Plasma Phase transition [[1]](#footnote-1)\*)

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1,2,3Norman G.E., 1,2,3Saitov I.M.

1JIHT RAS, Moscow, Russia, saitovilnur@gmail.com
2NRU HSE, Moscow, Russia, genri.norman@gmail.com
3MIPT (NRU), Dolgoprudny, Russia

Experimental methods for the generation and diagnostics of nonideal plasma and warm dense matter, which have become possible in recent years, are reviewed. Modern theoretical methods used to solve the problem of fluid-fluid phase transitions, including the plasma phase transition (PPT), are considered. Both the methods of quantum modeling and the results obtained within the framework of the chemical model of plasma are analyzed. Particular attention is paid to the phase transition in the fluid hydrogen/deuterium at high pressures. The results for helium, aluminum, cesium, cerium, ion and exciton plasmas, and some other substances are also considered.

**Experiments.** The equipment and diagnostic techniques that made it possible to start an experimental study of these issues appeared only in the 1990s. The existence of the PPT has been confirmed in a number of experiments, starting with the unique "explosive" experiments carried out at the Russian Federal Nuclear Center in Sarov, on the quasi-entropic compression of deuterium up to megabar pressures [1]. Subsequent work is divided into dynamic (shock waves, Z-pinch, NIF) and static (diamond anvils). An experimental phase diagram of hydrogen at high pressures is presented.

**Chemical model of plasma and phase transition in fluid hydrogen.** The development of the chemical model of plasma in describing the phase transition in hydrogen plasma is considered. The main attention is paid to the modern SAHA-D chemical model and the phase transition in warm dense hydrogen within this model [2, 3].

**Ab initio approaches.** The Kohn-Sham density functional theory (DFT) and the used exchange-correlation functionals are briefly described. In the quantum method of molecular dynamics, special attention is paid to electrical conductivity and optical properties. The Monte Carlo method for path integrals is touched upon, the path integral molecular dynamics method is considered more detailed.

**The PPT in fluid hydrogen.** A review of the results of the ab initio modeling is presented. The study of the ionization of molecules during a phase transition in a fluid hydrogen is singled out. The method is based on the analysis of proton-proton pair correlation functions, which are calculated in the range of hydrogen densities where a phase transition is expected. The results revealed a transition mechanism in which two processes occur simultaneously: a sharp decrease in the concentration of H2 molecules and the appearance of molecular ions with interproton distances as in H2+ and H3+. The transition is accompanied by a sharp increase in electrical conductivity. Complete dissociation and ionization occur only with further compression, and smoothly. The results of the DFT modeling indicate the transition of a fluid molecular hydrogen to an atomic fluid state upon compression through the formation of an intermediate state containing molecules, atoms, and proton clusters (including molecular ions).

**Triple point.** For the transition under consideration, the triple point is located on the melting line to the right of the maximum of this curve in the temperature T - pressure P coordinates. The known liquid-liquid phase transitions in other substances [4] have concomitant solid-solid phase transitions of a similar nature. In this connection, phase transitions in crystalline hydrogen near the melting line at high pressures are considered. Crystal structures with an interproton distance of 0.92 Å, characteristic of the stable hydrogen ion H3+, have been revealed in solid hydrogen. Thus, it can be assumed that during the melting of the resulting atomic structure of solid hydrogen, various proton clusters, including ionic-molecular ones, can be present in the resulting conducting hydrogen fluid.

**Metastable warm dense hydrogen.** The existence of metastable states is an important argument in favor of the fact that this is a first-order phase transition. Such states during the phase transition of warm dense hydrogen to the conducting state were discovered in the framework of the quantum method of molecular dynamics. Distinctive features include a relatively small jump in density during the transition and a significant overlap in density of the equilibrium branch of one phase and the metastable branch of the other on the isotherm of the dependence of P on the specific volume *V*, which corresponds to the prediction [5, 6]. In the region of overlap, the isotherm, due to its slope, turns out to be a three-valued function (three values of *P* correspond to one value of *V*), which distinguishes it from the single-valued *P(V)* van der Waals isotherm. This three-valuedness can be considered a distinctive feature of the PPT in a singly ionized plasma since it is due to the three-component composition of such a plasma and the presence of ionization equilibrium. This nature of the isotherm was initially discovered in the framework of a chemical model, but was subsequently confirmed by calculations using DFT.

**A new class of phase transitions.** This feature of phase transitions associated with ionization or dissociative equilibrium allowed the authors of [7] to put forward a hypothesis about the existence of a new class of phase transitions—dissociative and plasma—with the same topology of phase characteristics, which goes back to [8, 5, 6]. The specificity of the PPT phase diagram is that the critical point in the *P-V* coordinates lies in pressure below the two-phase states. While for curves of phase equilibrium on van der Waals type diagrams in *P-V* coordinates, the critical point is located above all two-phase states at the top of the wide dome of the binodal and spinodal. In contrast, the line of coexistence of phases in a hydrogen fluid in the *P-V* coordinates looks like a long, inclined, curved and very narrow tongue extended towards low pressures. Therefore, estimates of the critical temperature for heated dense hydrogen cannot be accurate and range from 1500 to 4000 K in various theoretical works. The Widom line is discussed.

**Nuclear quantum effects (NQEs).** The influence of the NQE in a fluid hydrogen/deuterium is considered. This effect affects the dynamics of protons, which leads to a decrease in the phase equilibrium pressure. The influence of the NQE weakens with increasing temperature. The influence of this effect on the size of the region of metastable states in the hydrogen fluid in the framework of DFT, on the position of the region of the phase transition to the conducting state, and on the structure of crystalline hydrogen is also considered.

**Criteria for the plasma nature of the phase transition in hydrogen.** Particular attention is paid to the similarity of the phase transition in the fluid hydrogen with the PPT [8, 5, 6] and differences from it. Three features are a direct indication of the PPT. 1. Density jump accompanied by a sharp increase in electrical conductivity due to ionization. 2. Strong overlap of the metastable and stable branches of the isotherm with the appearance of a region of three-valued dependence of *P* on *V*. 3. Negative slope of the phase coexistence line on the *T-P* plane. This line is limited by the critical point as *P* decreases and by the triple point on the melting line at high *P*. The differences between the real phase transition and the prediction [8, 5, 6] are associated with the high density and molecular composition of heated dense hydrogen. The transition leads not only to local partial ionization of H2 molecules, but also to a change in the structure of the ionized phase compared to the molecular one. The structural nature of the transition is rather complicated, since the transition gives rise to multiproton complexes with interatomic distances equal to the distances not only in H2+, but also in H3+.

**PPT in other substances.** In addition to hydrogen, the PPT is considered in systems of multielectron atoms: helium, aluminum, cesium, silicon, etc. Theoretical works, the experiment is only for helium, where, however, the obtained experimental parameters *T* and *P* turned out to be outside the region where the phase transition is supposed. Phase transitions adjacent to PPT, such as liquid-liquid, are affected. Studies of the PPT in other substances did not reveal any features that are new compared to PPT in hydrogen/deuterium. In this case, both similarities with the PPT in hydrogen/deuterium and differences from it are observed: (a) all transitions are associated with ionization, this is mandatory, both single and multiple ionizations are considered, (b) the metastable branches of the isotherm are poorly studied, (c) phase equilibrium curves *T(P)* can have both negative and positive slopes, (d) critical temperatures lie in a wide temperature range, (e) all triple points lie on the melting line, (f) the transition can lead not only to ionization, but also to a change in the structure of the ionized phase compared to the non-ionized one, (g) phase transitions associated with ionization, with a triple point on the melting line, are also observed in a solid.

A detailed presentation of the issues raised in the report is presented in the review [9]. We thank R.A. Sartana, together with whom work was done on the metastable states of warm dense hydrogen. This work was supported by the Russian Science Foundation grant 18-19-00734.

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