

Final Project Report

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Extreme Condition Hydrogen Phase States

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ABSTRACT: Hydrogen, being one of the most abundant and simplest elements, holds complicated yet promising potential in phase states only known to be accessible through extreme conditions. Molecular dynamic (MD) simulations are used to model hydrogen molecules in extreme conditions due to the difficulty of physically creating the necessary environments for investigation. This research utilizes a recently developed model (Cheng, B., et. al., 2020) which accurately captures the phase behavior of hydrogen in the environment range of interest. This study verifies a phase transition from solid to liquid state occurs under high temperatures and pressures. Using hydrogen phase diagrams derived throughout the literature, the most probable transition and model-capable conditions were selected as a focus for simulation. Radial distribution functions are not solely sufficient to show this transition, however, it is observed that atoms in the liquid phase are packed tighter than those in the solid phase, in agreement with previous discoveries (Zong et al., 2020). Additionally, mean squared displacement is evaluated as a function of temperature and analyzed in an attempt to find where a phase transition may occur. The results of this research expand on the quest to understand elements of the universe as well as progress the capabilities and validation of molecular modeling methods at conditions inaccessible to experimentation. Knowledge and eventual access to various phases of hydrogen will open future possibilities ranging from room-temperature superconductors to powerful rocket propellants, to understanding the nature of giant planets in the solar system. The methods used here to develop knowledge of hydrogen phases through molecular dynamic simulations are transferable to the discovery of phase behavior of different elements in the future.

KEYWORDS: *Hydrogen, Molecular Dynamics, Phase Behavior, LAMMPS*

INTRODUCTION

Many scientists throughout history embark on the quest to understand what makes up the universe. Of the identified elements, hydrogen is one of the simplest and most abundant, making it a great candidate for the starting line of the journey. The characterization of how hydrogen will undergo phase transition is a topic of great controversy, but also desire. Harnessing the ability to navigate across the phase spectrum of hydrogen will grant access to great future applications in fields such as energy, engineering, and even astrophysics.

One major application interest of scientists in recent years is metallic hydrogen, the “holy grail” of high-pressure research (Wigner and Huntington, 1935). It has been theorized that at extreme pressures hydrogen may undergo an insulator-to-metal transition, forming a metallic state. This state of hydrogen has many properties/applications of interest such as a room-temperature superconductor and powerful rocket fuel. This is only one example of the great potential of hydrogen.

This study joins the quest for understanding the phase behaviors of hydrogen by using molecular modeling techniques. Molecular dynamic simulations allow such studies to create extreme

apparatus conditions such as high pressure and temperature states. This study will utilize the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to reinforce previously characterized transitions from liquid to solid molecular state hydrogen (Dias and Silvera, 2017; Zong et al., 2020). The model used for this study is validated for temperatures ranging from 600 K to 3000 K and pressures from 100 GPa to 400 GPa. This range is precisely where previously characterized transition zones should occur, however, the previous study using this model had a focus towards a liquid-liquid transition (Cheng, et. al., 2020).

METHODOLOGY

Modeling

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is used in this study to predict and observe the behaviors of hydrogen on the molecular level due to the extreme conditions of interest. Commonly, ab initio molecular dynamics (AIMD) simulations are used for precise modeling from first principles using quantum mechanical information. However, these models hold an outstanding computational cost due to the sophistication of calculations such as electronic degrees of freedom. To combat this barrier, Cheng, et. al., 2020 developed neural-network-based machine-learned potentials (MLP) learned from electronic-structure references. The MLP used in this study is based on the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The model was trained and validated enabling orders of magnitude speed-up of extreme condition hydrogen simulations. The MLP force field requires the LAMMPS NNP interface. This is a neural network potential package (n2p2) that is compatible with the MLP provided in the supplementary material of Cheng, et. al., 2020.

Simulations were centered around simple pressure and temperature control using NPT integration for deterministic dynamics. Pressure is controlled with a Nose/Hoover pressure barostat, and temperature is controlled with a Nose/hoover thermostat replication of the isothermal-isobaric ensemble. Temperature is relaxed at 0.02 ps and pressure is relaxed at 500 ps to allow for reasonable equilibration time.

A time step of 0.2 femtoseconds was used to match the validated model, allowing negligible drift in conserved quantities for the system. Equilibration simulations in this study were run for 0.02 nanoseconds. It should be noted that the validated model simulated 0.4 ns for study, however, due to the computation cost, reduced simulation time was used. Congruent with the validated model, the simulation box holds 1728 atoms (Figure. 1) which were determined to sufficiently converge potential energy, volume, and molecular fraction. The simulation box was set as periodic in all three directions.

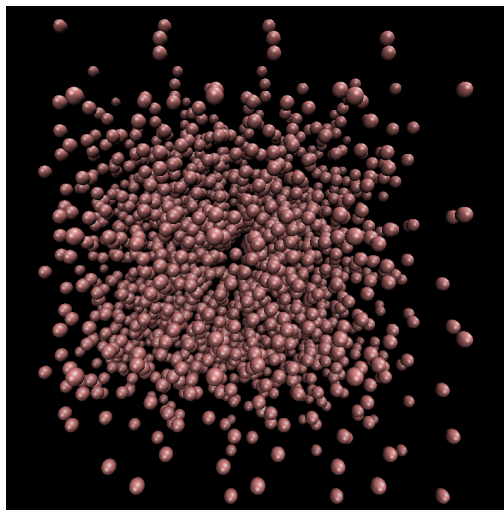


Figure 1. Simulation Box: Initial Configuration

Simulations

In order to identify phase behavior of hydrogen, two analysis techniques are used. The first method is the radial distribution function (RDF). This function describes relative density as a function of radial distance from a given atom. RDF is commonly used as a way to identify phase structure through organization of molecules in space. The second metric used is the mean square displacement function (MSD). The MSD function provides the average square of displacement of all particles. MSD allows a method of tracking molecular motion, providing the average displacements throughout a simulation time. Next, the simulation details for each metric are provided.

The goal of the RDF is to identify how the density of molecules varies as a function of the distance from a reference molecule. LAMMPS provides an RDF compute command that is utilized for this calculation. The computation follows Equation 1. where $\rho(r)$ represents the local density and ρ represents the overall density of atoms (volume).

$$g(r) = \frac{\rho(r)}{\rho}$$

Equation 1. Radial Distribution Function

The complete expression given by Equation 2. encompasses N , number of atoms in an interval $r \pm \Delta r/2$; Ω , volume of shell dr .

$$g(r) = \frac{\langle N \left(r \pm \frac{\Delta r}{2} \right) \rangle}{\Omega \left(r \pm \frac{\Delta r}{2} \right)} \frac{1}{\rho}$$

Equation 2. Radial Distribution Function (Complete)

To obtain meaningful RDF expressions for the phase behaviors of hydrogen, simulations were run at temperatures of 800 Kelvin (K) and 3000 K. The lower temperature was selected to represent hydrogen in molecular solid form based on widely accepted phase diagrams previously derived for hydrogen (Zong et al., 2020). The higher temperature represents hydrogen in a liquid state. These temperatures were tested at pressures of 100 GPa and 300 GPa. The variation in pressure should still hold phase differences in the different temperatures, however, the transition is expected to be at a lower temperature for higher pressure. It is important to note these simulation conditions are well within the validated range of the hydrogen potential used.

The expectation of the MSD is to display an obvious increase in the liquid phase compared to the solid phase. LAMMPS provides an MSD compute command that is utilized for this calculation. The computation follows Equation 3. where N is the number of particles, $r^{(i)}(0) = r_0^{(i)}$ is the reference position of the i^{th} particle, and $x^{(i)}(t)$ is the position of the i^{th} particle at time t .

$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \sum_i (r^{(i)}(t) - r^{(i)}(0))^2$$

Equation 3. Mean Squared Displacement

Simulations were performed at incremental temperatures as follows: 600 K, 700 K, 800 K, 900 K, 1000 K, 1100 K, 1200 K, 1300 K, 1400 K, 1500 K, 1600 K, 1700 K, 1800 K, 1900 K, 2000 K. Each simulation held a pressure of 300 GPa. This temperature range was selected to identify some change in MSD value that may indicate the solid-to-liquid transition of hydrogen in extreme conditions.

RESULTS AND DISCUSSION

RDF is evaluated at the last frame of the simulations described in the preceding section. Figure 2. displays the RDFs for the 800 K (solid) and 3000 K (liquid) simulations at 100 GPa and 300 GPa.

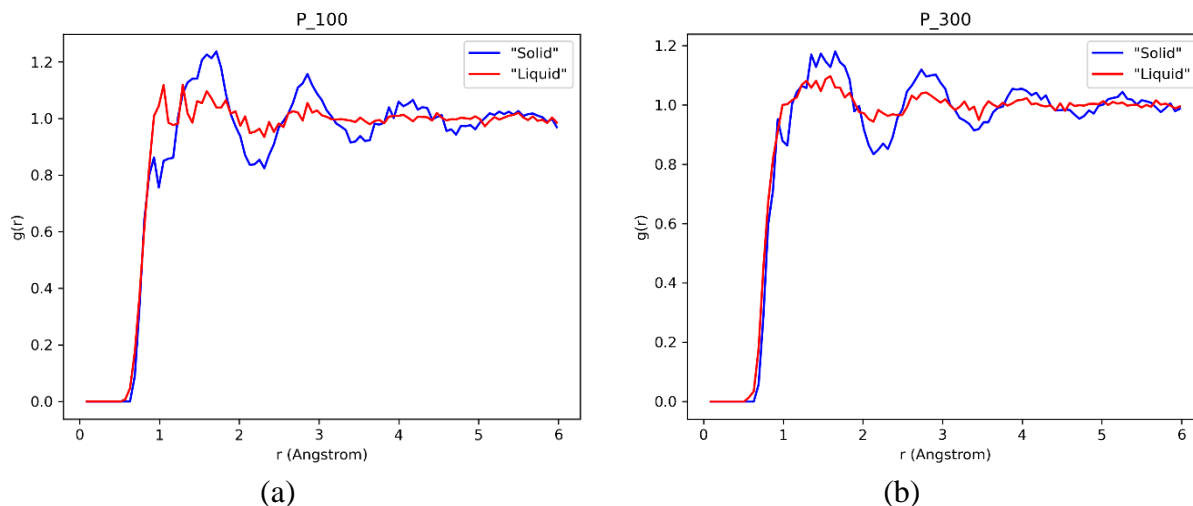


Figure 2. RDF for (a) 100 GPa, (b) 300 GPa

It should be noted that under extreme environmental conditions, the RDF is not solely sufficient in determining phase behavior. This observation is evident in the provided data. The “solid” phase hydrogen does not display the characteristic distinct peaks of what is normally observed in a molecular solid. However, these RDFs provide more subtle details into the behavior of hydrogen in simulated conditions. It is noticed that the amplitude of the peaks in the “liquid” curves are less than the amplitude of the peaks in the “solid” curves, indicating atoms in the liquid phase of hydrogen are atomically packed closer and more densely than the solid phase. This information is consistent with previous observations (Zong et al., 2020), where the space between atoms is observed to be less in the liquid phase than the interatomic space of the solid phase. This conclusion is expected and follows what is known about the solid and liquid phases in this pressure-temperature domain. This is considered a minor validation of the identity and pressure-temperature characteristics of the solid vs liquid phase. While RDF does not provide much additional information besides what is commented on here, it is gratifying to observe the consistency between these results.

The MSD data for the simulations at 300 GPa described in the preceding section are evaluated by plotting the MSD at the last step of each temperature interval into a master plot seen in Figure 3.

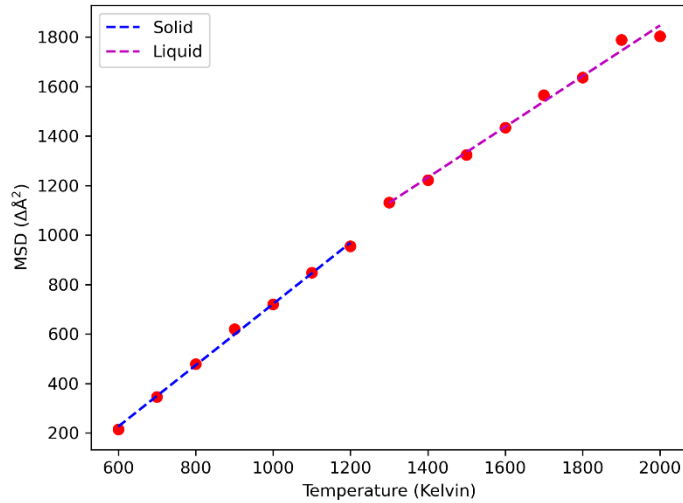


Figure 3. MSD for temperature increments at 300 GPa

The plotted MSD data values from the temperature incrementation are difficult to decipher. One potential explanation for the non-obvious transition zone that is expected is the simulation equilibration. Some systems may not reach a consistent temperature state converging to the value that is specified. Due to computational cost described in the modeling section the data provided here should be taken as a rough interpretation of true results.

Figure 3. possesses two fitted dotted lines to identify differing trends in the data. Data points that are within the range of 600 – 1200 K are grouped as they fit a linear relationship well. These points are identified to be in the solid phase, as they hold the relatively lower temperatures that are expected throughout the literature. Data points within the range of 1400 – 2000 K are fitted to represent a portion of the liquid phase which is expected at the higher temperatures. It is observed that the liquid phase line fit is not as precise as the solid phase fit. This can be interpreted as the motion of particles in the liquid phase is much greater and unpredictable creating a region where MSD measurements may have greater variability.

To conclude the observations of Figure 3., the separation of the fitted lines represents the solid-to-liquid transition zone. Due to the nature of this analysis as well as the physical hydrogen behavior, it cannot be determined at what specific temperature this transition occurs. However, in general agreement with the literature, the solid-to-liquid transition is determined to occur between 1200 – 1400 K. If changes to the dataset such as smaller incrementations of temperature as well as longer simulation equilibration were implemented, it is expected that a much clearer and precise solid-to-liquid transition zone could be observed.

CONCLUSIONS

The over-arching objective of this research is to demonstrate how the use of molecular dynamics simulations can help in the development of understanding elements that make up the universe. Here, MD simulations were conducted using particles parameterized by a potential force field that had been machine-learned from first-principal methods. The validation of this model represents a significant milestone of this study, as it empowers scientists to forecast the behaviors of systems under circumstances that are otherwise inaccessible for experimental analysis. In this specific instance, the focus was on hydrogen, and the validation offers a crucial affirmation that the obtained results are grounded in meaningful data.

Phase characteristics of hydrogen are identified in this study; however, the conclusions only represent a mere portion of the true phase diagram that is targeted. It is observed that hydrogen, in the liquid phase, atomically packs closer than hydrogen in the solid phase. This is a non-trivial observation and an important one to see replicated within a simulation. Additionally, at a pressure of roughly 300 GPa, the solid-to-liquid transition of hydrogen is determined to exist within the temperature span of 1200 – 1400 K.

As previously stated, the validation of this model alone is of great importance to the quest of understanding elements that make up the universe. Harnessing an element such as hydrogen to its full potential, with fully accessible phase transitions could lead to great inventions and discoveries, some of those including high-power rocket fuels, room-temperature superconductors, and even planetary characterization. Furthermore, this research opens the door to the continuation of the characterization of hydrogen following methods not limited to what is described here. The remarkable versatility demonstrated by the model used in this study exemplifies the profound benefits of constructing validated models, parameterized with machine-learned information, in the investigation of systems where experimental constraints impede progression in discovery.

Please contact the author at ArmanMoussavi2027@u.northwestern.edu for any supplementary material/information not provided

RECOMMENDED READING

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