

PROPERTIES OF DENSE HYDROGEN

Allocation: Blue Waters Professor/100 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 is 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 results. We have also explored the transition between molecular and atomic hydrogen at lower temperatures, in the solid phase.

RESEARCH CHALLENGE

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 to understand 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 motions are quantum and correlated.

It has long been an open question [1] 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].

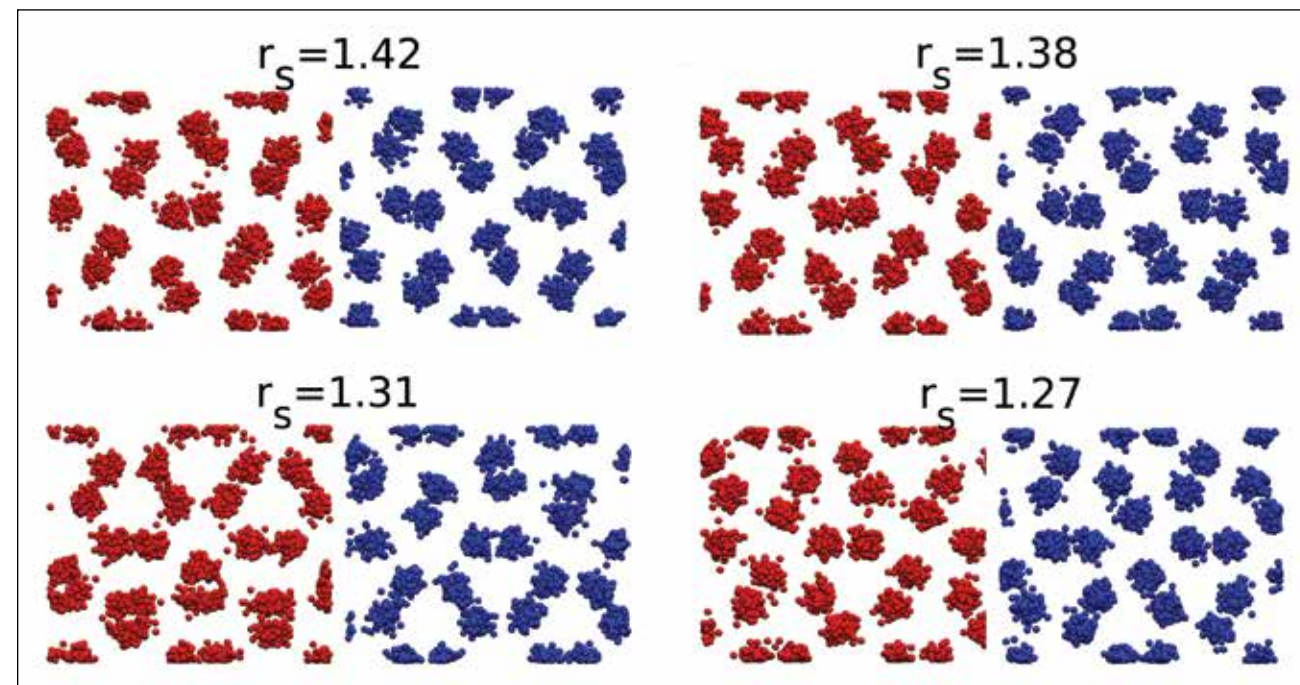


Figure 1: Typical snapshots of molecular hydrogen approaching the transition to atomic hydrogen [7]. Shown are the positions of the protons: in red from Path Integral Molecular Dynamics within density functional theory energetics, and in blue from coupled electron ion simulations. r_s is the average inter-proton distance in units of Bohr radii.

Recent experiments [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. In addition, recent experiments have probed the solid phase leading up to the atomic transition [7] and the melting temperature.

METHODS & CODES

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 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 200°K up to 5,000°K, and at relevant pressures, 100GPa (gigapascals) to 500GPa.

RESULTS & IMPACT

For temperatures below 2,000°K we observe [5] 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].

In recent unpublished work [7], we performed a detailed study of solid molecular hydrogen at temperatures between 200°K and 414°K and pressures between 180GPa and 520GPa, to understand the detailed crystal structures, the melting temperature of the solid and the transition into the metallic/atomic phase. There has been a recent controversial report of the experimental observation of this transition [6]. Shown in the figure are snapshots of a layer of one of the crystal structures (Cmca12) as it evolves from 180GPa to 420GPa.

Our calculations are needed to validate both our computational method and to resolve the different experimental measurements. It is essential for progress in the high-pressure community to resolve 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 being observed, composed largely of hydrogen and helium under extreme conditions. As a byproduct of our simulation, we are also judging the accuracy of various density functionals and force-fields for the simulations of these systems.

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.

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), pp. 4953–4957.