

METASTABLE STATES OF WARM DENSE HYDROGEN

Genri E. Norman,^{1,2,3} Ilnur M. Saitov,^{1,2,3} & Roman A. Sartan^{2,3,*}

¹The National Research University Higher School of Economics, Myasnitskaya Street 20, Moscow, 101000, Russia

²Joint Institute for High Temperatures of RAS, Izhorskaya Street 13 Bld. 2, Moscow, 125412, Russia

³Moscow Institute of Physics and Technology (State University), Institutskiy Per. 9, Dolgoprudny, Moscow Region, 141700, Russia

*Address all correspondence to: Roman A. Sartan, Joint Institute for High Temperatures of RAS, Izhorskaya Street 13 Bld. 2, Moscow, 125412, Russia; Tel.: +7 495 485 8545; Fax: +7 495 485 7990, E-mail: r.sartan@gmail.com

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Warm dense hydrogen is investigated by *ab initio* molecular dynamics simulations in the region of fluid–fluid phase transition. The method of getting adjacent metastable states is developed. The metastable states are successfully obtained in the region of densities from 0.920 to 0.970 g/cm³ and pressures from 1850 kbar to 2150 kbar along an example of 1000 K isotherm. The states have similar pair correlation function as equilibrium ones before the transition. The existence of metastable states provides possible physical reasons of the remarkable differences between phase transition parameters obtained by three experimental groups.

KEY WORDS: metastable states, plasma phase transition, density functional theory

1. INTRODUCTION

The first-order fluid–fluid phase transition is observed in warm dense hydrogen in shockwave (Fortov et al., 2007; Mochalov et al., 2017) and diamond anvil cell (Dzyabura et al., 2013; Ohta et al., 2015; Zaghoo et al., 2016) experiments. The jump of density is reproduced by *ab initio* calculations (Lorenzen et al., 2010; Morales et al., 2013, 2010; Norman and Saitov, 2017; Scandolo, 2003). The phase transition properties obtained from the calculations are close to the experimental ones.

Norman and Saitov (2017) introduced an idea that the lower density phase consists of molecules H₂, while the higher density phase is formed by molecular ions H₂⁺ and H₃⁺. The supposed ionization process at the phase transition correlates with the prediction of plasma phase transition (Ebeling and Norman, 2003; Norman and Starostin, 1968, 1970a,b), that is caused by an abrupt change of the degree of ionization with the rise of density in non-ideal plasma.

The metastable states are predicted by Biberman and Norman (1969); Norman and Starostin (1970b). Calculations made by Biberman and Norman (1969); Norman and Starostin (1968, 1970a,b) are based on a primitive chemical model with the lowering of ionization potential. The obtained isotherm differs from the classical van der Waals profile by relatively small density jump and sloped shape with a significant overlap by density of two branches of metastable states. A modern chemical model is applied to the plasma phase transition problem in the recent theoretical work made by Starostin et al. (2016). Obtained isotherm has a similar shape as it calculated by Biberman and Norman (1969); Norman and Starostin (1970b). The jump of density is also less than the overlap of two metastable branches. The metastable states cover an interval greater than 10 Mbar (Starostin et al., 2016).

In this paper, the metastable states are calculated within the framework of the density functional theory (DFT) approach using the VASP plane-wave code (Kresse and Furthmüller, 1996a,b; Kresse and Hafner, 1993, 1994; Kresse and Joubert, 1999). Section 2 lists briefly chosen parameters and describes the phase transition and two-phase states.

In Section 3, the method of getting the metastable states is described. The significance of metastable states is considered in Section 4, since this phenomenon is important for the discussion of the remarkable difference in results between three experimental groups: shockwave (Fortov et al., 2007; Mochalov et al., 2017), diamond anvil cell (Dzyabura et al., 2013; Ohta et al., 2015; Zaghoo et al., 2016), Z -pinch (Knudson et al., 2015) and current national ignition facility (NIF) results.

2. PHASE TRANSITION

The fluid–fluid phase transition in hydrogen is studied along isotherms in various works. The main distinction between the approaches is related to different *ab initio* methods: quantum Monte Carlo (Morales et al., 2010), DFT with the Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1996) functional (Lorenzen et al., 2010; Norman and Saitov, 2017), DFT with path integral molecular dynamics for ions and vdW-DF1 and vdW-DF2 (Dion et al., 2004) exchange correlational functionals (Knudson et al., 2015; Morales et al., 2013). Although the region varies, the transition is reproduced by all these methods; the change of structure is accompanied with jumps of density and conductivity.

We use the PBE exchange–correlation functional, since it reproduces experimental (Dzyabura et al., 2013; Ohta et al., 2015; Zaghoo et al., 2016) pressures and temperatures. The supercell contains 512 atoms, time step is 0.5 fs. Pressures, temperatures, and pair correlation functions (PCFs) $g(r)$ are averaged over all configurations of molecular dynamics (MD) trajectory. The length of the trajectory is 4–10 ps. More details are described by Norman and Saitov (2017).

The calculated equilibrium isotherm $T = 1000$ K is shown in Fig. 1(a). The changes of hydrogen structure are shown along the isotherm in Fig. 1(b) by means of PCFs. At lower densities, the PCF has a distinct peak $g_{max\ 1}$ at $r = 0.74$ Å, which corresponds to the interatomic distance between atoms in H_2 . It is evidence of the molecular phase. Therefore, an abrupt change of the value of $g_{max\ 1}$ can be used as a notice of the phase transition.

Two-phase point is a specific case. The point describes the system at densities where the phase transition takes place (i.e., at the plateau on the isotherm). We consider the dependence of pressure $P(t)$ and $g_{max\ 1}(t)$ on time along equilibrium MD trajectory (see Fig. 2), in order to determine the phase of the system. Beside common fluctuations (with a period of 6–7 fs), there are non-periodical oscillations (with duration of 150–700 fs). The oscillations of both values correlate with each other: $P(t)$ and $g_{max\ 1}(t)$ have extremes at the same time. The maximums correspond to the molecular phase, while the minimums refer to the state after the phase transition. Thus, we can conclude that the hydrogen changes its phase along one and the same trajectory.

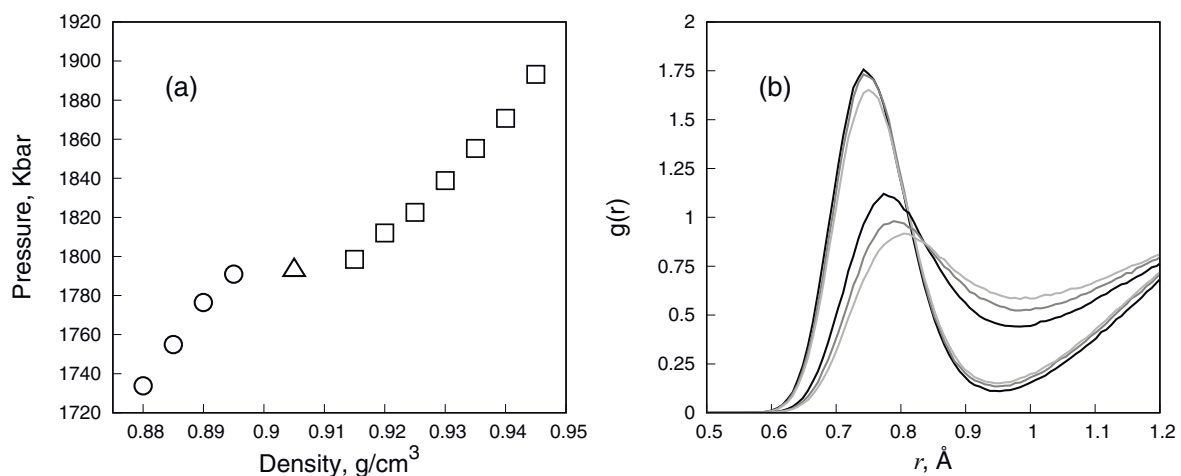


FIG. 1: Equation of state (a) and PCFs (b) along the 1000 K isotherm. Circles describe molecular phase, squares describe the phase after the transition, the triangle is a two-phase point (a). Lines from top down refer to densities: 0.880 g/cm³, 0.890 g/cm³, 0.900 g/cm³, 0.915 g/cm³, 0.925 g/cm³, 0.935 g/cm³ (b)

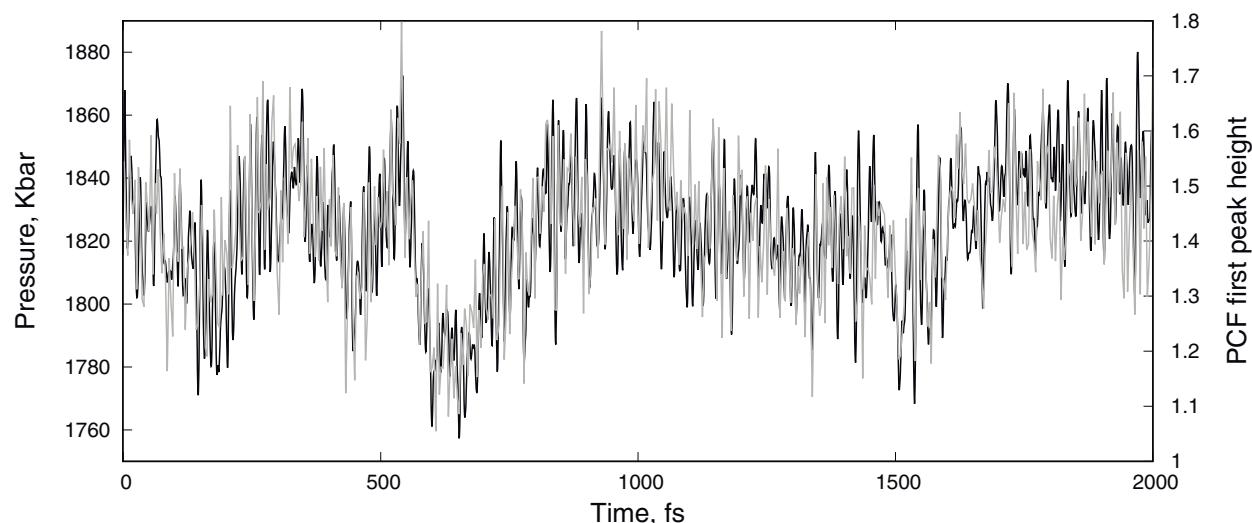


FIG. 2: Fragment of a MD trajectory of a two-phase point. Black line is pressure, gray line is the height of the first PCF peak $g_{max\ 1}$. The $g_{max\ 1}$ is calculated as mean value of $g(r)$ of one step at interval $r = [0.72:0.76]$

3. METASTABLE STATE

Modeling of metastable states is an unexplored problem so far. There are two main points that let us obtain the metastability: the selection of particular initial configurations (coordinates and velocities of ions) and turning off the thermostat. The procedure is as follows.

Firstly, we choose a particular moment of time on the two-phase trajectory and turn off the thermostat. As it is shown in Section 2, the hydrogen changes its state along two-phase trajectory. If the thermostat is shut down at extremes of $P(t)$ and $g_{max\ 1}(t)$, the system can “hook” the metastability. Then, the MD run is simulated from these initial conditions. Figure 3 demonstrates $P(t)$ of two calculations, with and without thermostat after the first rise of pressure. The trajectory with the thermostat has a decrease after the first increase; the following oscillations continue as the system remains to be two-phase. The trajectory without thermostat conserves pressure and molecular structure.

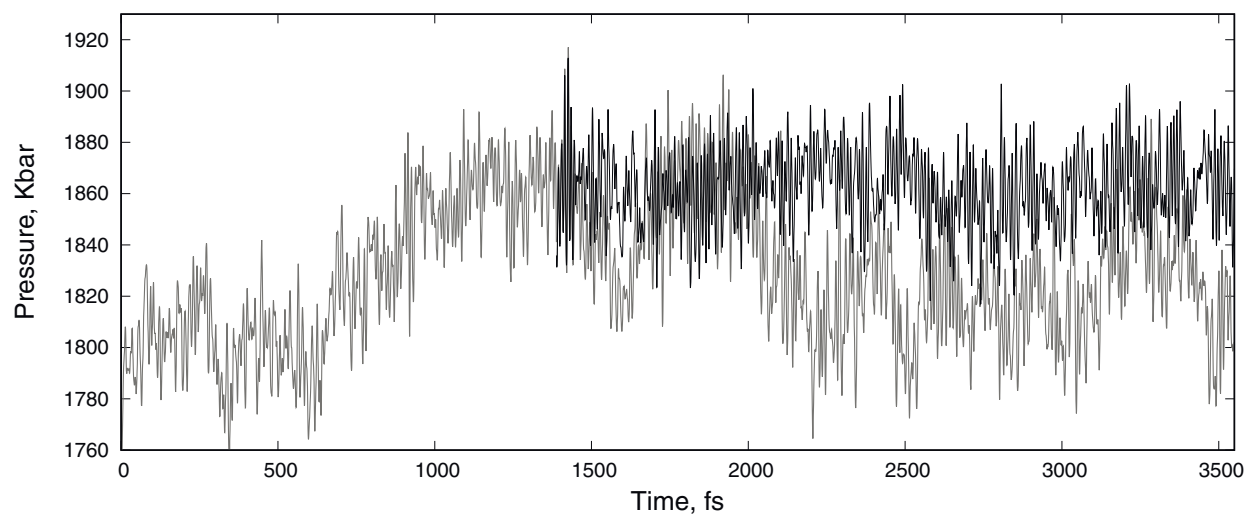


FIG. 3: Fragment of a MD trajectory of a two-phase point. Gray line corresponds to a trajectory with the thermostat, black line corresponds to a trajectory without the thermostat after $t = 1400$ fs

The described algorithm is not always successful. Quite often, the system stays at the two-phase state. Also, there is another problem: turning off the thermostat can lead to a change of average temperature. If the new trajectory is not a two-phase one, the relaxation to a new value will start directly after the thermostat is turned off; after the relaxation, the average temperature is maintained. The deviation from the start temperature is usually less than 25 K.

To get the metastable state at higher density a certain configuration is used of the MD run obtained for the lower density. The start from two-phase point allows modeling metastability only for the densities, where the phase transition takes place, while the change of cell size of metastable configuration allows one to continue the isotherm further. The thermostat is also kept switched off. If the temperature of the new point differs no more than 25 K from 1000 K, the configuration of the point can be used as a start for the next one.

The results are shown in Fig. 4(a). We managed to prolong the molecular phase from 0.900 to 0.969 g/cm³ by consequently decreasing the size of the supercell as it is described above. Turning off the thermostat leads to moderate dispersion around 1000 K that does not exceed 15 K. The metastable branch of isotherm overlaps by pressure of the equilibrium branch at the interval larger than 300 kbar. It is important that the first derivative of the metastable branch does not decrease with the density. So, the branch could reach 300 Mbar, that is, the pressures in *Z*-machine experiments (Knudson et al., 2015). The existence of metastable states at higher pressures is also confirmed by Starostin et al. (2016).

Figure 4(b) shows the isotherm of plasma phase transition, calculated in the primitive chemical model (Biberman and Norman, 1969; Norman and Starostin, 1970b). The results of this paper correlate qualitatively with the these features, as the overlap of the isotherm by density is several times more than the jump of density at the phase transition. The shape is in agreement with findings obtained in modern chemical model (Starostin et al., 2016). Such behavior of the isotherm is also not uncommon for some crystal–liquid phase transitions (Kuksin et al., 2007).

The existence of the third stable line between the branches is not yet confirmed.

Metastable and equilibrium sets of PCFs are presented in Fig. 5. The PCFs profiles of metastable set are similar to ones of molecular phase. As one can see in the inset of Fig. 5, the metastable branch prolongs the molecular phase. It confirms that metastable warm dense hydrogen remains molecular at higher densities. Thus, both stable and metastable phases of fluid hydrogen are possible to model in the same region of pressures and temperatures.

4. POSSIBLE PHYSICAL REASONS OF EXPERIMENTAL DATA SCATTER

Both chemical model calculations and DFT modeling point to the existence of metastable states of molecular phase of warm dense hydrogen (and deuterium) in the wide range of pressures. It permits one to introduce an idea, which

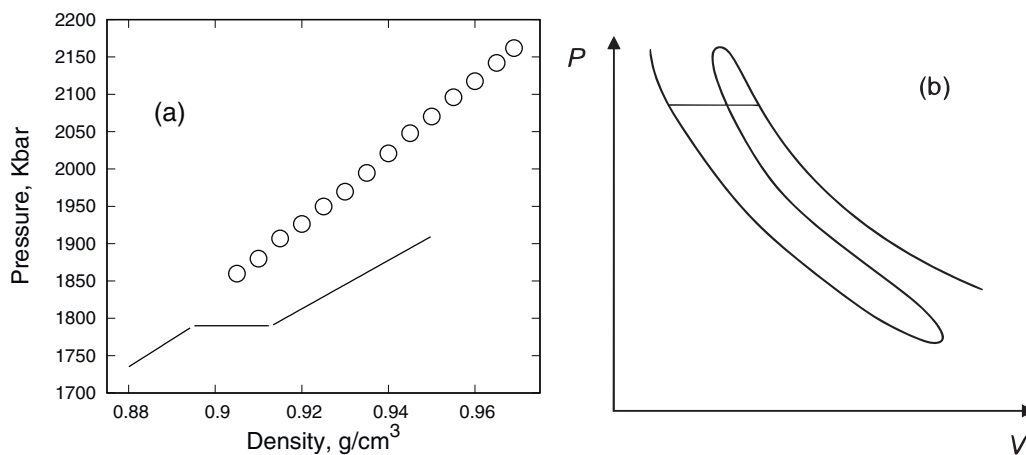


FIG. 4: Equation of state calculated with DFT (a) and in chemical model (Biberman and Norman, 1969; Norman and Starostin, 1970b) (b). Lines are equilibrium part of isotherm, points are metastable states (a)

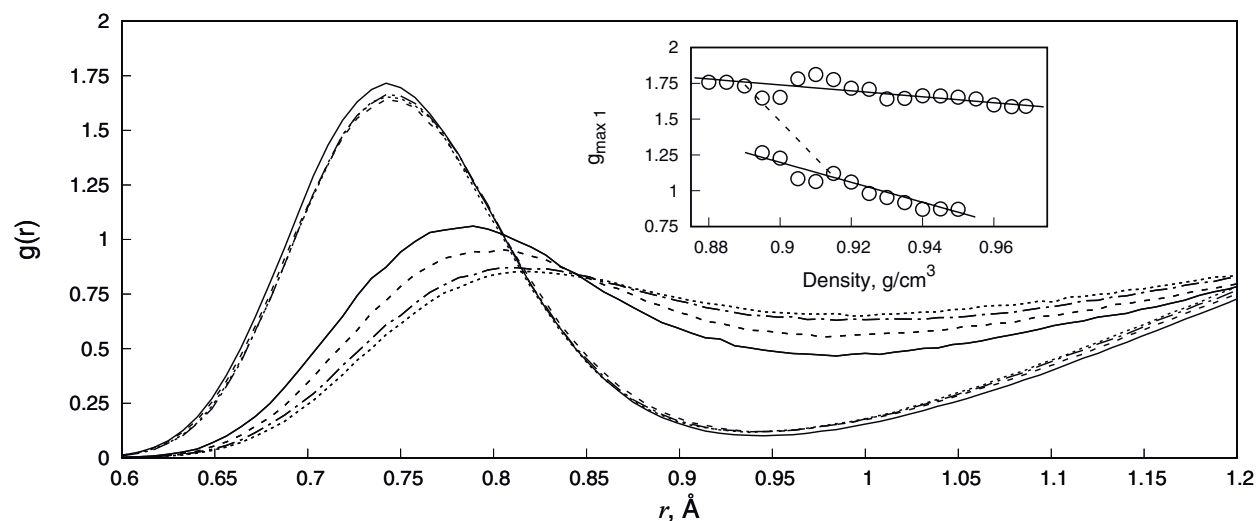


FIG. 5: Pairs of PCFs for metastable and equilibrium states. Full lines are for 0.920 g/cm^3 , dotted lines for 0.930 g/cm^3 , bar-dotted lines for 0.940 g/cm^3 , small dotted lines for 0.950 g/cm^3 . The values of $g_{max 1}$ are presented in the inset for metastable and equilibrium states by points, dashed line corresponds to phase transition, full lines are drawn in order to guide the eye

explains possible physical reasons for the challenging difference between shock wave, diamond anvil cell, and Z -machine experimental results for parameters of the fluid–fluid phase transition in warm dense hydrogen. In fact, we regard it as inconceivable that the highly skilled experimentalists of the top-level laboratories could commit such blunders. Is it possible that shock wave (Fortov et al., 2007; Mochalov et al., 2017), diamond anvil cell (Dzyabura et al., 2013; Ohta et al., 2015; Zaghoo et al., 2016), and Z -machine (Knudson et al., 2015) are correct despite the striking discrepancy between their experimental results?

Metastable states open an opportunity window to solve the problem. It is the effect of different compression (heating) rates. The faster the compression (heating) rate the farther from the equilibrium transition and closer to the spinodal is the point of the experimental transition. The rate at the Z -machine is orders of magnitude higher than in diamond anvil cell experiments. Therefore, Z -machine results could be shifted closer to the spinodal with respect to the diamond anvil cell results. It would explain the difference between two sets of measurements of phase transition pressures.

Such an effect is demonstrated for the carbon melting (Orehhov and Stegailov, 2015). The absence of a consensus on its melting temperature at normal conditions has existed for many years. Orehhov and Stegailov focus on the kinetics of graphite melting and show that the experimental puzzles can be resolved by considering the graphite melting as a process in the non-equilibrium superheated solid. The unusually slow melting kinetics results in the existence of the superheated graphite and thus biases the measurements of its equilibrium melting temperature.

Marcus Knudson (Sandia national laboratory) reported new Z -machine results in his talk at the warm dense matter (WDM) conference in Vancouver in April 2017. They extended Z -machine measurements to the higher temperatures with respect to Knudson et al. (2015). It turned out that Z -machine points became closer to the diamond anvil cell points with the increase of temperature. Such a behavior is a typical one for the positional relationship of spinodal and phase coexistence curves. Intersection of the extrapolation of two sets of points is expected about 5000 K. It gives an estimate of the critical point of the plasma (fluid–fluid) phase transition in warm dense hydrogen.

Peter Celliers (Lawrence Livermore national laboratory) reported new NIF results in his talk at the same WDM conference in Vancouver in April 2017. Experimental points, which he showed, interposed between the diamond anvil cell and Z -machine points. It does not contradict the idea presented in this section. The metastable region obtained in this paper covers the pressures of the NIF experiment.

A phenomenon of metastability is an inherent indication of the first-order nature of a phase transition. To check the existence of metastable states is important in particular when the volume drop is relatively small, as in the case

of the liquid–liquid phase transitions. To resolve the problem, the kinetics of the transitions in melts of Se and S is investigated at different cooling rates (Brazhkin et al., 1992, 1997). Superheating and supercooling of the liquid phases are observed. Shifts of the transition curves are obtained. The lifetimes of the metastable states are estimated.

Scatter of experimental data for the coexistence curve of the phase transition in warm dense hydrogen is not a chaotic one, but has a regular character. It could be considered as a crucial test of the first-order nature of the phase transition in warm dense hydrogen (and deuterium).

5. CONCLUSIONS

Metastable states of warm dense hydrogen are studied by quantum molecular dynamics based on density functional theory in the region of fluid–fluid phase transition. The problem is analyzed by calculating equation of states and pair correlation functions. The main results are as follows:

1. The procedure of modeling of the metastable states is developed. The metastable states can be obtained by choosing certain particular initial configuration and turning off the thermostat.
2. The molecular phase is prolonged to densities far beyond the equilibrium density jump region. The metastable branch of the isotherm overlaps the equilibrium branch by density at the interval of 0.05 g/cm^3 , that is 2.5 times more than density jump at the phase transition. The pressure range of metastability studied is more than 300 kbar, while the difference between pressure of the metastable and equilibrium states at the same density is approximately 150 kbar. The pair correlation function conserves its shape along the 1000 K isotherm, that confirms the preservation of the molecular phase.
3. The existence of the metastability could explain serious discrepancy between different experimental results on the phase transition parameters.

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