Metastable states of fluid–fluid phase transition in warm dense hydrogen

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Abstract. The warm dense hydrogen is studied by means of the \textit{ab initio} molecular dynamics simulation in the region of fluid–fluid phase transition. The metastable states of two isotherm of 700 and 1000 K are calculated. The metastable ranges by pressure are 470 and 320 kbar respectively. The existence of metastability is a strong criterion that the transition is a first order phase transition.

1. Introduction

In the region of high temperatures (of thousands of kelvins) and high pressures (of thousands of kilobars), warm dense hydrogen becomes conducting. The transition to conducting state is observed experimentally in [1] for the first time for deuterium. The discontinuity in density is registered, which points to the first order transition. In the following experiments, the first order nature of the transition is confirmed [2–4]. However, there is a point of view, that even the rise of conductivity can be continuous [5]. The pressure–temperature region of the phase transition is also varies, the parameters differ by several times among these experiments.

The accompanying metastable states of the warm dense hydrogen can be used as a criterion, that the transition is of the first order [6]. The existence of metastable states is predicted in [7,8] using the simple chemical model and in [9], where the modern chemical model is applied.

This paper focuses on obtaining the metastable states of warm dense hydrogen by means of density functional theory (DFT). Two isotherms of 700 and 1000 K are investigated. The structure of hydrogen is analyzed by pair-correlation functions (PCFs).

The paper is structured as follows. Section 2 lists the primary parameters of the \textit{ab initio} simulation. In section 3, the main features of the phase transition is presented. Section 4 is devoted to obtaining the metastable states. The results are presented in section 5.

2. Method

The calculations are performed within the framework of quantum molecular dynamics with the use of density functional theory, which is performed by means of VASP code [10–12]. The temperatures calculated are 700 and 1000 K, the density ranges up to 1.1 g/cm\textsuperscript{3}. The
Figure 1. PCFs of 700 K of different densities: 0.990 (blue), 1.005 (cyan), 1.030 (violet) and 1.045 g/cm$^3$ (pink).

applicability of VASP for even higher temperatures and densities discussed previously [13, 14].

The efficiency of using VASP is observed in [15–17].

The supercell contains 512 atoms; the $k$-grid consists of a single Baldereschi mean value point [18]. The validity of using of the one $k$-point is shown in [19]. The Perdew–Burke–Ernzerhof [20] exchange-correlation functional is used, since it reproduces the results of the experiments [2–4]. The initial configuration is simple cubic. The time step is 0.5 fs, the simulations last for 4–15 ps.

3. The phase transition

The fluid–fluid phase transition in warm dense hydrogen is investigated in different works by various $ab$ $initio$ approaches, such as DFT-MD (molecular dynamics) [19, 21], DFT with path integral molecular dynamics for ions [22, 23], quantum Monte-Carlo [24]. All these methods successfully reproduce the transition, although they predict different parameters of it.

At the dielectric state, hydrogen is molecular [19, 21]. This fact is reflected on PCFs $g(r)$ (figure 1). The first peak $g_{\text{max}1}$ at $r = 0.74$ Å corresponds to interatomic separation in the $\text{H}_2$ molecule. A number of molecules decay as hydrogen passes the transition and becomes conducting [19, 21]; it is characterized by the decrease of $g_{\text{max}1}$. Thus, the height of the first peak of PCF can be used as a criterion of the phase. The high values (more than 1.5) correspond to the dielectric phase; the low values correspond to the conducting phase (less than 1.1).

4. Metastable states

The equilibrium states can be obtained by relaxing the system with the thermostat from the simple cubic initial configuration. In order to achieve the metastability, we select the initial configuration in a certain way and turn off the thermostat.

4.1. The selection of initial configuration

The simple cubic initial configuration is used to calculate the non-molecular phase, the two-phase region and the molecular phase at densities up to 1.015 and 0.910 g/cm$^3$ for 700 and 1000 K.
4.2. The impact of the thermostat

The thermostat is necessary, if the simple-cubic initial configuration is used. But in order to get metastable states, it should be turned off. Under the influence of the thermostat the hydrogen is able to lose metastability.

Figure 2 demonstrates pressure as a function of time $P(t)$ in two calculations of a two-phase point. While the thermostat is on, which corresponds to the canonical $NVT$ ensemble, the pressure amplitude is high. In this case, the hydrogen changes its phase from one to another. Turning off the thermostat and going over to the microcanonical $NVE$ ensemble at the peak of pressure (the $g_{max}(t)$ also has a peak at such moments of time) allows saving molecular phase. This procedure also allows obtaining metastable states in the range of densities where the transition takes place without changing the size of supercell.

It is worth to note, that the suitable initial configuration and the turning off of the thermostat do not always lead to metastability. Not infrequently, the hydrogen loses molecular state or the temperature changes by 20–40 K after the change of density; such cases are not included in next graphs. Hydrogen can also “move” to equilibrium branch of the isotherm without any changes of the supercell size at high densities, which are close to the border of the metastable region. The last is explained by short lifetime (less than 4 ps) of metastable states near the border.

5. Results

The calculated isotherms 700 and 1000 K are shown in figure 3. Although the region of the phase transition strongly depends on the temperature, the equilibrium and metastable branches respectively. However, in order to obtain the molecular metastable state, the initial configuration should correspond to the molecular state beforehand. The coordinates and velocities of ions are taken from the equilibrium states or from the obtained metastable ones. Changing the size of the supercell, it is possible to calculate another density and save the state. We reproduce the metastable branch of the isotherm by consequently changing the supercell volume and relaxing configurations at every new density.
Figure 3. Equation of states of 700 (red) and 1000 K (orange) isotherms. Circles refer to the results obtained in this paper, triangles refer to the results obtained in [19]. In the inset, the equation of states calculated in [7, 8] is shown.

Figure 4. The values of the height of the first peaks of PCFs for 700 (triangles) and 1000 K (circles) isotherms.

of two isotherms are located along the straight lines that are similar for both temperatures. The average deviation of the temperature does not exceed 13 K from given ones. The two-phase points between the branches have a notable scatter by pressure.

The PCFs have high first peaks along metastable branches, that confirms hydrogen saving molecular phase (figure 4). Despite $g_{\text{max}}$ monotonically decreases with the density, the values are notably higher, than for the equilibrium state.
The isotherms are similar to ones predicted in works [7,8] (the inset in figure 3) and [9]. The distinctive features of the isotherms are the sloped shape and relatively small jump of density. The existence of the third stable line between the branches has not been confirmed yet.

The pressure and the density of the transition are the same as ones obtained in [19], since the calculation parameters are similar. However, in contrast to the current work, there is no metastable region for 1000 and only the beginning of it for 700 K in [19]; also, the existence of metastable states is not discussed in [19].

The metastable region size by pressure in this paper is 470 and 320 kbar for 700 and 1000 K respectively; the difference between pressure of the metastable and equilibrium states at the same density is approximately 150 kbar. While the density discontinuity at the transition is small (less than 3%) and does not clearly points to the first order nature of the transition, the existence of notable metastable region is a strong criterion that the transition is of the first order.

6. Conclusion
The metastability of warm dense hydrogen is investigated by quantum molecular dynamics within the framework of density functional theory. The equation of states is calculated in the region of fluid–fluid phase transition for temperatures of 700 and 1000 K. The metastable ranges by pressure are 470 and 320 kbar for 700 and 1000 K respectively. The existence of metastable states points out that the phase transition is a first order transition.

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References
[1] Fortov V E, Ilkaev R I, Arinin V A, Burtzev V V, Golubev V A, Iosilevskiy I L, Khrustalev V V, Mikhailov A L, Mochalov M A, Ternovoi V Y and Zhernokletov M V 2007 Phys. Rev. Lett. 99 185001
[2] Dzyabura V, Zaghoor M and Silvera I F 2013 Proc. Natl. Acad. Sci. U. S. A. 110 8040
[3] Obta K, Ichimaru K, Emaga M, Kawaguchi S, Shimizu K, Matsuoka T, Hirao N and Ohishi Y 2015 Sci. Rep. 5 16560
[4] Zaghoor M, Salamat A and Silvera I F 2016 Phys. Rev. B 93 155128
[5] McWilliams R S, Dalton D A, Mahmood M F and Goncharov A F 2016 Phys. Rev. Lett. 116 255501
[6] Norman G E and Saitov I M 2016 J. Phys.: Conf. Ser. 774 012015
[7] Biberian L M and Norman G E 1969 High Temp. 7 767
[8] Norman G E and Starostin A N 1970 J. Appl. Spectrosc. 13 965
[9] Starostin A N, Gryaznov V K and Filippov A V 2016 JETP Lett. 104 696
[10] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[11] Kresse G and Hafner J 1994 Phys. Rev. B 49 14251
[12] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[13] Levashov P R, Sin’ko G V, Smirnov N A, Minakov D V, Shemyakin O P and Khishchenko K V 2010 J. Phys.: Condens. Matter 22 505502
[14] Minakov D V, Levashov P R, Khishchenko K V and Fortov V E 2014 J. Appl. Phys. 115 223512
[15] Stegailov V V, Orekhov N D and Smirnov G S 2015 HPC hardware efficiency for quantum and classical molecular dynamics Parallel Computing Technologies: Int. Conf. on Parallel Computing Technologies ed Malyshkin V pp 469–73
[16] Stegailov V and Vecher V 2017 Efficiency analysis of Intel and AMD x86 64 architectures for ab initio calculations: A case study of VASP Parallel Processing and Applied Mathematics: Int. Conf. on Parallel Processing and Applied Mathematics ed Wyzykowski R, Dongarra J, Deelman E and Karczewski K pp 430–41
[17] Stegailov V and Vecher V 2018 Efficiency analysis of Intel, AMD and Nvidia 64-bit hardware for memory-bound problems: A case study of ab initio calculations with VASP Supercomputing: Russian Supercomputing: Russian Supercomputing Days ed Voevodin V and Sobolev S pp 81–90
[18] Baldereschi A 1973 Phys. Rev. B 7 5212
[19] Lorenzen W, Holst B and Redmer R 2010 Phys. Rev. B 82 195107
[20] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[21] Norman G E and Saitov I M 2017 Dokl. Phys. 62 294
[22] Knudson M D, Desjarlais M P, Becker A, Lemke R W, Cochrane K R, Savage M E, Bliss D E, Mattsson T R and Redmer R 2015 Science 348 1455
[23] Morales M A, McMahon J M, Pierleoni C and Ceperley D M 2013 Phys. Rev. Lett. 110 065702
[24] Morales M A, Pierleoni C, Schwegler E and Ceperley D M 2010 Proc. Natl. Acad. Sci. U. S. A. 107 12799