THE LIQUID-LIQUID TRANSITION IN DENSE HYDROGEN

Allocation: Blue Waters Professor/240 Knh
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EXECUTIVE SUMMARY

The phase diagram of high-pressure hydrogen is of great interest for fundamental research, planetary physics, and energy applications. A first-order phase transition in the fluid phase between a molecular insulating fluid and a monoatomic metallic fluid has been predicted. The existence and precise location of the transition line are relevant for planetary models. Recent experiments reported contrasting results about the location of the transition. Theoretical results based on density functional theory are also very scattered. We performed highly accurate coupled electron-ion Monte Carlo calculations of this transition, finding results that lie between the two experimental predictions, close to that measured in diamond anvil cell experiments but at 25–30 GPa higher pressure. The transition exhibited a discontinuity in the specific volume, a sudden dissociation of the molecules, a jump in electrical conductivity, and loss of electron localization, all indications of a weak first-order transition.

INTRODUCTION

The properties of hydrogen under extreme conditions of pressure and temperature are of great interest for fundamental research, planetary physics, and energy applications [1]. Hydrogen accounts for much of the visible mass in the universe. The properties of hydrogen and helium are needed for understanding the giant planets (Jupiter and Saturn), but experiments under the relevant conditions are challenging. Even though hydrogen is the first element in the periodic table, calculating its properties is not simple since both the electronic and protonic correlations are quantum and correlated.

There is a long-standing question [1] regarding how hydrogen makes a transition from a molecular insulating state to an atomic metallic state as pressure and temperature are increased. A first-order phase transition in the fluid phase between a molecular insulating fluid and a monoatomic metallic fluid has been predicted [2]. Recent studies [3-4] reported contrasting results about the location of the transition different by a factor of two (in pressure). Theoretical results based on density functional theory are also very scattered and hence not predictive [5]. These findings motivated us to repeat our earlier calculations on Blue Waters, to better control the convergence and utilize recent improvements in methodology.

METHODS & RESULTS

Over the past decade, we have developed new Quantum Monte Carlo simulation methods to treat quantum systems at low temperature. The quantum Monte Carlo method we use (Coupled Electron Ion Monte Carlo) works with the full interaction between the electrons and protons and treats both particles fully quantum mechanically. In contrast to density functional calculations, all effects of electronic correlation are explicitly included. This concept is particularly important in hydrogen, because of possible self-interaction effects, difficulty in treating the hydrogen bond breaking and the large van der Waals interactions. We model hydrogen with about 100 electrons and protons in a periodic cell. Special methods are used to extrapolate accurately to the thermodynamic limit. With our method, we simulated hydrogen for temperatures in the range of 200K to 5000K, and at relevant pressures, 100GPa to 500GPa.

We find pressures for the transition that lie between the two experimental predictions, close to that measured in diamond anvil cell experiments, but at 25–30 GPa higher. This observation is shown for both hydrogen and deuterium (Fig. 1). The transition along a line of constant temperature exhibited a discontinuity in the specific volume, a sudden dissociation of the molecules, a jump in electrical conductivity, and loss of electron localization. For temperatures below 2000K, we observe a first order transition between an insulating molecular liquid and a denser metallic atomic liquid. Our predicted transition pressures are intermediate between the two experimental observations [3,4]. Future work will be to perform further simulations and analysis to understand the divergent results of the experiments and the unusual properties of the molecular and atomic liquid. New experiments using the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory have also been recently performed though the results are proprietary.

Our calculations are needed to validate our computational method and to resolve the different experimental measurements. It is essential for progress in the high-pressure community to determine the difference between the experiments and computation. After validation, the method can be used with more confidence in modeling the wide variety of astrophysical objects observed, composed largely of hydrogen and helium under extreme conditions.

WHY BLUE WATERS

Without access to Blue Waters we would not have been able to perform this study because of the computational demands of the simultaneous treatment of quantum electrons and protons.

NEXT GENERATION WORK

Our method is highly amenable to next generation systems. We would be able to perform more such calculations and systems containing elements heavier than hydrogen and helium, essential not only in astrophysics but for materials as well. We will also be able to compute other properties relevant for modeling planetary interiors.

PUBLICATIONS AND DATA SETS

Pierleoni, C., et al., Liquid-liquid phase transition in hydrogen by coupled electron-ion Monte Carlo simulations, *Proc. Nat. Acad. Science (US)* 113 (2016), p. 4953-4957.

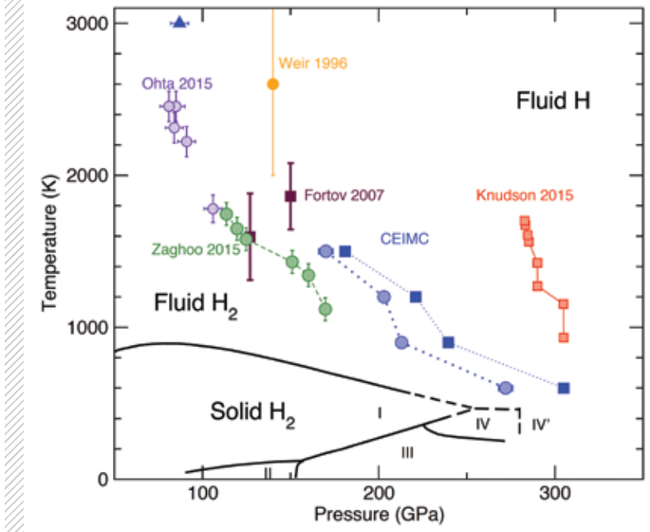

FIGURE 1: The predicted phase diagram (temperature versus pressure) of dense hydrogen. The blue circles (hydrogen) and squares (deuterium) show the results from the Blue Waters calculation [5]. The red squares [3] and green circles [4] show the different experimental measurements.