Molecules ionization at phase transition in warm dense hydrogen

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Abstract. An idea is suggested that the fluid–fluid phase transition in warm dense hydrogen is related to the partial ionization of molecules H\textsubscript{2} with formation of molecular ions H\textsuperscript{+}\textsubscript{2} and H\textsuperscript{+}\textsubscript{3}. Conventional ab initio quantum modeling is applied. Proton pair correlation functions (PCF) obtained are used for the nonconventional diagnostics of the phase transition and elucidation of its nature for temperatures 700–1500 K. Short- and long-range changes of PCFs are studied. H\textsubscript{2} molecules ionization and molecular ions H\textsuperscript{+}\textsubscript{2} and H\textsuperscript{+}\textsubscript{3} appearance is revealed. The validity of the soft sphere model is tested for the long-range order.

1. Introduction

The problem of the fluid–fluid phase transition in warm dense hydrogen (deuterium) is studied experimentally in top laboratories during last decade. Both generation and diagnostics of the matter need the best technique. Three diverse experimental approaches are applied: shock-wave reverberation deuterium experiments [1,2], laser-driven shock waves in a hydrogen sample pre-compressed in a diamond anvil cell [3–8] and a series of breakthrough dynamic compression experiments on liquid deuterium performed at the Sandia Z machine [9].

Both [5–7] and [1] focus on the observation of the first-order phase transition that should separate two distinct coexisting phases of hydrogen or deuterium which differ in density and conductivity. The results [1] can be adjusted to the coexistence curve derived from observations [5–7]. Any specific volume drop is not found in either [10, 11] or [3, 4]. It is curios that their criteria of metallization give points in the same area as the observations [1, 5–7] of the specific volume drop do. Sandia Z machine observations [9] give points which are far from those of both [3–7] and [1,10,11]. We agree with a conclusion [12] that the origin of the disagreement is unclear at present.

Experimental results [1, 3, 5, 10, 11] motivate theoretical studies [9, 12–25]. Properties of warm dense hydrogen are investigated by means of ab initio molecular dynamics and quantum simulation techniques based on either density functional theory (DFT) or path integral Monte-Carlo. The phase transition is found and the first-order nature of this transition is confirmed. The coexistence curve calculated is close to the measured one. Phase transition nature is in the focus of the discussion. Two main issues are considered: metallization under hypnosis of [26] and pressure dissociation H\textsubscript{2} \rightarrow 2H. Plasma phase transition is also mentioned but without any attachment to a particular ionization reaction.
The objective of this letter is to elucidate the nature of the phase transition in warm dense hydrogen.

2. Method
We apply DFT. The VASP plane-wave code [27–30] is used. The Kohn–Sham set of equations with the PAW potential is solved. The generalized gradient approximation for the exchange and correlation part of the density functional is used. The type of the functional is PBE [31]. Pressure, proton–proton pair correlation function (PCF) (another term “radial distribution function, RDF”) are calculated. The results are averaged over the set of ion configurations. These configurations are obtained within the framework of the quantum molecular dynamics. The forces acting on ions are evaluated via the Hellmann–Feynman theorem.

Depending on the particle density in the computational cell, the trajectories have 4000–20000 steps with the time step 0.5 fs. The values of pressure at each time step is used for averaging. From 10 to 20 statistically independent [32] configurations are chosen for averaging of PCF.

The cutoff of the plane basis set is 1200 eV, which provides the convergence of the results. The number of particles is 512 in the simple cubic computational cell with the periodic boundary conditions. The Baldereschi mean value point [33] is used for the calculation of pressure, which provides the same values of pressure as $3 \times 3 \times 3$ Monkhorst–Pack [34] k-mesh, as it is shown in [19].

The range of densities studied is $\rho = 0.4$–1.2 g/cm$^3$. Two temperatures $T = 1000$ and 1500 K are considered. Calculations are performed in the canonical ensemble with the Nosé–Hoover thermostat [35,36], which controls the ionic temperature. The electron temperature coincides with the ion temperature and is established by the Fermi–Dirac distribution.

The approach we use is a conventional approach which is applied in many works of other authors. However, three new methods of a nonconventional treatment of the PCFs obtained are suggested to elucidate the character and nature of the phase transition.

3. Pair correlation functions
Proton–proton PCFs $g(r)$ are calculated in the hydrogen density area, where the phase transition is expected, to reveal its nature. Results are presented in figures 1, 2. Figure 1 shows that PCF changes slowly with increase of the density in the range of distances greater than 2 Å. No indication of a phase transition is found. However, the situation changes drastically for distances smaller than 2 Å. PCFs are shown in figures 2(a, b) in a large scale for distances smaller than 2 Å for two temperatures and a set of densities. It is evident that the values of $g(r_{\text{max}})$ and $g(r_{\text{min}})$ are changed dramatically in the narrow density range of the expected phase transition, $r_{\text{max}}$ and $r_{\text{min}}$ are the values of distance where the function $g(r)$ has its first maximum and first minimum. The values of $g(r_{\text{max}})$ decrease and the values of $g(r_{\text{min}})$ increase sharply in this density range.

To emphasize the character of $g(r)$ changes, plots of $g(r_{\text{max}})/g(r_{\text{min}})$ are presented in figure 3(a) for $T = 1500$, 1000 and 700 K. We use data [19] for $g(r)$ at 700 K. Strongly pronounced jumps of $g(r_{\text{max}})/g(r_{\text{min}})$ are obtained for all three temperatures just at the same conditions where our calculations point to the density jumps. However, the latter jumps are weakly pronounced ones as compared with jumps in figure 3(a). So, the jumps of $g(r_{\text{max}})/g(r_{\text{min}})$ can be considered as a sensitive diagnostics of the phase transition of the first order. Note that the number of particles used in modeling is relatively small; it results in a certain smoothing of the jumps both in figure 3(a) and for density.

On the contrary, the value of the ratio $g(r_{\text{max}})/g(r_{\text{min}})$ varies smoothly with the density as it is evident from figure 3(b), $r_{\text{max}}$ and $r_{\text{min}}$ are the values of distance where the function $g(r)$ has its second maximum and second minimum. So, all the phase transition events happen only
Figure 1. Pair correlation functions for warm dense hydrogen at temperature $T = 1500$ K for two densities $\rho = 0.68$ g/cm$^3$ and $\rho = 0.9$ g/cm$^3$. The average distances between molecules for the lowest and highest densities are depicted by the black and red arrows respectively.

in the space which is occupied by the H$_2$ molecules. The long-range order does not respond to the phase transition.

One can conclude that the phase transition is of the structural character, and the structure changes abruptly only at the short-range distances at that. The results for the higher temperatures, density jumps and a discussion of the critical point location will be given elsewhere. We analyze here only the character and nature of the phase transition.

4. Formation of molecular ions H$_2^+$ and H$_3^+$

The values of both $r_{\text{max}1}$ and $r_{\text{min}1}$ do not almost depend on temperature, the value of $r_{\text{max}1}$ being almost equal to the interatomic distance $d_{\text{H}_2} = 0.74$ Å in the H$_2$ molecule. The value of $r_{\text{min}1}$ is in the range of the interatomic distances $d_{\text{H}_2^+} = 1.06$ Å and $d_{\text{H}_3^+} = 0.92$ Å in the molecular ions H$_2^+$ and H$_3^+$ [37]. The value of $g(r_{\text{min}1})$ is close to zero before the phase transition. Maximum values of $g(d_{\text{H}_2})$ and zero values of $g(d_{\text{H}_2^+})$ and $g(d_{\text{H}_3^+})$ mean that warm dense hydrogen is a molecular fluid before the phase transition in a complete agreement with all the conclusions in the literature.

The values of $g(d_{\text{H}_2})$ decrease and the values of $g(d_{\text{H}_2^+})$ and $g(d_{\text{H}_3^+})$ increase sharply in the narrow density range where the phase transition takes place. It means that the number of H$_2$ molecules decreases sharply and the number of molecular ions H$_2^+$ and H$_3^+$ appears correspondingly at the phase transition.

To expose more obviously that it is this effect that takes place at the phase transition, the following procedure is suggested. Let $g_1(r)$ and $g_2(r)$ denote the PCFs which are the closest from the calculated ones to the phase transition before and after it. The results for the function $\Delta g(r) = g_2(r) - g_1(r)$ are presented in figure 4. The function $\Delta g(r)$ is close to zero for $r > 2$ Å. It confirms the aforesaid conclusion that the long-range order does not respond to the phase
Figure 2. Pair correlation functions for warm dense hydrogen at temperatures \(T = 1000\) (a) and 1500 K (b) for a number of densities. The lines are drawn through points in order to guide the eye here and in the subsequent figures. Distances between protons in the hydrogen molecule \(H_2\) (0.74 Å) and in molecular ions \(H_3^+\) (0.92 Å) and \(H_2^+\) (1.06 Å) are depicted by arrows.

transition. However, the most important result is that the function \(\Delta g(r)\) has a deep minimum at \(r = d_{H_2^+}\) and a strongly pronounced maximum at \(r = d_{H_3^+}\). An extended wing adjoins to the maximum to the right of it. The wing covers the distances about \(r = d_{H_2^+}\). It means that the number of \(H_2\) molecules decreases abruptly and the number of molecular ions \(H_2^+\) and \(H_3^+\) appears indeed correspondingly at the phase transition.

The results presented show that neither Wigner metallization with the formation of protons and electrons, nor dissociation with the formation of atomic hydrogen take place at the phase transition, contrary to the widespread assumptions. The absence of the metallic conductivity in this range of temperature and densities is recently reported in experiments [8].

One can conclude that the nature of the phase transition is of electronic origin since it is related to the abrupt ionization of molecules. However, the change of electronic structure results in the structural changes as well, since the interatomic distances \(d_{H_2^+}\) and \(d_{H_3^+}\) are larger than \(d_{H_2}\). The latter factor would be of no importance for conventional strongly coupled plasma densities, but becomes essential for such a close packed system as warm dense hydrogen.
Figure 3. The dependencies of the functions $g(r_{\text{max}1})/g(r_{\text{min}1})$ (a) and $g(r_{\text{max}2})/g(r_{\text{min}2})$ (b) on density for temperatures 700 K (crosses (a) and solid line (b)), 1000 K (circles (a) and dashed line (b)) and 1500 K (squares (a) and dash–dotted line (b)).

5. Soft sphere approximation for long-range order

Proceed with a long-range order of the warm dense hydrogen at the fluid–fluid phase transition. It turns out that the PCFs obtained can be modeled for $r$ larger than 2 Å by the soft sphere PCFs at the number densities which are equal to the total number density of H$_2$, H$_3^+$ and H$_2^+$ (Figure 5). The latter value remains to be close to constant at the phase transition. The soft sphere repulsion is taken in the form $r^{-12}$ with the repulsion “diameter” about 0.8–0.9 Å at the temperatures needed. It does not contradict to the intermolecular H$_2$–H$_2$ interaction potential which is calculated in [38] for the interaction at low temperatures. Thus, we can conclude that the long-range order of warm dense hydrogen corresponds to the soft sphere model in the area of the fluid–fluid phase transition.

Such a “downcast appearance” of the PCFs indicates an absence of any nucleation in warm dense hydrogen at the phase transition, contrary to the Brazhkin-type phase transitions [39, 40] where chains and other clusters are observed. It should not seem strange, since critical temperature of the liquid–vapor transition is 33 K for hydrogen. The state of warm dense hydrogen is so far from this temperature that any analogy with phenomena in liquids, in particular nucleation, is rather doubtful. Hydrogen is the only substance where a fluid–fluid transition is observed. All the Brazhkin-type phase transitions are liquid–liquid transitions.

One can suggest that since the fluid–fluid phase transition in warm dense hydrogen is of the first order, it might have its specific nucleation therefore. However, the phase transition
Figure 4. Functions $\Delta g(r) = g_2(r) - g_1(r)$ for temperatures 700 K, $g_{1.06}(r) - g_{1.0}(r)$; 1000 K, $g_{0.92}(r) - g_{0.9}(r)$; and 1500 K, $g_{0.8}(r) - g_{0.77}(r)$. Subscripts show the density values, for which PCFs are taken for each temperature.

Figure 5. Example of PCF for $T = 1000$ K and density 0.92 g/cm$^3$. Solid curve presents simulation results; dashed curve is a soft sphere model.

considered is an electronic one and is related to the local partial ionization of H$_2$ molecules with formation of H$_2^+$ and H$_3^+$ molecular ions. It is not driven by any long-range interparticle interaction and does not go through a nucleation which is possible in the presence of a long-range interparticle interaction. This analysis gives an additional support to the aforesaid conclusion that the long-range order of warm dense hydrogen does not respond to the phase transition discussed. All the events are concentrated in H$_2$ molecules and are not accompanied by a nucleation. This is one more peculiarity of the phase transition.

Comparison of the transition in warm dense hydrogen with Brazhkin-type liquid–liquid transitions in melts shows that the phase transition in warm dense hydrogen differs from them and is a particular exceptional case. A certain analogy can be drawn to the plasma phase transition predicted in [41–43], since the latter is also driven by the ionization but in classical
picture. The differences are in quantum nature of ionization and in structural changes which are inherent for a close packed system as warm dense hydrogen.

6. Triple point
It follows from the figure 3(a) that the size of the $g(r_{\text{max}1})/g(r_{\text{min}1})$ jumps decreases with increase of temperature. So, the existence of the critical point is evident. However, the size of the jumps increases with decrease of temperature. Therefore, one can expect a fluid–fluid–solid triple point on the melting curve at high temperatures predicted in [42,43], rather than a lower critical point.

The interatomic distance in the $\text{H}_2$ molecule is smaller than the interatomic distance in the molecular ions $\text{H}_2^+$ and $\text{H}_3^+$. Therefore, the ionization of molecules results in an increase of the specific volume of warm dense hydrogen at the fluid–fluid phase transition. It gives an explanation of the negative slope of the coexistence curve $P(T)$ of the phase transition which is observed experimentally [5–7]. Remember that warm dense hydrogen is an only exceptional case when both fluid–fluid and melting curves are abnormal with negative slopes of $P(T)$ near the expected fluid–fluid–solid triple point.

The liquid–liquid phase transitions in selenium and other substances [40] use to have adjacent solid–solid phase transitions of the same nature with a solid–solid–liquid triple point on the melting curve at high temperatures. It is located at higher pressure with respect to the corresponding liquid–liquid–solid triple point. Now, the fluid–fluid phase transition in warm dense hydrogen assumes the same status as the transition from dielectric to conducting solid hydrogen is observed experimentally [44] after many decades of searches. It should be studied if the crystalline lattice is formed by protons [26] or $\text{H}_2^+$ and/or $\text{H}_3^+$ molecular ions.

7. Conclusions
In this work, ab initio molecular dynamics and quantum simulation techniques based on the density functional theory are used to calculate proton–proton PCF in the range of temperatures and densities where the phase transition is observed in warm dense hydrogen experimentally. Three new methods of treatment of the PCFs obtained are suggested elucidating the character and nature of the phase transition. The following results are obtained.

The phase transition is of the structural character, and the structure changes abruptly at the short-range distances of the PCFs at that. All the phase transition events happen only in the space which is occupied by the $\text{H}_2$ molecules.

The number of $\text{H}_2$ molecules decreases abruptly and the number of molecular ions $\text{H}_2^+$ and $\text{H}_3^+$ appears at the phase transition. The phase transition considered is of the electronic nature and is related to the local partial ionization of $\text{H}_2$ molecules with formation of $\text{H}_2^+$ and $\text{H}_3^+$ molecular ions. The ionization nature of the transition is typical for plasmas. However, the change of electronic structure of dense hydrogen results in the structural changes since the interatomic distances $d_{\text{H}_2^+}$ and $d_{\text{H}_3^+}$ are larger than $d_{\text{H}_2}$. The latter factor would be of no importance for conventional strongly coupled plasma densities, but becomes essential for such a close packed system as warm dense hydrogen.

The long-range order of warm dense hydrogen PCFs does not respond to the phase transition. The long-range order corresponds to the soft sphere model from the second maximum of PCF.

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