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# Phase transition in dense low-temperature molecular gases

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## Abstract

This work is devoted to an analysis of the thermodynamic and transport properties of high-density low-temperature gases and plasmas. The results of two independent theoretical methods are discussed and compared: path integral Monte Carlo data and results from a new chemical model which takes into account free charged particles, atoms, molecules and molecular ions. The two approaches show good agreement for the equation of state of hydrogen up to the multimegabar range. At low temperature, both show indications of a first-order phase transition. Furthermore, based on the chemical model the electrical conductivity of dense hydrogen and deuterium and the deuterium shock hugoniot are computed. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Recent experiments on dense hydrogen and deuterium [1–4] have revealed unusual behavior of the electrical conductivity [1,2] and of the deuterium shock hugoniot [3,4] in the megabar pressure range. The results of Refs. [1,2] demonstrated a drastic increase, of about five orders of magnitude, of the conductivity of hydrogen in a narrow pressure range,  $p = 10^5\text{--}2 \times 10^6$  atmospheres. The measurements were performed in the temperature range  $(4.5\text{--}10) \times 10^3$  K. Further, the measured deuterium hugoniot [3,4] displayed a strong density increase at megabar pressure

and mass densities of  $0.5\text{--}1.0 \text{ g cm}^{-3}$ , which remains puzzling from the point of view of first-principle theories, e.g., [5].

Such a behavior of thermodynamic and transport properties points to qualitative changes in the plasma and to a possible first-order phase transition which is accompanied by rapid or even jump-like changes in the chemical composition and density. In fact, the first prediction of a phase transition in a low-temperature plasma (PPT) was given by Norman and Starostin [6]. Numerous subsequent papers investigated this important subject (see, e.g., [7–10]), where the main attention was devoted to the Coulomb interaction between free charges. However, the interaction between the neutrals was, in most studies, neglected or treated in a very simplified way, although some indications of their importance for the critical parameters of the PPT in partially ionized hydrogen or hydrogen–helium mixtures were found, e.g., [10].

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Therefore, the present Letter gives a detailed analysis of the neutral–neutral and neutral–charged particle interaction in dense plasmas in the megabar pressure range. We present a comparative analysis of the thermodynamic properties and of the conductivity of hydrogen and deuterium in the above parameter range based on two methods: first, quantum Monte Carlo simulations for hydrogen [11–14] and, second, using a chemical model for a multicomponent nonideal hydrogen and deuterium plasma [15]. It is demonstrated that the discussed above experimental observations can be explained by the existence of a new phase transition in dense hydrogen and deuterium. We present the critical temperature and coexistence line, compute the hydrogen conductivity and the deuterium hugoniot which are compared to the experimental results.

## 2. Quantum Monte Carlo simulations

For the simulations we used a recently developed [11–14] efficient path integral Monte Carlo (PIMC) approach which allows to analyze dense degenerate plasmas in a broad range of temperatures and densities, and which was also successfully applied to trapped electrons [16,17], for details of the PIMC concept, see Ref. [14]. The simulations were performed with 50 electrons and 50 protons by minimizing the free energy  $F = -k_B T \ln Z$ , where  $Z$  is the properly anti-symmetrized fermionic canonical partition function. All thermodynamic functions of interest are computed by the usual differentiation of the logarithm of  $Z$  with respect to the thermodynamic variables (temperature, volume, etc.).

To evaluate  $Z = \text{tr } \rho$ , the trace of the  $N$ -particle density operator has to be computed. However, for the high-density and low-temperature situations of interest to the present work, the plasma is nonideal, and  $\rho$  is not known. Therefore, we use the path integral concept [18] allowing us to express the exact density matrix in terms of a product of known high-temperature density matrices  $\rho_{\text{ht}}$ . The main difficulty of the simulations is the need to anti-symmetrize  $\rho$  giving rise to a poorly converging sum of  $N!$  terms of alternating sign. In a recently developed new path integral representation for  $\rho$  [11,12], the sum over the permutations is recast into a determinant which is evaluated with high efficiency by using standard linear al-

gebra techniques. The second key ingredient is the use of the correct quantum pair potential (the Kelbg potential, for a justification see Refs. [14,22]) for the electron–electron and electron–ion interaction.

Using this simulation technique, we computed the hydrogen pressure isotherms (equation of state) in the temperature range between  $T = 10,000$  and  $50,000$  K, see below.

## 3. Chemical model

In Ref. [15] a new chemical model for nonideal plasmas with chemical reactions was presented which will be applied to dense plasmas in the megabar pressure range. Here we outline only the main properties of this model. For a nonideal partially ionized/partially dissociated plasma all relevant chemical species are included. In particular, for hydrogen ( $A = \text{H}$ ) and deuterium ( $A = \text{D}$ ) we include the following six species:  $e$ ,  $A$ ,  $A^+$ ,  $A^-$ ,  $A_2$ ,  $A_2^+$ , which goes far beyond most previous studies where usually the contributions from  $A^-$  and  $A_2^+$  are neglected. As our results show these two components may be of comparable abundance to free electrons and protons in dense hydrogen underlining the importance of the present study.

In order to compute thermodynamic quantities, the corrections due to interaction between all species have to be accounted for in a systematic and consistent way. In particular, the contributions due to interactions involving neutrals ( $n$ ) are represented by a sum over powers of the density including all pair and triple  $e$ – $n$  and  $n$ – $n$  interactions. The corresponding second and third virial coefficients were computed in Refs. [19,20] using Hill pseudo-potentials. The  $e$ – $n$  and  $n$ – $n$  pseudo-potentials were derived from Lenard–Jones type potentials, cf. Eqs. (4), (6) of Ref. [19]. In the interaction between charged particles we took into account that the electrons bound in atoms and molecules do not contribute to the continuous part of the spectrum.

We underline that the full account of all second and third virial coefficients in the free energy and equation of state gives us the principal possibility to obtain the critical data of the phase transitions in dense plasmas. In particular, our model correctly reproduces the low-temperature liquid–gas transition in molecular hydrogen, with a critical temperature of about 50 K.

Furthermore, as will be shown in the next section, our model predicts a new first-order phase transition in dense hydrogen. Finally, we mention that, to keep the complex system of coupled mass action laws solvable, the Coulomb interaction between charged particles and quantum diffraction effects of the electrons are included only to leading order. Therefore, the results are expected to be less reliable at high free electron densities above the Mott point.

After discussing the theoretical methods we apply them to the thermodynamic and transport properties of dense plasmas. We will focus on the chemical model and will compare them to recent experimental data in Section 5. Since these data are limited to the region around the Mott transition, we take advantage of the quantum Monte Carlo results which serve as an additional test for the thermodynamic predictions of the chemical model in Section 4.

#### 4. Numerical results. Comparison of the analytical results and PIMC simulations. Dissociation phase transition

We first compute the equation of state of dense hydrogen, cf. Fig. 1. Overall, the chemical model and the PIMC simulations show satisfactory agreement. First, up to moderate densities,  $\rho \leq 0.1 \text{ g cm}^{-3}$  for  $T = 10,000 \text{ K}$  and  $\rho \leq 1 \text{ g cm}^{-3}$  for  $T = 50,000 \text{ K}$ , the chemical model is expected to be accurate, which is confirmed by the excellent agreement with the PIMC simulations. This extends well into the region where a large fraction of bound states is present, e.g., [12,13].

The most interesting feature in Fig. 1 is the appearance of van der Waals-like loops in the pressure isotherms for low temperatures, clearly indicating a phase transition. Fig. 2 gives a more detailed analysis of the transition region. Similar as for a classical first-order gas–liquid transition, the van der Waals loops become steeper with decreasing temperature, the instability region is enclosed by line 8 in Fig. 2—the spinodal. The critical temperature is approximately 50,000 K which is roughly the dissociation energy of hydrogen molecules and molecular ions  $\text{H}_2^+$  (similar results are obtained for other molecular systems as well). In fact, our analysis showed that the main trend during the transition is a rapid dissociation of  $\text{H}_2$

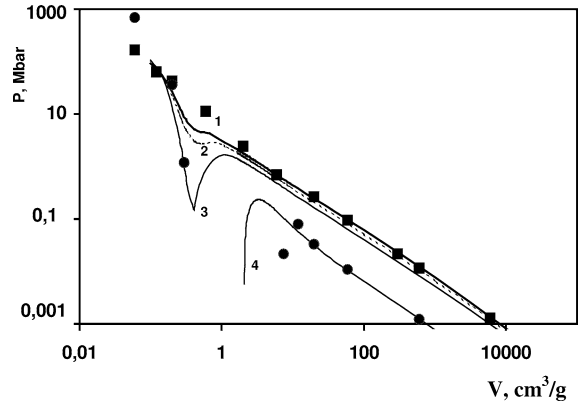


Fig. 1. Pressure isotherms for hydrogen plasma. Numbers denote results of the chemical model, symbols are path integral Monte Carlo data. Temperatures (in 1000 K): 50 (1 and full squares), 45 (2), 38 (3), 10 (4 and full circles).

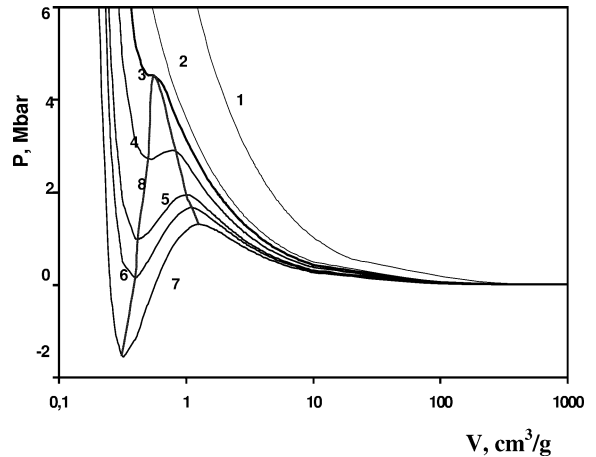


Fig. 2. Phase transition in hydrogen plasma. Temperatures (in 1000 K): 60 (1), 55 (2), 50 (3), 45 (4), 40 (5), 38 (6), 35 (7). Also shown is the spinodal (line 8, connecting the pressure extrema of different isotherms).

molecules. This is accompanied by a strong growth of the fraction of atoms, electrons, protons and  $\text{H}^-$  [24]. Formally, the reason is a strong growth of the magnitude of the second virial coefficients describing the heavy particle interactions. The remaining interactions, including the Coulomb interaction play, in this parameter region, only a minor role. In contrast, turning off the heavy particle interactions in our model leads to vanishing of this “dissociation” phase transition. We underline that this transition is essentially

different from the frequently discussed plasma phase transition, e.g., [6–10], where the Coulomb interaction is dominant leading to a critical temperature approximately three times lower.

It is interesting to compare these findings with the Monte Carlo simulations in this parameter range. In fact, it turned out that the simulations for  $T = 10,000$  K do not converge in a density interval around  $\rho = 1 \text{ g cm}^{-3}$ , which can be seen by the gap in the pressure isotherm, cf. dots in Fig. 1. The simulation data are surprisingly close to the results of the chemical picture even in the vicinity of the instability region. Moreover, in this density–temperature region close to the Mott point, the simulations also show a substantial fraction of trions ( $\text{H}^-$ ) and even larger bound complexes (clusters) which indirectly supports the findings of the chemical model. This may indicate that, indeed, the fraction of free electrons is smaller than predicted by previous models which neglected these complex particles. Furthermore, the Monte Carlo simulations show an instability also at  $T = 20,000$  K where the instability interval is narrower than for 10,000 K. The determination of the critical temperature requires more extensive computations and will be reported elsewhere [24].

## 5. Comparison with experimental data

Our results predict that during the discussed phase transition the concentration of charged carriers (electrons, protons, trions) increases by three orders of magnitude. Therefore, a direct consequence of the phase transition should be a drastic increase of the electrical conductivity of the plasma. In fact, such a conductivity increase has been observed experimentally, cf. the Introduction. In Ref. [1] a drastic reduction of the plasma resistance for pressures around one megabar was reported. In Fig. 3 we plot the experimental data of Ref. [1] (squares) together with several theoretical models for the conductivity. The figure shows that closest to the experiment, around densities of  $1 \text{ g cm}^{-3}$ , is the hopping mechanism [21] which is due to a resonant exchange (“quantum diffusion”) of bound electrons between atoms and ions. Further, the hopping mobility of the electrons exponentially depends on density since the hopping time is determined by the wave function overlap integral

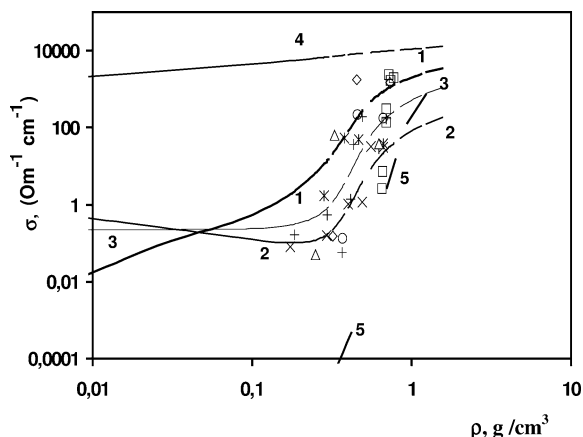


Fig. 3. Electrical conductivity of dense hydrogen plasma in the megabar range and  $T = 10,000$  K. (1) Hopping conductivity, (2) gas-kinetic model, (3) Drude result, (4) minimal metallic conductivity, (5) hopping conductivity for  $T = 4,500$  K. Open squares—experimental data from Ref. [1], remaining symbols—experimental points from Ref. [2].

of electrons in the molecular ion  $\text{A}_2^+$ . Other mechanisms, such as the gas kinetic one yield not more than 10% of the hopping conductivity. Further, the minimal metallic conductivity (assuming that all electrons have become conduction electrons) gives about an order of magnitude too large results (see Fig. 3). Notice, however, that all shown theoretical models predict the conductivity jump to occur at significantly lower (by a factor of about 2.5) densities than the experiment.

A large amount of experimental data for hydrogen in the temperature range of 4,500–10,000 K is given in Ref. [2] and also exhibits a strong conductivity increase for densities between 0.2 and  $0.8 \text{ g cm}^{-3}$ . This corresponds to measured pressure in the range 0.4–0.7 Mbar. All experimental data points are located in between the two hopping conductivity isotherms for 4,500 and 10,000 K, cf. Fig. 3, confirming reasonable agreement of our theoretical model with the measurements (unfortunately, experiments [1–4] did not measure the temperature). Interestingly, this range of parameters is just inside the theoretical two-phase region, cf. Fig. 2.

Let us now turn to the another interesting experimental observation—the anomalous behavior of the deuterium shock hughoniot [4]. Fig. 4(a) shows the experimental data and our theoretical results. As one can see, the agreement of the low pressure branch

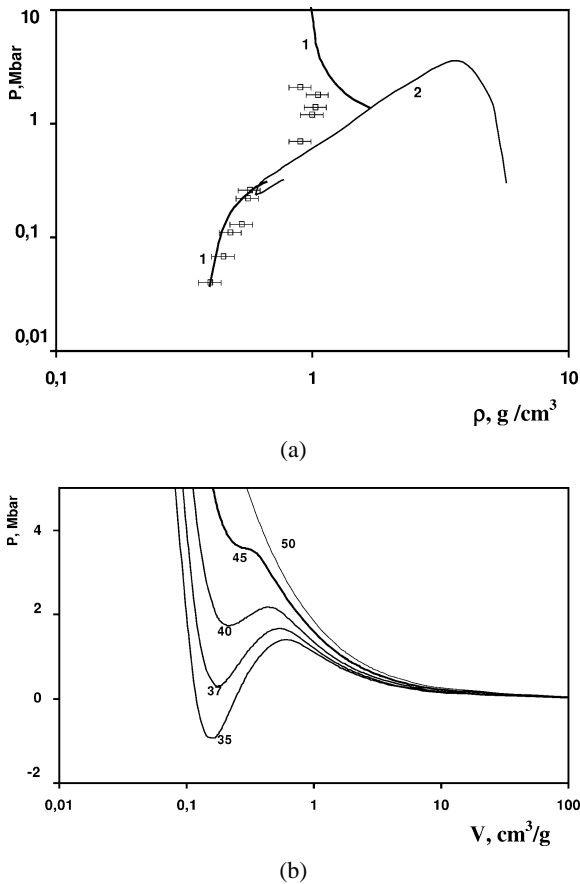


Fig. 4. Deuterium plasma phase diagram. (a) Shock hugoniot (1), gas boundary of the two-phase region (2) and experimental data [3] (symbols). (b) Deuterium pressure isotherms. The numbers in the figure denote the temperature in 1000 K.

( $T < 10,000$  K, lower part of curve 1) is very good. Furthermore, our calculations yield a density jump on the hugoniot around  $\rho = 0.6 \text{ g cm}^{-3}$ . For temperatures between 6,000 and 35,000 K our model does not have a stable gas phase solution on the shock hugoniot. While a density jump is apparent in the experimental data around  $\rho = 0.6 \text{ g cm}^{-3}$  as well, it is significantly smaller than in our model. The reasons for this deviation are manifold and can be related to insufficient accuracy in the available data for the inter-molecular interaction, but also to the mentioned above simplified treatment of the charged particle interaction. The latter fact could also explain the too high pressure values in our model at the upper branch of the hugoniot.

We mention that the computed shock hugoniot and the density jump, in particular, are strongly affected by the mentioned above phase transition (the unstable region is below curve 2 in Fig. 4(a)). The corresponding deuterium pressure isotherms show a similar van der Waals loop, as can be seen in Fig. 4(b). This could allow for a new theoretical explanation of the experimentally observed (and still puzzling from the theoretical point of view) strong compressibility change of shocked deuterium.

## 6. Summary and conclusions

In the present Letter, an investigation of the equation of state of hydrogen and deuterium in the sub-megabar and megabar pressure range was given using path integral Monte Carlo simulations and a recently developed multicomponent chemical picture. Both methods yield discontinuous changes of the concentrations of the various particle species for temperatures below the molecular dissociation energy. The instability behavior was found to be dominated by the interaction between neutrals and can be interpreted as a new “dissociation phase transition”. The associated jump in the concentration of the charged particles at pressures around 1 Mbar was found to be accompanied by a drastic conductivity increase which has been clearly observed in a number of experiments. Our analysis showed that, in this parameter range, the governing charge transport mechanism is hopping conductivity (quantum diffusion of bound electrons).

An important advantage of the present chemical model is its broad applicability to dense molecular fluids. As another illustration we show in Fig. 5 the equation of state of dense low-temperature oxygen. Again there is a phase transition with a critical temperature around 45,000 K which is near the dissociation energy of the molecular ion  $\text{O}_2^+$ .

As was mentioned above, the most important feature of our chemical model is the careful treatment of the interaction between neutrals and the inclusion of additional heavy particles, such as  $A^+$  and  $A_2^-$ . The important role of these complex particles at pressures below and around 1 Mbar was confirmed by the quantum Monte Carlo simulations which, moreover, clearly demonstrated the existence of even larger weakly bound clusters [25]. In future work, we will

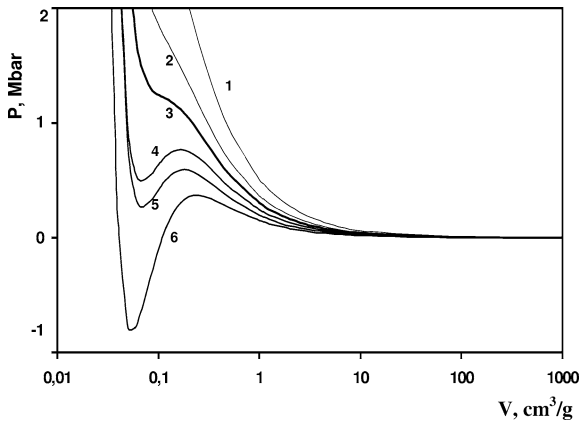


Fig. 5. Pressure isotherms of oxygen. Temperatures in 1000 K: 60 (1), 50 (2), 45 (3), 40 (4), 35 (5) and 30 (6).

study these phenomena more in detail. At still higher pressures, where charged particles are dominant, the present chemical model can only give estimates. In particular, the results above the conductivity increase have to be regarded as preliminary. In future work the presented chemical model will be improved by a more advanced treatment of the Coulomb interaction and of electron degeneracy, e.g., by using Padé approximations [23].

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