Hydrogen-helium demixing from first principles: From diamond anvil cells to planetary interiors

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Hydrogen-Helium Demixing From First-Principles: From Diamond Anvil Cells to Planetary Interiors

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An accurate determination of the immiscibility of helium in hydrogen has a direct impact on the understanding of the interior structure and of the evolution of Jovian planets. We extend our previous work on hydrogen-helium mixtures (Ref.[12]) to lower pressures and lower temperatures, across the molecular dissociation regime in hydrogen, to the low pressure molecular liquid. Using density functional theory-based molecular dynamics together with thermodynamic integration techniques, we calculate the Gibbs free energy of the dense liquid as a function of pressure, temperature, and composition. We address the importance of the non-ideal entropy of mixing in the solubility of helium in hydrogen and find that it is critically important in the molecular regime. The resulting demixing temperatures smoothly connect measurements done in diamond anvil cells to the high temperature and pressure conditions found in giant planet interiors.

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I. INTRODUCTION

The properties of hydrogen-helium mixtures have a significant impact in the study of the structure and evolution of planets, in particular for gas giants like Jupiter and Saturn whose composition are over 90% hydrogen and helium[1,2]. The details of the planetary models are controlled by the global properties of the phase diagram of the mixture, in particular by the existence of phase transitions at high pressure. The problem of helium solubility in hydrogen has an equally important role in the correct description of planetary interiors. If helium is immiscible at some point in the planet's interior, the heavier helium rich droplets would descend deeper in the planet through gravitational differentiation, producing an additional energy source which could help explain the current discrepancies between the observed luminosity of Saturn and the one predicted by homogeneous evolutionary models[3,4].

At relatively low pressures, demixing in the H_2-He mixture was observed in experiments at room temperature by Streett up to 10 kbar[5], by van den Bergh and Schouten up to 75 kbar[6] and by Loubeyre et al. up to 80 kbar[7]. Subsequent Gibbs ensemble Monte-Carlo calculations with interaction potentials that were used by Schouten *et al.*[8] to predict helium demixing up to 2500 K and 1 Mbar are consistent with the room temperature experimental measurements. In this case, the demixing of helium is due to the differences in the interaction potentials of like and unlike species.

After decades of intense theoretical focus, significant progress was made recently on the problem of helium solubility in liquid metallic hydrogen at high pressure. Using first-principles simulation methods based on density functional theory (DFT), two independent calculations[9–13] produced similar predictions on the critical temperatures of immiscibility at pressures above 3 Mbar, where the demixing of helium is clearly related to the fact that hydrogen is metallic under these conditions while pure helium still exhibits a large band gap. This demixing will occur until the temperature or pressure is high enough to metallize helium as well or until the temperature is high enough to entropically favor mixing.

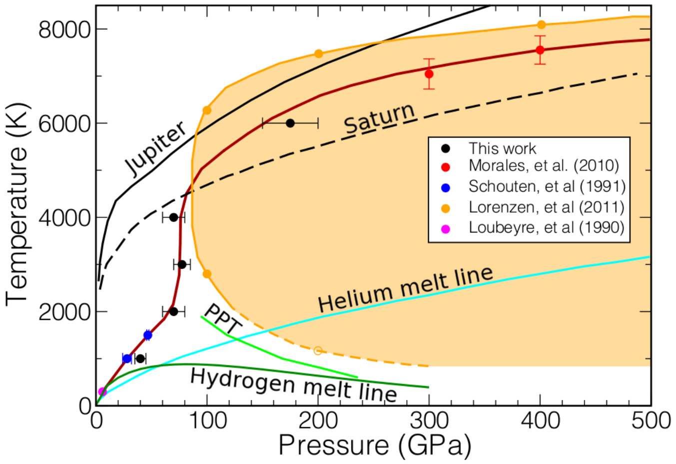

FIG. 1: Schematic phase diagram of hydrogen-helium mixtures at high pressure, for a helium concentration of 8%. The blue circles are the low pressure results obtained with the effective potential of Schouten *et al.*[8]. The yellow circles show the critical temperature reported by Lorenzen *et al.*[14], with the corresponding immiscible region represented by the shaded yellow region. The black circles are the results of the present work while the red circles are the results from our previous calculations[12]. The location of the liquid-liquid phase transition in hydrogen[16,17] (light green) is presented along with the melting lines of pure hydrogen (dark green) and pure helium (cyan).

In a subsequent publication, Lorenzen et al.[14] extended their DFT-MD simulations to lower pressures between 1 and 2 Mbar into a region where atomic and molecular hydrogen are in coexistence (i.e. molecular bonds exist but don't last very long). However, their results for the demixing temperature are inconsistent with low pressure experimental work and with the predictions of Schouten *et al.*[8] based on potentials fitted to the low pressure experimental data. One possible reason for the inconsistency at low pressure may be found in their use of the metallization criteria as the main drive for immiscibility in all regions. The aim of this paper is to explore the impact of this assumption. We use a similar approach as described in our previous work[12] using thermodynamic integration to account for any non-ideal entropy of mixing and obtain a critical temperature for helium demixing that is consistent with early experimental work[5–7].

II. RESULTS

A. Non-Linear Entropy

The central quantity in the study of the miscibility properties of a binary compound is the Gibbs free energy of mixing, where a function of mixing is defined by: $A_{mix}(x) = A(x) - xA(1) - (1-x)A(0)$ and $A(x)$ is any thermodynamic quantity for a mixture at a composition given by x, the fraction of one of the components, helium in our case. With knowledge of the Gibbs free energy of mixing, we can obtain critical compositions of mixing using the equal tangent construction. Unfortunately, the calculation of Gibbs free energies is not a trivial task, particularly using first-principles simulation methods. The problem lies in the fact that the entropy is not directly accessible to direct simulation methods, since it can not be expressed as an ensemble average. The remaining part of the Gibbs free energy, the energy and pressure, can be directly obtained from simulation, which leads many to make use of a linear mixing approximation (LM) for the entropy. In the LM approximation, the mixing entropy is obtained assuming mixing of non-interacting species and is given by (in units of k_B): $S^{LM}_{mix}(x) = x\ln x + (1-x)\ln(1-x)$. With the exception of our recent work[12], where we present direct free energy calculations of hydrogen-helium mixtures using thermodynamic integration, the LM approximation has been universally applied in the study of hydrogen-helium mixtures at high pressures. In the following, we demonstrate how the LM approximation can led to incorrect conclusions regarding the accuracy of DFT-based approaches in describing the properties of hydrogen-helium mixtures, especially for mixtures with high helium concentrations at high pressure.

The upper panel of Figure 2 shows the difference in the Gibbs free energy of mixing between our direct free energy calculations[12] and the results of Lorenzen *et al.*[13] using the LM approximation, as a function of composition for several temperatures at a pressure of 400 GPa.

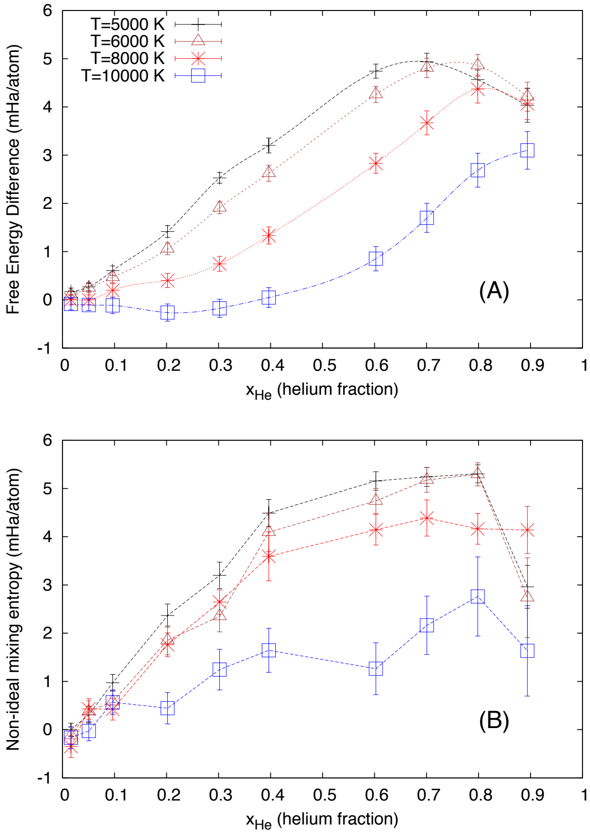

FIG. 2: Upper panel: Difference in the Gibbs free energy of mixing between our direct free energy calculations[12] and the results of Lorenzen *et al.*[13]. Lower panel: Non-ideal mixing entropy as a function of composition, at a pressure of 400 GPa, for various temperatures. In both figures, lines are guide to the eye.

Two key features are prominent in this comparison; the free energies agree very well at low helium fractions, and the agreement worsens with either increased amounts of helium or decreasing temperatures. While small deviations between the two calculations are always expected due to differences in the choice of simulation parameters including: system size, treatment of the electron-proton interaction (pseudo-potentials, PAW), grids in density and temperature, k-points, plane-wave cutoffs, etc; most of the discrepancies come from the approximated treatment of the entropy of the mixture. The use of the linear mixing approximations leads to a deep minimum of the mixing free energy at high helium fractions[13]. This leads to an incorrect evaluation of the slope in the equal tangent construction, which in turns leads to small deviation in the resulting critical composition. This translates in a difference in the de-mixing temperature of $\sim 1000K$.

The large non-ideal contribution to the entropy can be understood by looking at the structural properties of the liquid, in particular at the hydrogen-hydrogen correlation as the amount of helium is varied. Figure 3 shows the

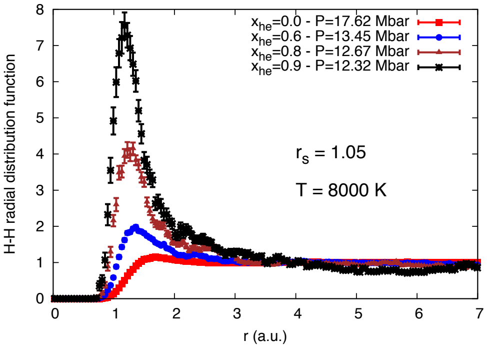

FIG. 3: H-H pair correlation function for a hydrogen-helium mixture, at T=8000 K, for a series of of helium fractions at a density given by r_s=1.05. A very strong dependence in the height and shape of the first peak with helium fraction is observed. Figure taken from Morales, *et al.*,[12]

hydrogen-hydrogen pair correlation function for mixtures of various compositions at a temperature of 8000 K and a density given by $r_s = 1.05$. The structure of hydrogen is strongly influenced by the helium concentration, a molecular-like peak builds up smoothly with increasing helium concentration ($x_{He} \to 1$). Although at low x_{He} hydrogen is in the monoatomic fully ionized state, an effective proton-proton attraction reminiscent of molecular bonding develops upon increasing x_{He}, even at the high pressures and temperatures found in the core of the planets. Under these conditions, helium is not ionized; this inhibits the delocalization of the hydrogenic electrons, enhancing the formation of weak molecular bonds. Such weak attraction gives proton pairs with short lifetimes, as also inferred from direct inspection of the MD trajectories.

The effects of the weak proton-proton attraction on the internal energy of the mixture should be accurately captured by the work of Lorenzen *et al.*[13], since the enthalpy of the mixture is calculated through direct MD simulations. The effects on the entropy, on the other hand, will not be adequately described in the LM approximation since it doesn't take into account changes in the chemical environment with varying composition. In fact, this approximation assumes that the chemical state of the system does not change with composition. In order to better understand the implications of the LM approximation on the Gibbs free energy of mixing, we calculate the non-linear contribution to the mixing entropy, defined as: $\Delta S_{mix} = S(x) - S_{mix}^{LM}(x)$. ΔS_{mix} measures how much the mixing entropy deviates from ideal behavior[20]. The lower panel of Figure 2 shows the non-ideal mixing entropy at a pressure of 400 GPa for various temperatures. The magnitude of the non-ideal mixing entropy closely resembles the magnitude of the free energy difference between direct free energy calculations and mixing free energies obtained with the LM approximation. While this approximation is reasonably accurate with low amounts of helium and/or higher temperatures, it becomes very poor for large helium fractions producing an artificially stable helium-rich mixture.

B. H-He Miscibility at Low Pressure

In order to understand helium miscibility in low pressure hydrogen, we extended the free energy calculations to lower pressures. Instead of integrating the equation of state across the regime of molecular dissociation, which would require very fine grids in density and temperature to accurately capture all the features present in the free energy surface, we make use of the Coupling Constant Integration (CCI) approach to calculate the free energy of the mixture at a temperature of 1000 K and a density given by $r_s = 2.0$, which corresponds to a pressure of $\sim$ 16.5 GPa for pure hydrogen and $\sim$ 9.4 GPa for pure helium. Our reference system consists of a collection of hydrogen molecules and helium atoms interacting through effective potentials. The potential corresponding to the hydrogen molecules is divided into two terms, an intramolecular term obtained from the Kolos Wolniewicz (KW) ground state potential energy calculation of the dimer[15], and an intermolecular term centered at the center of mass of the molecule. The H_2-H_2, H_2-He and He-He potentials were obtained from a fit of the exp-6 potentials used by Schouten *et al.*[8] with a Yukawa potential form. Following our previous free energy calculations[12], we perform a coupling constant integration, for a series of compositions, between the system described by DFT and the reference system. This was followed by a second coupling constant integration between the reference system and a system of non-interacting helium atoms and hydrogen molecules, where the intramolecular part of the hydrogen molecule interaction is left unaltered to avoid crossing any first-order transitions produced by bond breaking. The free energies of the ideal system can be calculated analytically. Combining the resulting free energies with the equation of state of the mixture on a grid of pressures and temperatures, we can expand the Gibbs free energy of the mixture in both temperature and density axes.

Figure 4 shows the Gibbs free energy of mixing as a function of composition along the T=1000 K isotherm, for pressures between 20-60 GPa. While at low pressures the system is fully miscible, as the pressure is increased an immiscible regime appears, which subsequently expands with increasing pressure.

Figure 1 shows a schematic phase diagram of a mixture with 8% of helium, representing conditions similar to those expected in the interior of Jupiter and Saturn. In addition to the melting lines of the pure elements[14,18], the figure also shows isentropes corresponding to recent interior models of Jupiter and Saturn[19]. The critical temperature of immiscibility from the recent work of Lorenzen *et al.*[14] is compared with the present work. There is a reasonable agreement in the critical temperature and its pressure dependence at higher pressures, when hydrogen

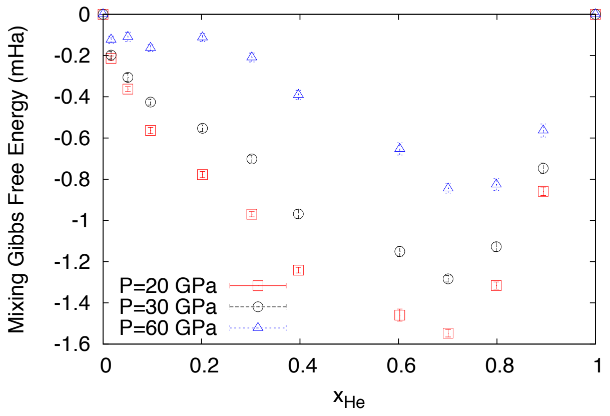

FIG. 4: Gibbs free energy of mixing as a function of helium fraction, for various pressures at a temperature of T = 1000 K. The demixing transition transition for compositions above 10-15% is seen between pressures of 20-30 GPa, while the transition below compositions of 10% occurs above 30 GPa, but clearly below 60 GPa.

exists in a conducting atomic state; this is expected from previously published work[12,13]. At lower pressures, there is a marked difference in the predictions of the immiscible regime. Based on an estimation of the metallization of pure dense fluid hydrogen, Lorenzen *et al.* predict a miscible mixture in the liquid phase at all temperatures for pressures below 100 GPa. Our work predicts an immiscible regime that approaches the melting line of molecular hydrogen in the limit of low pressure. In this regime, demixing is not driven by metallization of hydrogen, which is at odds with Lorenzen *et al.* conclusion. In fact, our calculations predict an immiscibility temperature that agree very well with the model calculations of Schouten *et al.*[8] around 50 GPa, and are consistent with an extrapolation to the experimental measurements of Loubeyre *et al.*[7] at 8 GPa.

We should mention that for small enough helium fractions at temperatures around 1000 K, close to the melting line of hydrogen, we have not considered mixed solid phases whose free energy will be comparable to those of the liquid. This represents a much more demanding calculation due to the need to determine the structure of the solid at each composition, in addition to free energy calculations for each structure. Since mixed solid phases will only exists at the lowest temperatures, we decided to ignore this in the current work. Nevertheless, the current predictions represent the most accurate calculations of helium miscibility in high pressure hydrogen to date. The observed immiscible regimes are at low enough temperature to be accessible with diamond anvil cell techniques.

From the point of view of planetary modeling, this work represents an important step forward in the correct description of helium distribution inside hydrogen-rich planets. In addition to explaining the observed helium depletion on the surface of the planets, this work predicts immiscible regimes inside Saturn which would help explain the current discrepancies between evolutionary models and observed surface temperatures in the planet[3,4]. While the previous work of Lorenzen *et al.* presented a picture of helium miscibility in strong disagreement with low pressure measurements and model calculations, our work is in good agreement with all existing data. This not only gives strong support to the ability of DFT to properly describe the equation of state of the mixture at high pressure, it also clearly demonstrates the need for accurate free energy calculations. Our work suggests that equations of state used in planetary modeling should be produced from these type of direct free energy calculations instead of more common mixing approaches that do not properly describe the mixture close to the dissociation regime of hydrogen. Finally, our work demonstrate the need for a reinvestigation of planetary interiors with models that properly account for helium segregation and inhomogeneous helium distributions, combined with first-principle derived equations of state.

Acknowledgments

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