{ g cm}^{-3}$ and $5000\text{--}15\,000\text{ K}$. The SFVT produces pressure and temperature dissociation varying continuously as either the density or temperature increases.

Figure 6 shows the concentration of atomic and molecular nitrogen as a function of density at $11\,000\text{ K}$. Between $\rho = 0.1$ and 0.8 g cm^{-3} , it shows strong recombination as described in the law of mass action. At higher densities, strong non-ideal correlation effects come into play, decreasing the dissociation energy and favoring molecular dissociation. Temperature dissociation effects are clearly displayed by the low-density part of the isotherm sequence. Note that the nitrogen molecules are the dominant species in the density range $\sim 0.1\text{--}3.1\text{ (g cm}^{-3}\text{)}$; nitrogen atoms are the dominant species outside this density range.

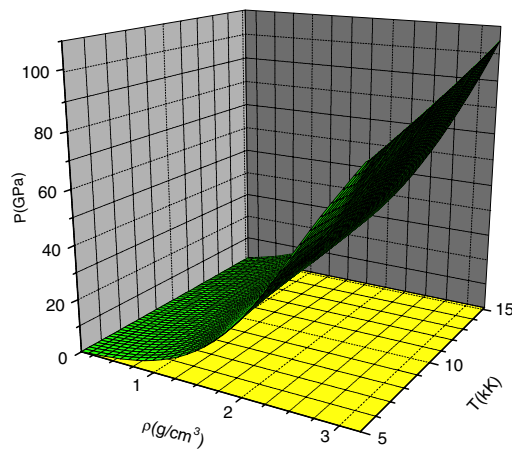


Figure 7. Surface of pressure of fluid nitrogen as a function of density and temperature.

The equations of state of the fluid N–N₂ mixtures in the temperature range 5000–15 000 K and density range 0.1–3.2 g cm⁻³ have been predicted. The surface of the pressure of fluid nitrogen as a function of density and temperature is shown in figure 7. As can be seen, the pressure at low densities, about 0.1–1.5 g cm⁻³, strongly depends on the temperature, while in the intermediate density region, about 1.5–2.5 g cm⁻³, the pressure of fluid nitrogen increases with increasing density and temperature. At even higher densities, the pressure increases with density slightly more strongly.

4. Conclusion

The present self-consistent fluid variational theory has been successfully applied to treat dissociation processes of fluid molecules and to determine the equation of state of a mixture of fluid nitrogen/hydrogen atoms and molecules over a wide range of temperatures and densities. An important feature of the current model is the introduction of correction of the dissociation energy by fulfilling self-consistently when minimizing the free energy in the condition of chemical equilibrium for the reaction $A_2 \rightleftharpoons 2A$. The quantities $\Delta\mu^{\text{cor}} = \mu_2^{\text{cor}} - 2\mu_1^{\text{cor}}$ are given by the interactions with the chemical potentials and yield a shift of chemical equilibria compared with the ideal Saha equations. They can be interpreted as lowering of the respective dissociation energies with increasing density, which leads to pressure dissociation. The SFVT produces pressure and temperature dissociation varying continuously as either the density or temperature increases.

Acknowledgments

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