Ionization of Molecules at the Fluid—Fluid Phase Transition in Warm Dense Hydrogen

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Abstract—The problem of the fluid—fluid phase transition in warm dense hydrogen/deuterium has been studied experimentally and theoretically in the best laboratories in the last decade. However, the nature of the phase transition remains unclarified. In this paper we put forward the new idea that H₂ molecules are ionized at the phase transition to produce molecular and ions

\[ \text{H}_2^+ + \text{H}_2^+ \]

Three different techniques were used in the experiments [1–5]: shock reverberation [1], shocks generated by a laser pulse in hydrogen precompressed in a diamond anvil [2–4], and dynamic compression of liquid deuterium in a Z-pinch [5]. We agree with the opinion [6] that the reason why the results [5] differ remains unclear. The goal of both [1] and [2–4] was to show that the two phases differing in conductivity is separated by a transition that is a first-order phase transition.

Experimental results have initiated theoretical works. We will point out the latest ones [5–9]. The properties of warm dense hydrogen have been investigated by the methods of ab initio molecular dynamics and quantum simulations using the density functional theory and quantum Monte Carlo. A first-order phase transition was detected; the coexistence curve turned out to be close to the measured one. Opinions about the nature of the phase transition differ: under the hypnosis of the well-known 1935 paper by Wigner and Huntington attempts were made to associate it with hydrogen metallization, an alternative is the dissociation by pressure \( \text{H}_2 \rightarrow 2\text{H} \), a plasma phase transition is also mentioned (see [8]).

The goal of this paper is to clarify the nature of the phase transition in warm dense hydrogen.

Ab initio molecular dynamics and a quantum computing technique based on the density functional theory are applied. The VASP package is used. The proton—proton pair correlation functions \( g(r) \) (PCFs) and the pressure are calculated in the range of hydrogen densities where the phase transition is expected. The results are averaged over the set of equilibrium ion configurations.

We will emphasize that random distributions of protons are chosen to be the initial conditions in our molecular-dynamics calculations. This means that the structures that, as we will see, are formed when the molecular-dynamics trajectories reach an equilibrium are not fed in any way into the calculations but are formed by themselves in view of the quantum nature of the calculations.

As we see, the approach used here is a conventional one and has been applied previously in the works of other authors. However, to reveal the character and nature of the phase transition, we used three new methods of processing the results for \( g(r) \).

THE PAIR CORRELATION FUNCTIONS

To clarify the nature of the phase transition, we calculated the proton—proton PCFs \( g(r) \) in the range of densities where this transition is observed experimentally. The results show that the PCFs change smoothly and slowly with increasing density for distances \( r > 2 \text{ Å} \). No evidence for the phase transition was found in this range of distances. The situation changes abruptly for distances \( r < 2 \text{ Å} \).

In Fig. 1 the range of distances \( r < 2 \text{ Å} \) is presented on a large scale for two temperatures and a set of densities. The PCF values \( g(r_{\text{max}}) \) and \( g(r_{\text{min}}) \) are seen
to change radically in the narrow range of densities where the phase transition is expected, $r_{\text{max}1}$ and $r_{\text{min}1}$ are the distances at which the function $g(r)$ has the first maximum and the first minimum. The values of $g(r_{\text{max}1})$ decrease, while the values of $g(r_{\text{min}1})$ increase sharply in this narrow range of densities.

To emphasize the pattern of changes in $g(r)$, Fig. 2 presents the density dependences of $g(r_{\text{max}1})/g(r_{\text{min}1})$. Pronounced jumps of the function $g(r_{\text{max}1})/g(r_{\text{min}1})$ were obtained at temperatures $T = 1500$, 1000, and 700 K in the same place where our calculations point to density jumps. However, the latter are much less pronounced. Such a behavior of $g(r_{\text{max}1})/g(r_{\text{min}1})$ is expected up to the triple point, if it exists. Note that the number of particles used in our calculations is relatively small, resulting in some smoothing of the jumps in both $g(r_{\text{max}1})/g(r_{\text{min}1})$ and density at the phase transition.

It can be seen from the same Fig. 2 that, at the same time, the function $g(r_{\text{max}2})/g(r_{\text{min}2})$ changes smoothly with increasing density in the entire range of densities considered, $r_{\text{max}2}$ and $r_{\text{min}2}$ are the distances at which the function $g(r)$ has the second maximum and the second minimum. Thus, all of the events occurring at the phase transition unfold locally only in the region of space occupied by H$_2$ molecules. The long-range order, starting from the second maximum, does not respond in any way to the phase transition.

It can be concluded that the phase transition under consideration is structural in character, with all abrupt structural changes occurring only in the short-range order, without affecting in any way the long-range one. The results for temperatures above 1500 K and the critical point will be considered separately. Here we analyze only the character and nature of the phase transition.
The values of \( r_{\text{max1}} \) and \( r_{\text{min1}} \) are almost independent of the temperature. The value of \( r_{\text{max1}} \) is equal to the distance between the protons \( d_{H_2} = 0.74 \) Å in an H\(_2\) molecule. The value of \( r_{\text{min1}} \) lies in the range of distances between the protons \( d_{H_2}^+ = 1.06 \) Å and \( d_{H_3} = 0.92 \) Å for molecular H\(_2^+\) and H\(_3^+\) ions [10]. The values of \( g(r_{\text{min1}}) \) are nearly zero up to the phase transition. The maximum values of \( g(d_{H_2}) \) and the nearly zero values of \( g(d_{H_2}^+) \) and \( g(d_{H_3}) \) suggest that warm dense hydrogen is a molecular fluid up to the phase transition, in agreement with the opinion established in the literature.

The values of \( g(d_{H_2}) \) decrease sharply, while the values of \( g(d_{H_2}^+) \) and \( g(d_{H_3}) \) increase sharply in a narrow range of densities near the phase transition. This means that the concentration of H\(_2\) molecules falls, while the concentration of H\(_2^+\) and H\(_3^+\) rises sharply at the phase transition.

To reveal this effect more clearly, we propose the following procedure. Denote the PCFs at the densities closest to the phase transition, before and after it, by \( g_1(r) \) and \( g_2(r) \), respectively. The results for the function \( \Delta g(r) = g_2(r) - g_1(r) \) are presented in Fig. 3.

The function \( \Delta g(r) \) is nearly zero for \( r > 2 \) Å. This confirms the above assertion that the long-range order does not feel the phase transition. However, the main result is that the function \( \Delta g(r) \) has a deep minimum at distance \( r = d_{H_2} \) and a pronounced maximum at distance \( r = d_{H_2}^+ \). An extended wing covering \( r = d_{H_2} \) is adjacent to this maximum on the right. Thus, at the phase transition the concentration of H\(_2\) molecules indeed decreases sharply and molecular H\(_2^+\) and H\(_3^+\) ions emerge.

The presented results show that, contrary to the available assumptions, there is neither the Wigner metatization to produce protons and electrons nor the dissociation by pressure to produce atomic hydrogen. The latest measurements [11] also suggest the absence of metallic conduction in this region.

Note that the phase transition under consideration is electronic in nature, because it is attributable to abrupt ionization of molecules. However, a change in the electronic structure also leads to a change in the spatial structure, because the distances between the protons \( d_{H_2} \) and \( d_{H_3} \) are larger than \( d_{H_2} \).

### THE SOFT-SPHERE APPROXIMATION FOR THE LONG-RANGE ORDER

Let us return to the long-range order in warm dense hydrogen at the fluid–fluid phase transition. The PCFs found at \( r > 2 \) Å turned out to be well modeled by the PCFs for a system of soft spheres with a diameter close to 0.8–0.9 Å and a concentration equal to the total concentration of H\(_2\), H\(_2^+\), and H\(_3^+\), which does not change greatly at the phase transition (Fig. 4). The repulsion between soft spheres was chosen in the form \( r^{-12} \) in the range of energies corresponding to the temperatures under consideration. This form is consistent with the intermolecular H\(_2\)–H\(_2\) interaction potential calculated in [12] for low temperatures. Thus, the long-range order in warm dense hydrogen near the fluid–fluid phase transition corresponds to the soft-sphere approximation.

Such a “dull” character of the long-range order suggests the absence of any cluster formation at the phase transition, in contrast to the Brazhkin phase transition [13], where chains and other structures are observed. This is not surprising, because the critical temperature of hydrogen is 33 K. The states of warm dense hydrogen are so far from this temperature that no cluster-formation phenomena inherent in the liquid state are expected here. Hydrogen is the only material where the fluid–fluid phase transition is observed; all Brazhkin phase transitions are liquid–liquid ones.

It could have been assumed that since the fluid–fluid phase transition is a first-order one with its criti-
cal point, peculiar nucleation could occur near its coexistence curve. However, this transition is electronic and is associated with the local partial ionization of H₂ molecules to produce H⁺ and H₂⁺ ions. The transition is not attributable to any classical long-range attraction and, hence, does not pass through cluster formation, which is possible only in the presence of such an interaction. Thus, we obtain one more argument for our conclusion that the long-range order does not respond to this transition. All events refer to H₂ molecules and are not accompanied by any nucleation. This is yet another peculiarity of the transition.

Comparison with the Brazhkin liquid–liquid phase transitions [13] shows that the fluid–fluid phase transition in warm dense hydrogen differs from them and is a unique transition. Some analogy can partly be drawn with the prediction from [14], because the phase transition also attributable to ionization but in a purely classical picture is considered there.

THE TRIPLE POINT

It follows from Fig. 2 that the jump of the function $g(r_{\text{max}})/g(r_{\text{min}})$ decreases with increasing temperature. Therefore, the existence of a critical point is obvious. At the same time, this jump increases monotonically with decreasing temperature. Thus, one might expect the two-phase coexistence curve to end not with the lower critical point but with the fluid–fluid–solid triple point on the melting curve at high temperatures. This triple point was also predicted in [14], because the phase transition also attributable to ionization but in a purely classical picture is considered there.

| $\Delta g(r)$ | $r$ (Å) |
|---------------|---------|
| -2.06 -1.06   | 2.0     |
| -0.92 -0.9    | 1.5     |
| -0.8 -0.77    | 1.0     |
| -0.5 1.0      | 0.5     |

*Fig. 3.* Function $\Delta g(r) = g_2(r) - g_1(r)$ for different: (1) 700 K, $g_{1.06}(r) - g_{1.0}(r)$; (2) 1000 K, $g_{0.92}(r) - g_{0.9}(r)$; and (3) 1500 K, $g_{0.8}(r) - g_{0.77}(r)$. The indices indicate the hydrogen densities at which the difference was found.

leads to an increase in the specific volume at the fluid–fluid phase transition in warm dense hydrogen. This explains the negative slope of the coexistence curve $P(T)$ obtained in the experiments [2–4] for this phase transition. Recall that hydrogen is the only example of a material for which the phase equilibrium curves $P(T)$ both for melting and for the fluid–fluid phase transition have a negative slope near the triple point on the melting curve at high temperatures.

The liquid–liquid phase transition in selenium and other materials [13] has an accompanying solid–solid phase transition of a similar nature. The corresponding solid-solid-liquid triple point is located on the melting curve in pressure above the liquid–liquid–solid triple point. Until recently, no such accompanying transition from the dielectric to conducting state of solid hydrogen has been observed. Only recently [15] has this transition been detected experimentally after many decades of unsuccessful searches. However, it remains unclear what charges form the crystal lattice of the conducting state of solid hydrogen: the protons, as Wigner and Huntington assumed, or the molecular H⁺ and/or H₂⁺ ions.

Thus, we applied the method of quantum molecular dynamics using the density functional theory to calculate the proton–proton PCFs in the range of hydrogen temperatures and densities where the fluid–fluid phase transition is expected. We proposed three new methods of processing the pair correlation functions to clarify the nature and character of the fluid–fluid phase transition. The following conclusions can be drawn from the results obtained.

The phase transition is structural in character, with only the short-range order undergoing abrupt
changes. All phase transition events occur in the volumes occupied by individual H₂ molecules.

At the phase transition the number of H₂ molecules decreases sharply and molecular H²⁺ and H³⁻ ions emerge instead. The phase transition is electronic in nature, because it is associated with the local partial ionization of H₂ molecules to produce molecular H²⁺ and H³⁻ ions. The ionization nature is typical for a plasma. However, a change in the electronic structure of warm dense hydrogen also leads to structural changes, because the distances between the protons in H²⁺ and H³⁻ ions are larger than those in an H₂ molecule.

The long-range order of the proton—proton pair correlation functions does not respond to the phase transition. The long-range order can be described in terms of the soft-sphere approximation, starting from the second maximum.

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