Ionization-dissociative phase transitions of the first order

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In this paper, we consider the plasma phase transition (PPT) phase diagram in the coordinates pressure P–specific volume V.

Chemical Models. The NormanStarosin1968 model is considered: a qualitative analysis of the features of $P(V)$ isotherms was carried out in BibermanNorman1969; for the quantitative one, we use the primitive Pade approximation. The SAHA-D model is presented by GryaznovIosilevskiy2009 and StarostinGryaznovFilippov2016 (two PPTs) results. A chemical model without ionization was applied in KhomkinShumikhin2014, 2022 (the two phases differ in the degree of dissociation of molecules).

Quantum molecular dynamics (QMD). The character of the $P(V)$ isotherms turned out to be the same: the "inverted" binodal. When approaching the critical temperature, the pressure drops, the binodal looks like a long, narrow, inclined and curved tongue, NormanSaitovSartan2019. Nuclear quantum effects within PIMD do not change the results.

Conclusions. The results for chemical models and QMD indicate three features of $P(V)$ isotherms of warm dense matter: (a) overlap of the metastable branch of one phase with the metastable and equilibrium branch of the other phase in a certain range of specific volume, (b) the phase transition pressure decreases as the critical temperature is approached, i.e. with increasing temperature (EbelingReichert1985 drew attention to this property of the PPT), (c) due to the three-valuedness of $P(V)$, in a certain range of the specific volume, there is an isolated region of metastable states (the results of QMD do not yet confirm, but do not contradict, this feature).

The physical nature of the transitions is common to all six cases: an ionization or dissociation jump. So, one can introduce a new type of phase transitions of the first order: ionization-dissociative ones.