Critical point and mechanism of the phase transition in warm dense hydrogen

I M Saitov and G E Norman

Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13
Bldg 2, Moscow 125412, Russia
E-mail: saitovilnur@gmail.com

Abstract. Ab initio quantum modeling is applied to calculate the equation of state and the proton-proton pair correlation functions in the range of hydrogen temperatures and densities where the fluid-fluid phase transition is expected. The estimation of the critical temperature of the fluid-fluid phase transition in warm dense hydrogen is obtained \( T_c \geq 4000 \) K. A two-step mechanism of the phase transition is suggested: the partial ionization of molecules to produce molecular ions \( H_2^+ \) and \( H_3^+ \).

1. Introduction

In this paper we have evaluated the critical temperature and suggested the mechanism of the phase transition in warm dense hydrogen. In the experiments [1–4] the phase transition in warm dense hydrogen was detected based on the measurements of various parameters such as conductivity and reflectivity. The density jump is observed in [1–3] in contrast to the other works. However, there are no clear experimental data concerning the parameters of the critical point.

Properties of the warm dense hydrogen are studied theoretically by quantum molecular dynamics within the framework of density functional theory (DFT) [4, 5] and the quantum Monte Carlo method [6–8]. The results obtained in these works for the phase equilibrium curves are in good agreement with experiment. The following estimations for the critical temperature of the phase transition are obtained: 1500 [5] and 2000 K [6].

There are various approaches for the explanation of the nature of the phase transition: the assumption of metallization based on [9], the pressure dissociation of hydrogen molecules \( H_2 \rightarrow 2H \), plasma phase transition is also considered [6, 10, 11].

The objective of this work is to clarify the nature and mechanism of phase transition in warm dense hydrogen and to estimate the critical point parameters.

2. Equation of state

The analysis of the equation of state is conventional method of the diagnostics of the first-order phase transition. Isotherms of warm dense hydrogen are calculated at temperatures of 1000, 1500, 2500 and 4000 K. The quantum molecular dynamics within the framework of the DFT is applied. VASP plane wave code [12–15] is used for the calculations. This is a conventional approach which is applied to study thermodynamic properties [16–18]. The method is described in [19] more detailed.
The results of calculating the pressure dependence on the density at \( T = 1000 \) K are shown in figure 1. As one can see from figure 1, there is a density jump on the 1000 K isotherm. Such jumps are found and also at higher temperatures. However, the magnitude of the density jump decreases with increasing of temperature and becomes comparable with the value of the pressure calculation error. This occurs due to the relatively small number of particles in the considered system. However, the density jump at the phase transition is accompanied by much more pronounced jumps of pair correlation functions (PCF) of protons [4]. Therefore, in the following sections we will use this method of diagnosis. It allows detect the phase transition, as well as also to investigate the character and nature of the changes taking place in the transition.

Concluding the discussion of figure 1, we note that it also shows the beginning of the isotherm of the metastable states, which continues the isotherm of equilibrium states. The existence of metastable states is clear evidence that the observed transition is a first-order phase transition, rather than an indication, for example, the Widom line. This fact is especially important for the phase transition with small values of the density jump.

It should be emphasized that the quantum molecular dynamics is not a quite adequate method for the investigation of metastable states. The reason is that the forces in this method are not calculated from a single potential surface. The disturbance arising in the calculation of forces leads to the destruction of metastable states. Therefore, the calculations can not be extended far from the binodal point.

The existence of metastable states is a clue point for the explanation of the strong difference between the results of the experimental data [1–3] and [4]. The metastable state can occur in the Z-machine [4] due to the ultra-fast heating of deuterium. In this case, the results of [4] could be considered as evidence that the authors [1–3] and [4] observe the same phase transition. It is shown in [20], where the phase transitions in liquid–liquid selenium and sulfur are considered, that phase transition points are shifted by increasing of the rate of cooling or heating.

3. Critical point

The PCFs calculated at temperatures 2500 and 4000 K are shown in figure 2 in a large scale for distances smaller than 2 \( \text{Å} \) for the set of densities. It is evident that the values of \( g(r_{\text{max}_1}) \) and \( g(r_{\text{min}_1}) \) are changed dramatically in the narrow density range of the expected phase transition, \( r_{\text{max}_1} \) and \( r_{\text{min}_1} \) are the values of distance where the function \( g(r) \) has its first maximum and

![Figure 1. The dependence of pressure on density at temperature \( T = 1000 \) K. The solid line corresponds to the pressure of phase equilibrium.](image-url)
Figure 2. Proton–proton PCFs for warm dense hydrogen at temperatures $T = 2500$ (a) and $4000$ 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.

4. Mechanism of the phase transition

The value of $r_{\text{max1}}$ being almost equal to the interatomic distance $d_{H_2} = 0.74$ Å in the $H_2$ molecule. The value of $r_{\text{min1}}$ is in the range of the interatomic distances $d_{H_2^+} = 1.06$ Å and $d_{H_3^+} = 0.92$ Å in the molecular ions $H_2^+$ and $H_3^+$ [22]. The values of $g(d_{H_2})$ decrease and the values of $g(d_{H_2^+})$ and $g(d_{H_3^+})$ increase sharply in the narrow density range where the phase
transition takes place. It means that the number of H\textsubscript{2} molecules decreases and the number of molecular ions H\textsuperscript{+}\textsubscript{2} and H\textsuperscript{+}\textsubscript{3} appears correspondingly at the phase transition.

Let consider the function \(\Delta g(r) = g_2(r) - g_1(r)\), where \(g_1(r)\) and \(g_2(r)\) are the values of the PCF, which are the closest from the calculated ones to the phase transition before and after it. The results are presented in figure 4.

One can see that the function \(\Delta g(r)\) has a deep minimum at \(r = d_{\text{H}_2}\) and a strongly pronounced maximum at \(r = d_{\text{H}_2^+}\). An extended wing adjoins to the maximum to the right of it. The wing covers the distances about \(r = d_{\text{H}_2^+}\). It also notifies that the number of H\textsubscript{2} molecules decreases abruptly and the number of molecular ions increases correspondingly at the phase transition.

On the basis of these results the following mechanism of the phase transition in warm dense hydrogen can be assumed, consisting of two stages. The first stage is a partial ionization of molecular hydrogen to form molecular ions H\textsuperscript{+}\textsubscript{2}:

\[
\text{H}_2 \rightarrow \text{H}_2^+ + e. \tag{1}
\]

The next step is the formation of ions H\textsuperscript{+}\textsubscript{3}. By analogy with the case of a rarefied gas plasma H\textsuperscript{+}\textsubscript{3} ions are formed by the reaction of hydrogen molecules with ions H\textsuperscript{+}\textsubscript{2}:

\[
\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}. \tag{2}
\]

It should be noted that the function \(\Delta g(r)\) at temperatures 2500 and 4000 K has two maxima. As it is mentioned earlier, the first maximum corresponds to the contribution of H\textsuperscript{+}\textsubscript{3}. Then, based on (2) we can assume that second peak is the contribution of the hydrogen atoms.

Figure 3. The dependencies of the functions \(g(r_{max1})/g(r_{min1})\) on density for temperatures 700 (crosses), 1000 (circles), 1500 (squares), 2500 (diamonds), 4000 K (triangles).
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, $g_{0.92}(r) - g_{0.9}(r)$; 1500 K, $g_{0.8}(r) - g_{0.77}(r)$; 2500 K $g_{0.6}(r) - g_{0.55}(r)$; 4000 K $g_{0.475}(r) - g_{0.45}(r)$. Subscripts show the density values, for which PCF’s are taken for each temperature.

5. Conclusions
In this work the DFT approach is used to calculate pressure and proton–proton pair correlation functions in the range parameters where the phase transition is observed in warm dense hydrogen experimentally. The following results are obtained.

The estimation of the critical temperature of the fluid–fluid phase transition in warm dense hydrogen is obtained $T_c \geq 4000$ K.

A two-stage mechanism of the first-order phase transition related to the partial ionization of H$_2$ molecules to form molecular ions H$_2^+$ is suggested. The second stage is the reaction of H$_2$ molecules with H$_2^+$ ions to form an ion H$_3^+$. Thus, the nature of the phase transition combines ionization, i.e. plasma transition and change in the structure of dense matter.

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