Structure properties of warm dense hydrogen

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Abstract. The warm dense hydrogen is studied by the ab initio molecular dynamics in the region of the fluid–fluid phase transition. A method for calculating the properties such as concentration and lifetime of H$_2$ molecules is developed. As warm dense hydrogen passes the transition, the concentration of H$_2$ molecules decreases smoothly, while the lifetime changes abruptly by several orders.

1. Introduction
The fluid–fluid phase transition in warm dense hydrogen is studied in a number of theoretical works [1–9] by means of the quantum molecular dynamics simulation. Despite quantitative discrepancies among the calculations, the transition is described qualitatively in the same way: at lower densities (temperatures), hydrogen is a dielectric molecular fluid, at higher densities (temperature) the structure of hydrogen changes and it becomes a conducting fluid. For brevity, I will denote the dielectric phase as phase I, and the conducting phase as phase II.

The structure changes are associated with the dissociation of H$_2$ molecules. The concentration of molecules is estimated in [1,2]. However, these estimations are performed for the supercritical region. In this paper, I consider temperatures below the critical one and propose an alternative method for concentration estimation. Additionally, an estimation of the H$_2$ molecules lifetime will be given.

The paper is structured as follows. Section 2 provides a brief description of the modeling parameters. Section 3 is devoted to the definition of “molecule” and its parameters. Section 4 describes the results obtained.

2. Method
The calculations are performed within the framework of quantum molecular dynamics with the use of density functional theory (DFT). The exchange–correlation functional chosen is Perdew–Burke–Ernzerhof [10].

The supercell contains 512 atoms; the $k$-mesh consists of a single Baldereschi mean value point [11]. The $3 \times 3 \times 3$ Monkhorst–Pack $k$-mesh is used for the conductivity calculations, which provides the convergence of the results. The time step is 0.5 fs, the simulations last for 4–10 ps. The DFT code used is the Vienna Ab initio Simulation Package (VASP) [12,13]. The applicability of VASP for high pressure and temperature calculations is discussed in [14].
Figure 1. Solid lines show pair correlation functions $g(r)$: red color—for $\rho = 0.88 \text{ g/cm}^3$; blue color—for $\rho = 0.95 \text{ g/cm}^3$ both at $T = 1000$ K. The dotted line is $g(r)$ of the first neighbor, where only the nearest atom was taken into account from the whole environment. The $g(r)$ of the nearest neighbor in phase I (where all atoms are paired into molecules) goes to zero at $\approx 1.0$ Å, i.e., in order to cover all possible bond lengths in the H$_2$ molecule, the $r_{\text{cut}}$ should be not less than 1.0 Å. On the other hand, the $g(r)$ of the nearest neighbor in phase II starts differ from the full $g(r)$ at $\approx 0.85$ Å, i.e., at $r_{\text{cut}} > 0.85$ Å some atoms will effectively have several bonds at once.

The frequency-depended conductivity is calculated with the use of the Kubo–Greenwood formula \[15, 16\]. Since the formula sets the conductivity to zero at zero frequency, the static conductivity is estimated using the value of conductivity at frequency $\omega = 0.5$ eV.

3. The definition of “molecule”
To analyze the properties of H$_2$ molecules, such as concentration, lifetime or interatomic bond length, it is necessary to formalize the concept of a “molecule”. The inaccuracy of the definition is the primary quantitative error of the calculated parameters.

The proposed definition of a molecule is based on geometry. Atoms are considered to be bonded, if the distance between them is less than some $r_{\text{cut}}$. $r_{\text{cut}}$ must be not less than the maximum amplitude of interatomic distance oscillations in the H$_2$ molecule. At the same time, $r_{\text{cut}}$ must be less than the distance, at which different molecules or single atoms can come closer without forming a bond. Otherwise the constructed bond will be “fictitious”. In practice, it is not possible to satisfy these requirements at the same time (figure 1).

In order to distinguish the “fictitious” bond from the “real”, I add the next condition: the atoms must perform at least one oscillation with respect to each other. The existence of such oscillation is checked by the second threshold $r_{\text{threshold}} < r_{\text{cut}}$. The bond is considered as “real” if the atoms were at least once closer than the $r_{\text{threshold}}$ during the existence of this bond. In [1], another additional condition is used, the atoms must make at least ten oscillations. This is checked by the time that the atoms spent next to each other, i.e., all short-lived bonds are simply discarded.

As the bonds are constructed, we need to define the lifetime $\tau$ and concentration $n$ of H$_2$ molecules.
I define the lifetime $\tau$ as

$$\tau = \frac{\langle N \rangle}{\langle \Delta N \rangle} \Delta t,$$

(1)

where $\langle \ldots \rangle$ means averaging over all configurations, $\Delta t$ is the molecular dynamics (MD) time step, $N$ is the total number of molecules and $\Delta N$ is the number of decayed molecules. The ratio $\langle \Delta N \rangle / \langle N \rangle$ has a sense of the average probability for each molecule to decay during one MD time step. To compute $\Delta N$, we need to count all bonds that exist at some moment of time and do not exist the next time step. Using formula (1), it is possible to determine the molecule lifetime even if it is longer than the molecular dynamics trajectory length (however the lifetime should be less than the trajectory length multiplied by $\langle N \rangle$).

In general, the true probability to decay depends on the lived time. It can be shown via the distribution of the molecule lifetime [figure 2(a)] for phase II. The positions of the first peaks are a multiple of the period of the interatomic distance oscillation in the molecule. It means that molecules are likely to decay exactly after the first oscillation, the second, etc.

Figure 2(b) supports the validity of the replacement of the true probability to decay, which depends on the lived time, by average probability to decay, that is used in formula (1). The lifetime calculated by formula (1) is close to mathematical expectation of the lifetime distribution, such as in figure 2(a). I assume, that the similarity of the mathematical expectation and $\tau$ will remain for phase I, where the lifetime is much more than the MD trajectory length.

The concentration of H$_2$ molecules $n$(H$_2$) is defined as

$$n$(H$_2$) = $2 \frac{\langle N \rangle}{A}$,

(2)

where $A = 512$ is the number of atoms in the supercell in the simulation.

Technically, in formulas (1) and (2), $N$ is the number of bonds constructed according to the described earlier algorithm, rather than number of molecules. If each atom has at most one bond, then $N$ coincides with the number of H$_2$ molecules; otherwise, formula (2) loses its physical meaning and the concentration can become greater than one.
The concentration can also be estimated using only \( g(r) \). The following method was proposed in [2], the concentration is the doubled value of coordination number \( K(r) = 0.748 \text{ Å} \), where

\[
K(r) = \frac{A - 1}{V} \int_0^r 4\pi r'^2 g(r')dr',
\]

where \( A \) is the number of atoms in the supercell, \( V \) is the volume of the supercell.

4. Results

Three isotherms of 700, 1000, and 1500 K are analyzed. The equation of state with metastable states [17–19] is shown in figure 3(a). The method of obtaining the metastable states in molecular dynamics simulation is described in [20].

I consider the example of four pairs of \( r_{\text{cut}} \) and \( r_{\text{threshold}} \): \( r_{\text{cut}} = 1.0 \) or 1.1 Å and \( r_{\text{threshold}} = 0.70 \) or 0.75 Å. The dependence of the lifetime of \( \text{H}_2 \) molecules on the density along isotherms is shown in figure 3(b).

The lifetime of the molecules decreases with density for each of the phases and drops sharply by 1–2 orders of magnitude during the phase transition from I to II. The lifetime of molecules is \( 10^3–10^5 \) fs and \( 10^1–10^2 \) fs, in phases I and II respectively. The quantitative estimation depends on density, temperature and the definition of “molecule”.

The changes of \( r_{\text{cut}} \) parameter have a large effect on the estimation of the lifetime in phase I, even when \( r_{\text{cut}} \) is greater than the (approximate) maximum amplitude of \( \text{H}_2 \) bond length oscillation. The fact is that the recombination of decayed molecule can occur right after the decay, and the atoms will stay at a relatively close distance next to each other during this process. Figure 4 shows an example of the evolution of the interatomic distance for one particular pair of atoms forming a molecule in phase I. The oscillations are disharmonious, and at 1850 fs the amplitude exceeds 1.2 Å. If \( r_{\text{cut}} \) is less than 1.2 Å, then the act of the decay will be recorded according to the described earlier algorithm. Otherwise, the atoms will be considered as bonded up to 3300 fs, where the decay of the molecule occurs without subsequent recombination.
Figure 4. The evolution of the interatomic distance in particular \( \text{H}_2 \) molecule in phase I. At 1850 fs, the decay and recombination of the molecule occur, at 3300 fs the final decay occurs.

Figure 5. (a) Concentration of \( \text{H}_2 \) molecules for different \( r_{\text{cut}} \) and \( r_{\text{threshold}} \); the symbols are the same as in figure 3(b). (b) Dependence of static conductivity on the degree of dissociation at \( r_{\text{cut}} = 1.1 \) Å and \( r_{\text{threshold}} = 0.70 \) Å.

The concentration of molecules in phase I is 100\% ± 0.5\% both for equilibrium and metastable states at any considered \( r_{\text{cut}} \) and \( r_{\text{threshold}} \) [figure 5(a)]. As warm dense hydrogen passes the phase transition, the fraction of molecules falls smoothly, rather than abruptly, even at temperatures that are less than critical one. The concentration does not go to zero even at high densities at \( r_{\text{threshold}} = 0.75 \) Å.

Figure 5(b) shows the dependence of static conductivity on the degree of dissociation \( Z \), calculated as \( Z = 1 - n(\text{H}_2) \). Only the values for \( r_{\text{cut}} = 1.1 \) Å and \( r_{\text{threshold}} = 0.70 \) Å are shown for sake of clarity. The dependence is similar for different temperatures. The dissociation of 5\% is enough to increase the conductivity by several orders of magnitude.

As warm dense hydrogen passes the phase transition the average interatomic distance in \( \text{H}_2 \bar{r} \) also changes [figure 6(a)]. The \( \bar{r} \) is slightly larger than the position of the first peak \( g(r) \), since the distribution of bond lengths differs from \( g(r) \) by a factor of \( r^2 \) and the distribution is asymmetric. The distributions of bond lengths \( h(r) \) for all variants of the parameters are shown
Figure 6. (a) The average bond length $\bar{r}$ in H$_2$ molecules for different $r_{\text{cut}}$ and $r_{\text{threshold}}$: the $\bar{r}$ is defined as the mathematical expectation of the distribution of the bond length; the symbols are the same as in figure 3(b). (b) The bold line is $g(r)$. The points are $h(r)$ multiplied by $4\pi r^2 n_0$. The symbols are the same as in figure 3(b). The lines connecting points are drawn in order to guide the eye.

in figure 6(b). In order to compare it with the $g(r)$, the distributions are multiplied by $4\pi r^2 n_0$, where $n_0$ is the average concentration of atoms in the supercell. For phase I (not shown in the figure), all distributions coincide with the nearest-neighbor $g(r)$ (see figure 1). For phase II, the distributions coincide with the $g(r)$ up to $r_{\text{threshold}}$, after noticeably less than $g(r)$ and terminate at $r_{\text{cut}}$.

In [2], the concentration is calculated by integrating (3) with $g(r)$ up to $r = 0.748$ Å, where 0.748 Å is the position of the $g(r)$ first peak in phase I. My data suggests 80% concentration even in phase I at $T = 1000$ K using this equation. This method also does not take into account the shift of average interatomic distance and the asymmetry of the bond length distribution.

I also calculate the lifetime and concentration of the hydrogen molecules, using the definition of “molecule” suggested in [1]. In [1], all bonds that live less than certain time $t_{\text{min}}$ are discarded. I consider the example of four pairs of parameters: $r_{\text{cut}} = 1.0$ or 1.1 Å and $t_{\text{min}} = 50$ or 100 fs (the authors of [1] use $t_{\text{min}} = 76$ fs and $r_{\text{cut}} = 0.954$ Å). For phase I, the difference between $t_{\text{min}} = 50$ and 100 fs is small, similar to different $r_{\text{threshold}}$ in the method proposed in this paper. For phase II, the lifetime reaches a stationary value with the increase of density, that is a little more than $t_{\text{min}}$. This is not surprising, since the definition of a “molecule” itself is associated with a minimum lifetime; therefore it is incorrect to determine relatively short lifetime by this definition. For $r_{\text{cut}} = 1.0$ Å, the concentration of molecules in phase I does not reach 100%; it is near 97–99%. The concentration reaches a stationary state value of 20% with the increase of density at $T = 1000$ K, $r_{\text{cut}} = 1.1$ Å and $t_{\text{min}} = 50$ fs; for all other pairs of parameters it comes to (almost) zero.

5. Conclusions

The structural properties of the conducting and dielectric phases of warm dense hydrogen are considered in the framework of the molecular dynamics method using the density functional theory. At the fluid–fluid phase transition, the lifetime of the H$_2$ molecules sharply changes
by several orders of magnitude, while the concentration of the H$_2$ molecules changes smoothly. Dissociation of 5% is sufficient to increase the conductivity by several orders of magnitude. The average interatomic distance in H$_2$ molecule also has an abrupt jump at the transition.

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References
[1] Vorberger J, Tamblyn I, Militzer B and Bonev S A 2007 Phys. Rev. B 75 024206
[2] Holst B and Redmer R 2008 Phys. Rev. B 77 184201
[3] Lorenzen W, Holst B and Redmer R 2010 Phys. Rev. B 82 195107
[4] Morales M A, Pierleoni C, Schweger E and Ceperley D M 2010 Proc. Natl. Acad. Sci. U. S. A. 107 12799
[5] Morales M A, McMahon J M, Pierleoni C and Ceperley D M 2013 Phys. Rev. Lett. 110 065702
[6] 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
[7] Norman G E and Saitov I M 2017 Dokl. Phys. 62 284
[8] Pierleoni C, Holzmann M and Ceperley D M 2018 Contrib. Plasma Phys. 58 99–106
[9] Mazzola G, Helgren R and Sorella S 2018 Phys. Rev. Lett. 120 025701
[10] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[11] Baldereschi A 1973 Phys. Rev. B 7 5212
[12] Kresse G and Hafner J 1993 Phys. Rev. B 47 558
[13] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[14] 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 505501
[15] Kubo R 1957 J. Phys. Soc. Jpn. 12 570
[16] Greenwood D A 1958 Proc. Phys. Soc. 71 585
[17] Skripov V P 1974 Metastable Liquids (New York and Toronto: J. Wiley)
[18] Debenedetti P G 1996 Metastable Liquids. Concepts and Principles (Princeton, NJ: Princeton University Press)
[19] Skripov V P and Faiizzullin M Z 2006 Crystal-Liquid-Gas Phase Transitions and Thermodynamic Similarity (Weinheim: Wiley-VCH)
[20] Norman G E, Saitov I M and Sartan R A 2018 Dokl. Phys. 63 313–6