ON THE DISSOCIATION EQUILIBRIUM OF H\textsubscript{2} IN VERY COOL, HELIUM-RICH WHITE DWARF ATMOSPHERES

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ABSTRACT

We investigate the dissociation equilibrium of H\textsubscript{2} in very cool, helium-rich white dwarf atmospheres. We present the nonideal chemical equilibrium solution for the dissociation of molecular hydrogen in a medium of dense helium. We find that at the photosphere of cool white dwarfs of $T_{\text{eff}} \approx 4000$ K, the nonideality results in an increase of the mole fraction of molecular hydrogen by up to a factor of $\sim 10$ compared to the equilibrium value for the ideal gas. This increases the H\textsubscript{2}-He collision-induced absorption (CIA) opacity by an order of magnitude and will affect the determination of the abundance of hydrogen in very cool, helium-rich white dwarfs.

Subject headings: dense matter — stars: atmospheres — white dwarfs

1. INTRODUCTION

Several very cool white dwarfs with suspected $T_{\text{eff}} < 4500$ K have been discovered recently (Farihi 2005; Kilic et al. 2006; Gates et al. 2004; Oppenheimer et al. 2001; Harris et al. 1999, 2001; Hodgkin et al. 2000; Ibata et al. 2000). Most of them are thought to possess helium-rich atmospheres with a very high He/H $> 10^3$ ratio (Bergeron et al. 2005; Kilic et al. 2006; Gates et al. 2004; Bergeron & Leggett 2002; Bergeron 2001; Oppenheimer et al. 2001; Hodgkin et al. 2000). In most cases, however, current atmosphere models fail to reproduce the observed spectra and photometry of these peculiar stars. The reason, and there may be more than one, for this shortcoming of the models is currently unknown. However, current models predict extreme physical atmospheric conditions for such stars, reaching densities of up to $2-3 \text{ g cm}^{-3}$. Under these conditions, the mostly ideal gas constitutive physics used in published atmosphere models is demonstrably inadequate. A careful look at the dense matter effects on the equation of state, chemistry, opacities, and radiative transfer is necessary to compute physically realistic models of these stars. Several of these effects have been studied previously, including refractive radiative transfer (Kowalski & Saumon 2004), the effects of fluid correlations on He$^-$ free-free and He Rayleigh scattering (Kowalski et al. 2005; Iglesias et al. 2002), and the ionization of warm, dense helium (Kowalski et al. 2005; Bergeron et al. 1995). In this contribution we present an additional correction that arises in the dense fluid, the solution for the dissociation of molecular hydrogen in dense fluid helium in the limit He/H $\gg 1$. The relative importance of these corrections varies considerably, and even more so when they are combined. As several more dense matter effects remain unexplored, it is premature to ponder their implications for the analysis of the coolest white dwarfs known and whether they will result in models that reproduce the data. Nonetheless, incorporating adequate constitutive physics in atmosphere models is a necessary step in reaching a proper understanding of these peculiar stars.

We introduce nonideal effects into the equilibrium dissociation of molecular hydrogen through a modification of the chemical potentials of H\textsubscript{1} and H\textsubscript{2} (§ 2). We find that the strong interactions in the dense, helium-rich atmosphere result in a significant decrease in the dissociation fraction of molecular hydrogen, with a corresponding change in the H\textsubscript{2}-He collision-induced absorption (CIA) opacity, which is a linear function of $n_{\text{H}_2}$. In § 3 we illustrate the impact of the interactions on the H\textsubscript{2}/H\textsubscript{1} ratio on a sequence of white dwarf atmosphere models with $T_{\text{eff}} = 4000$ K, a gravity of log $g = 8$ (cgs), and a homogeneous composition of He/H $= 10^2, 10^3,$ and $10^4$, where He/H is the number abundance ratio.

2. THE DISSOCIATION EQUILIBRIUM OF MOLECULAR HYDROGEN IN A DENSE FLUID

2.1. Theoretical Approach

The condition for chemical equilibrium (at a given density and temperature) for the dissociation reaction,

$$\text{H}_2 = 2\text{H} \uparrow \quad (1)$$

is given by (Cox & Giuli 1968, chap. 9),

$$\mu_{\text{H}_2} - 2\mu_{\text{H}} = 0, \quad (2)$$

where $\mu_i$ is a chemical potential of the species $i$ expressed as

$$\mu_i = E_{0,i} + k_B T \ln \frac{n_i h^3}{Z_i (2 \pi m_i k_B T)^{3/2}} + \mu_i^{\text{had}}. \quad (3)$$

In the above equation, $k_B$ is the Boltzmann constant, $h$ is the Planck constant, $T$ is the temperature, $E_{0,i}$ is the ground state energy, $n_i$ is the number density, $Z_i$ is the unperturbed internal partition function, and $m_i$ is the mass. The first two terms on the right-hand side of equation (3) represent the ideal contributions of translational and internal degrees of freedom, and $\mu_i^{\text{had}}$ is the nonideal contribution to the chemical potential arising from the interparticle interactions in the fluid. Setting $\mu_i^{\text{had}} = 0$, we recover the standard Saha equation for the dissociation of molecular hydrogen,

$$\beta^{\text{had}} = \frac{n_{\text{H}_2}}{n_{\text{H}_1}^2} = \frac{Z_{\text{H}_1}^2}{Z_{\text{H}_2}} \left( \frac{m_{\text{H}_2} h^3}{2 \pi m_{\text{H}_1} k_B T} \right)^{3/2} e^{D_0 / k_B T}, \quad (4)$$

where $D_0 = 2E_{0,\text{H}_1} - E_{0,\text{H}_2} = 4.478$ eV is the dissociation energy of the isolated hydrogen molecule. Even for trace species,
like H I or H2 in dense helium, the \( \mu^n_{\text{nid}} \) that arise from interactions with the atoms are not negligible and in principle should be comparable in magnitude to \( \mu^n_{\text{He}} \).

If we define the quantity \( \Delta I \) as

\[
\Delta I = \mu^n_{\text{H2}} - 2\mu^n_{\text{H1}},
\]

the nonideal equilibrium equation can be written in the form

\[
\beta = \frac{n_{H_2}}{n_{H_1}} = \frac{Z_{H_2}}{Z_{H_1}} \left( \frac{m_{H_2} h^2}{2\pi m_{H_1} k_B T} \right)^{3/2} e^{(D_{H_2} - \Delta I)/k_B T} \\
= \beta^n_{\text{H2}} e^{-\Delta I/k_B T}.
\]

Comparing equations (4) and (6), we see that the nonideal effects on the dissociation equilibrium can be interpreted as a change in the dissociation energy by a value of \( \Delta I \). For simplicity, we will follow this interpretation hereafter. We emphasize that this description of the nonideal contribution to the chemical equilibrium (eq. [6]) is identical to the occupation probability formalism of Hummer & Mihalas (1988) if there is only one bound state in the partition function (e.g., low-temperature H I) or if the \( \mu^n_{\text{H2}} \) is the same for all bound states \( j \) of the species \( i \) \( \mu^n_{\text{Hj}} = \partial f(T, n_j, \rho)/\partial n_j \) remains constant in eq. (2.17) of Hummer & Mihalas 1988. In both cases, the occupation probability can be factored out of the partition function and written as \( e^{-\Delta I/k_B T} \) (eq. [6]).

In the atmosphere of cool white dwarfs, hydrogen exists mostly as H2 and H I, and the H I/H2 ratio is governed by reaction (1) only. For a given temperature, density \( \rho \), and the atmosphere composition \( y = \text{He}/\text{H} \), the number densities of H2 and H I are

\[
n_{H_1} = \frac{-1 + \sqrt{1 + 8\beta n_\text{tot}}}{4\beta},
\]

\[
n_{H_2} = \beta n_\text{tot}^2,
\]

where

\[
n_\text{tot} = n_{H_1} + 2n_{H_2} = \frac{\rho}{m_{H_1} + y m_{\text{He}}}
\]

refers to the hydrogen species only.

2.2. Computation of the H2 Dissociation Equilibrium

The nonideal contributions to the chemical potentials of H I and H2 were obtained through the numerical solution of the Ornstein-Zernike equation in the Percus-Yevick (PY) approximation (Martynov 1992, chap. 5, 6, 10). For the H-He interaction, we use the pair potential of Shalabi et al. (1998), and for the H2-He interaction, the pair potential given by Ree (1983; see also Fig. 1). Both potentials are from ab initio quantum mechanical calculations and are in good agreement with the independent calculations of Tang & Yang (1990) for H-He and of Tao (1993) and Shafer & Gordon (1973) for H2-He. As we consider a helium-dominated mixture (He/H > 103), the H-I, H2-H, and H2-H2 interactions can be neglected.

High-pressure experiments have shown that ab initio pair potentials are too repulsive to describe dense systems in which N-body effects become important (Nellis et al. 1984; Ross et al. 1983). The softening of the pair potentials at high densities can only be quantified experimentally or, alternatively, estimated with N-body quantum mechanical calculations. Since neither are available for mixtures of trace hydrogen in helium, we resort to ab initio potentials. The net effect on the dissociation equilibrium depends on the relative softening of the potentials (eq. [5]) and is therefore less sensitive to N-body effects than the individual potentials. We also calculated the chemical potentials in the hypernetted chain approximation and found them to agree within 5% with the PY values up to 2 g cm\(^{-3}\). Since the PY approximation is better suited for short-range potentials, such as the ones we use here, we estimate that our PY calculations are reliable up to at least 2 g cm\(^{-3}\).

For the internal partition functions \( Z_i \), we use expressions for the electronic ground state of the unperturbed hydrogen molecule accounting for the vibrational/rotational excitations (Huber & Herzberg 1979), and set \( Z_{H_1} = 2 \) for hydrogen atoms. This approximation is justified as the electronic excitation energies of both species are large and for temperatures of a few thousand degrees, the populations of the excited electronic states are extremely small. However, there is significant thermal excitation of the rotational and vibrational levels of H2, and the effect of the dense medium on \( Z_{H_2} \) must be considered. Since the molecule does not have spherical symmetry, it is possible that its rotation modes will be hindered by interactions with neighbors at very high density. Furthermore, the energies of the vibrational levels, which are spaced by a mere 0.54 eV, could also be significantly shifted by these interactions. Both of these effects are discussed by Saumon & Chabrier (1991) and can be neglected under the present conditions. The use of the unperturbed rotational and vibrational levels of H2 is thus justified in the calculation of \( Z_{H_2} \).

More importantly, the excited rotational and vibrational levels of the H2 molecule may be differentially affected by the interactions. This relates to the general problem of the cutoff of the sum over states in the internal partition function and is the subject of an extensive literature. This truncation of the partition function sum is often described by an occupation probability formalism (Hummer & Mihalas 1988) and in the case of interactions between neutral particles, is generally described in the context of the volume occupied by each bound state. In the case of a diatomic molecule, the volume occupied increases with the rotational

![Figure 1](https://example.com/image.png)

**FIG. 1.**—H-He and H2-He pair interaction potentials. The dashed line represents the radius (horizontal axis) of a sphere whose volume equals the effective volume of two H atoms colliding with a kinetic energy of \( \frac{3}{2} k_B T \) (see text).
quantum number (centrifugal stretching) and with the vibrational quantum number (larger amplitude of vibration). The first effect is very small and can be safely neglected. We estimate the vibrational stretching by considering the change in the equilibrium internuclear separation of the molecule with the vibrational quantum number. Because of the anharmonicity of the potential, higher vibrational levels correspond to larger equilibrium separations and a larger average molecular volume. Based on the potential curve of the H2 molecule (Kolos & Wolniewicz 1965), we find that for \( T < 6000 \) K and densities of up to 2 g cm\(^{-3}\), the vibrational excitation is largely limited to the lowest five levels, and the partition function is reduced by a few percent when the larger volume of the excited states is taken into account. This is a small effect that can be neglected in view of the other uncertainties in the model, such as the \( N \)-body effects on the interaction potentials.

Thus, the use of the internal partition function of the isolated H2 molecule, with all states being affected identically by the interactions with He (eq. [6]) is a very good approximation.

3. RESULTS AND DISCUSSION

3.1. The H\(_2\) Dissociation Equilibrium in Fluid Helium

In general, the \( \Delta I \) defined by equation (5) is a function of the density of helium and the temperature (Fig. 2a), but is independent of the He/H ratio if H is a trace species (He/H > 10\(^2\)). For the conditions in white dwarf atmospheres, the temperature dependence is weak. The change in the dissociation energy \( \Delta I \) is negative, making H\(_2\) more stable in dense helium. This may be qualitatively understood by comparing the effective volume occupied by one H\(_2\) molecule to that of two H atoms in He. Let us assume that these effective volumes are the spaces around each of the particles where the energy of their interaction with He atoms is greater than the average thermal kinetic energy of the particles \( \frac{3}{2} k_B T \). This radius is the classical distance of closest approach in a collision. In Figure 1, we plotted the radius of a sphere whose volume equals the effective volume of two hydrogen atoms, as a function of \( k_B T \) (dashed curve). The corresponding radius for the hydrogen molecule is represented by the H\(_2\)-He potential (solid curve). The effective volume of H\(_2\) is smaller than that of two H atoms for \( k_B T < 1 \) eV. Since the exclusion of a greater volume results in a decrease of the entropy of He, H\(_2\) is more stable in

![Fig. 2.—(a) Variation of the effective dissociation energy \( D_0 - \Delta I \) as a function of the density of helium for temperatures of 3000 K (solid line), 4000 K (dotted line), and 5000 K (dashed line). (b) The density \( \rho \) at the photosphere of cool white dwarf atmosphere models of \( T_{\text{eff}} = 4000 \) K, \( \log g = 8 \) (cgs), and various He/H compositions.](image)

### Table 1

| \( \rho \) (g cm\(^{-3}\)) | \( \Delta I \) (eV) for \( T \) (K) |
|-------------------------|------------------|
|                         | 2000             | 4000             | 6000             | 8000             |
| 0.001                    | -0.001           | -0.001           | -0.001           | -0.001           |
| 0.010                    | -0.007           | -0.010           | -0.011           | -0.012           |
| 0.100                    | -0.083           | -0.108           | -0.120           | -0.127           |
| 0.250                    | -0.242           | -0.297           | -0.323           | -0.334           |
| 0.500                    | -0.579           | -0.668           | -0.697           | -0.702           |
| 0.750                    | -1.006           | -1.075           | -1.088           | -1.070           |
| 1.000                    | -1.471           | -1.494           | -1.469           | -1.414           |
| 1.500                    | -2.011           | -2.094           | -1.963           | -1.825           |
| 2.000                    | -2.189           | -2.387           | -2.192           | -1.988           |

![Fig. 3.—Density profiles of white dwarf atmosphere models of \( T_{\text{eff}} = 4000 \) K, \( \log g = 8 \) (cgs), and He/H composition of He/H = 10\(^6\), 10\(^4\), and 10\(^2\) (top to bottom).](image)
dense helium than two H atoms. In dense hydrogen we have the opposite situation, in which H2 is less stable at high density (leading to pressure dissociation of H2) because H2-H2 is more repulsive than the sum of the H-H and H-H2 interactions (Saumon & Chabrier 1991).

Numerical values for \( \Delta I \) obtained from our model are given in Table 1. Together with relations (6)–(9), this table allows for an easy implementation of the nonideal abundances of atomic and molecular hydrogen into white dwarf atmosphere codes.

The nonideal recombination of H becomes significant when \(-\Delta I/k_B T > 1\). For an atmosphere with \( T_{\text{eff}} = 4000 \) K, this will occur at the photosphere if \( \rho > 0.3 \) g cm\(^{-3}\), a density easily achieved in He-rich models. As \( D_0 - \Delta I \) increases with increasing helium density, a lower dissociation fraction will result. A strong deviation from the ideal gas abundance of H2 is expected.

### 3.2. The H2 Dissociation Equilibrium in He-Rich White Dwarf Atmospheres

We have applied the nonideal correction to the H2 dissociation equilibrium to very cool white dwarf atmospheres. To show the effect, we solved for the chemistry and opacity along fixed \( T_{\text{eff}} \) white dwarf atmosphere profiles of \( T_{\text{eff}} = 4000 \) K, a gravity of

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**Fig. 4.—**Left panels: Number density of atomic (solid lines) and molecular (dotted lines) hydrogen with (thick lines) and without (thin lines) the nonideal chemical equilibrium along the atmosphere profiles of Fig. 3. Right panels: Corresponding contributions to the photospheric opacity; H2-He CIA (solid lines), He free-free of Iglesias et al. (2002; long dashed lines), H+ bound-free and free-free (dotted lines), and Rayleigh scattering (short dashed lines).
log $g = 8$ (cgs), and various He/H ratios. Figure 3 shows the atmospheric density profiles. These profiles were obtained with a code that solves for static, plane-parallel, and LTE white dwarf atmospheres in thermal and hydrostatic equilibrium, accounting for refraction (Kowalski & Saumon 2004). The resulting new abundances of H$_2$ and H$_2$ in our models are given in Figure 4 (left panels). As expected, the amount of molecular hydrogen increases significantly throughout the atmosphere for He/H $> 10^{3}$, and H$_2$ can become the dominant hydrogen species at the photosphere.

The most important sources of opacity in helium-rich white dwarf atmospheres are He$^-$ free-free, Rayleigh scattering and H$_2$-He CIA (Hansen 2004). Several physical and chemical effects that alter these opacity sources have already been discussed: the change in the free-free opacity and the Rayleigh scattering of helium, as caused by the strong correlations in the dense fluid (Iglesias et al. 2002), the change in the number density of free electrons (Kowalski et al. 2005; Bergeron et al. 1995), the presence of heavy elements (Bergeron 2001), and the formation of trace species like He$^+$ (Malo et al. 1999) and HeH$^+$ (Harris et al. 2004). The effect of the nonideal chemistry of the H$_2$ dissociation on the opacity is shown in the right panels of Figure 4. The increase in number density of molecular hydrogen results in an increase of the H$_2$-He CIA opacity. This follows from the linear dependence of H$_2$-He CIA opacity on $n_{H_2}$. On the other hand, the H$^-$ bound-free and free-free opacities are reduced due to the decrease in the abundance of atomic hydrogen. Based on the atmospheric structures used here, the effects of the nonideal chemistry of H$_2$ in dense helium are maximal for He/H $\sim 10^3$. This arises from a competition between the need for a high He/H ratio to increase the nonideal effects by increasing the density at the photosphere (Fig. 2b) and the need for a high enough hydrogen content in the atmosphere so that H$_2$ (or H) contributes to the total opacity (Fig. 4, right panels).

The impact of the nonideal dissociation equilibrium of H$_2$ on the synthetic spectrum of a He-rich white dwarf model is shown in Figure 5. For a white dwarf atmosphere model of $T_{\text{eff}} = 4000$ K, log $g = 8$ (cgs), and He/H $= 10^3$, the rise in abundance of H$_2$ increases significantly the opacity in the infrared, causing a redistribution of the flux toward shorter wavelengths. This effect on the spectrum of cool white dwarfs is largest for $T_{\text{eff}} = 4000$–4500 K, where H$_2$ is partially dissociated. At lower effective temperatures, hydrogen exists mostly in molecular form, and the effect of the nonideal dissociation equilibrium on the spectrum vanishes at $T_{\text{eff}} \sim 3000$ K.

The determination of the He/H composition of very cool He-rich white dwarfs depends mostly on the relative He-H$_2$ CIA, and He$^-$ free-free opacities (Fig. 4, right panels). Since the nonideal recombination increases the CIA opacity, this effect, taken by itself, will result in a higher value for the He/H ratio inferred from a given stellar spectrum. On the other hand, current calculations for the ionization fraction of dense helium and the low-frequency behavior of the He$^-$ free-free opacity are uncertain, and the He$^-$ free-free opacity could be underestimated by as much as $\sim 2$–4 orders of magnitude (Kowalski et al. 2005). It is therefore too early to draw conclusions about the atmospheric composition of the coolest white dwarfs. However, we emphasize that, as the chemical equilibrium (eq. [6]) is not affected by the number of free electrons in the atmosphere, our solution for the nonideal abundance of H$_2$ will not be affected by weak ionization of He, and the results are limited only by the validity of the H$_2$-He and H-He interaction potentials.

The nonideal dissociation equilibrium in pure hydrogen atmospheres is discussed in Saumon & Jacobson (1999). As hydrogen is much more opaque than helium, the density at the photospheres of these stars is much smaller than for helium-rich atmosphere stars of the same effective temperature. The nonideal effects are therefore weaker and become important only in stars of lower effective temperature and/or higher gravity, where high densities are achieved. Saumon & Jacobson (1999) show that the nonideality matters in pure hydrogen atmospheres with $T_{\text{eff}} < 2500$ K. White dwarfs with hydrogen-rich atmospheres of such low effective temperatures have not yet been identified.

4. CONCLUSIONS

Recent discoveries of a number of cool white dwarfs with peculiar spectral energy distribution represent a challenge in the modeling of very cool white dwarf atmospheres, as the spectra of these stars cannot be fitted with existing models. We believe that the main reason of this shortcoming of the models is the poorly explored, extreme physical regime found inside these atmospheres. We presented a correction to the abundance of H$_2$ that arises from the strong interaction of hydrogen molecules and atoms in a dense fluid helium medium. We have found that in dense, helium-rich, cool white dwarf atmospheres, the formation of H$_2$ is more favorable than in the ideal gas description. For white dwarfs of $T_{\text{eff}} = 4000$ K and He/H $> 10^3$, the abundance of molecular hydrogen increases by an order of magnitude, with a corresponding increase in the H$_2$-He CIA opacity by the same factor. This improvement is a new, significant effect that must be included in realistic modeling of very cool white dwarf atmospheres.

We have shown that the nonideal effects affect strongly the abundances of even trace species in the atmosphere. This strongly suggests the necessity of revising the abundances of other trace species with significant opacity for similar effects. We expect that the study of their abundances and absorption processes in fluid helium will significantly improve our understanding of the atmospheric physics, composition, and evolution of the oldest and coolest white dwarfs.

I thank D. Saumon for useful discussions and the referee, P. Bergeron for suggestions that improved the clarity of the manuscript. This research was supported by the United States Department of Energy under contract W-7405-ENG-36.
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