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First-order liquid-liquid phase transition in dense hydrogen

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We use *ab initio* molecular-dynamics simulations to study the nonmetal-to-metal transition in dense liquid hydrogen. By calculating the equation of state of hydrogen at high pressures up to several megabars and temperatures above the melting line up to 1500 K we confirm the first-order nature of this transition at these temperatures. We characterize both phases based on equation of state data, the electrical conductivity, and the pair-correlation functions, which are all derived self-consistently from these simulations. We locate the respective transition line in the phase diagram and give an estimate for its critical point. We compare with available experimental data and other theoretical predictions.

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I. INTRODUCTION

The high-pressure phase diagram of hydrogen is of interest since it is of paramount importance for many applications in astrophysics. For instance, the description of the interior of Jupiter-like giant planets which consist mainly of hydrogen (and helium) is one of the great challenges today.[1–3] Despite of its simplicity and the enormous progress in studying this prototypical system experimentally and theoretically, some of the key elements of the high-pressure phase diagram of hydrogen are still under lively debate. The slope of the melting line[4–7] and the transition pressure to solid metallic hydrogen[8,9] are prominent examples. At $T=0$ K solid metallic hydrogen is expected to occur[10] at pressures higher than 4 Mbar which is experimentally still not feasible, even 75 years after Wigner and Huntington have predicted this phase.[11]

Another long-standing problem is closely connected with this nonmetal-to-metal transition if it appears at finite temperatures (FTs), i.e., in the liquid or at even higher temperatures in the plasma. More than 50 years ago Landau and Zeldovich[12] called first attention to this problem and proposed that the nonmetal-to-metal transition in mercury could induce additional first-order phase transitions in the fluid phase. Assuming that such a transition occurs also in fluid hydrogen, various high-pressure phase diagrams have been proposed since then. These were used to locate the boundary between a *molecular* and a *metallic* layer in Jupiter-like giant planets along their isentropes, see, e.g., Ref. 13. Especially, advanced chemical models have been developed that predict almost coherently a pronounced first-order phase transition driven by the electronic transition, mostly in the range of 10 000–15 000 K and at about 0.5 Mbar.[14–25] The consideration of Pauli blocking effects in such a chemical model[26,27] has lead to a substantially lower value for the critical temperature of that phase transition around 6450 K. Percolation theory has been applied to this particular problem in dense Coulomb systems as well.[28,29] However, this *plasma phase transition* has not been observed in high-pressure experiments yet[30] but a first signature has been reported;[31] for a recent review, see Ref. 32.

The observation of *liquid* metallic hydrogen[33] at temperatures of about 2500 K and a pressure of 1.4 Mbar, i.e., well below the transition pressure predicted for solid hydrogen, has initiated an intense search for a potential liquid-liquid phase transition. Liquid hydrogen at megabar pressures and temperatures of few thousand kelvin can only be probed with innovative and highly sophisticated techniques such as isentropic shock compression or laser heated diamond-anvil cells so that experimental data are rather sparse in this domain.

Alternatively, *ab initio* approaches based on density-functional theory[4,34–40] (DFT) or quantum Monte Carlo (QMC) simulations[40–43] have been applied to determine the high-pressure equation of state (EOS) of liquid hydrogen. These calculations have revealed many features of the high-pressure liquid. For instance, the transition from a molecular to an atomic fluid has been analyzed with respect to structural changes, and a prediction for a transition line as well as the high-pressure phase diagram have been given.[38,39]

Only few quantum simulations have predicted a phase transition so far.[35,44,45] However, the first conclusive evidence for a first-order liquid-liquid phase transition has been given only recently based on both QMC and FT-DFT-molecular-dynamics (MD) simulations by Morales *et al.*[40] They have analyzed their EOS data and derived a new high-pressure phase diagram with a liquid-liquid coexistence line and a critical point which is predicted near 2000 K and 120 GPa. They have also calculated the high-pressure melting line up to 200 GPa and predict an intersection with the liquid-liquid coexistence line (i.e., a new triple point) at about 700 K and 220 GPa (FT-DFT-MD) or 550 K and 290 GPa (QMC), respectively. Detailed information on the changes in the structural and electronic properties with density and temperature clearly shows that the nonmetal-to-metal transition in dense liquid hydrogen drives this first-order phase transition.

In this paper we present results for the EOS, the electrical conductivity, and the pair-correlation functions in liquid hydrogen which have been obtained independently by using FT-DFT-MD simulations. We confirm the first-order phase transition as reported by Morales *et al.*[40] but find a slightly different location for the critical point at about 1500 K and 140 GPa; we present the respective high-pressure phase diagram. Furthermore, we have performed extensive calculations of the electrical conductivity which shows a pronounced jump of up to four orders of magnitude when crossing the coexistence line. The transition from a molecu-

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lar to an atomic liquid is also reflected in respective changes in the pair-correlation functions. In addition, we have performed detailed convergence checks in order to study the influence of the particle number and of the time step duration in the FT-DFT-MD simulations on the results which have proven to be robust. It would be very desirable to check the new theoretical predictions experimentally, e.g., via isentropic shock compression and/or x-ray scattering techniques.[46]

II. THEORETICAL METHOD

The method used here combines a classical molecular-dynamics simulation for the ions and a quantum mechanical treatment of the electrons based on FT-DFT, which is implemented in the code VASP.[47] For each MD step the electronic density is calculated and the ions are moved according to the forces acting on them which are determined via the Hellmann-Feynman theorem. This procedure is repeatedly performed for several thousand time steps of 0.3–1 fs so that the total simulation time amounts up to 10 ps. The deviations in the equation of state data between the different time steps is below 1%, the transition pressure differs up to 2%. After the simulations have reached thermodynamic equilibrium, thermodynamic quantities such as the pressure and internal energy are derived from mean values averaged over the following several thousand time steps. Although simulations with 64 atoms already give a convergence of better than 1% compared to calculations with higher numbers in a wide density range, reaching convergence at or near to the phase transition is more difficult so that we have considered always 512 atoms in a cubic simulation box with periodic boundary conditions. We have also done convergence tests with up to 1024 atoms but no further changes in the results were obtained.

For the DFT calculations we used the generalized gradient approximation (GGA) exchange-correlation functional in the parametrization of Perdew, Burke, and Ernzerhof.[48] Convergence was checked with respect to the **k**-point sets used for the evaluation of the Brillouin zone and the energy cutoff for the plane-wave basis set. For the determination of the EOS data we chose the Baldereschi mean value point,[49] which reproduces the location of the phase transition calculated with a $3\times3\times3$ Monkhorst-Pack[50] **k**-point set much better than calculations at the Γ point. Together with an energy cutoff of 1200 eV we reach convergence of better than 1% compared to higher **k**-point sets and higher energy cutoffs. We calculated the electrical conductivity via the Kubo-Greenwood formula[51] for 20 snapshots of the simulations, where we used a $4\times4\times4$ Monkhorst-Pack **k**-point set for sampling the Brillouin zone.

In order to illustrate the important convergence issues, we present in Fig. 1 the results for the pressure at 1000 K and 1 g/cm^3 as function of the particle number used in the FT-DFT-MD simulations for different **k** points chosen for the integrals over the Brillouin zone. The widely used Γ point has in this case a very nonsystematic convergence behavior, which was already reported by Tamblyn *et al.*[39] Evaluation of the pair-correlation functions (see Sec. III C) shows different structures depending on the particle number, resulting in the different pressures in Fig. 1. In contrast, calculations employing the Monkhorst-Pack $3\times3\times3$ **k**-point set[50] do not show this behavior and are already converged within 0.5% using 64 atoms compared to calculations with 512 atoms. The results obtained with the Baldereschi mean value point[49] usually agree within 1% compared to the results of the $3\times3\times3$ **k**-point set, giving a very reasonable compromise between computational time and accuracy. Note that this peculiar convergence behavior is due to the rapid dissociation of the hydrogen molecules near the phase transition and not a general feature of the FT-DFT-MD method.

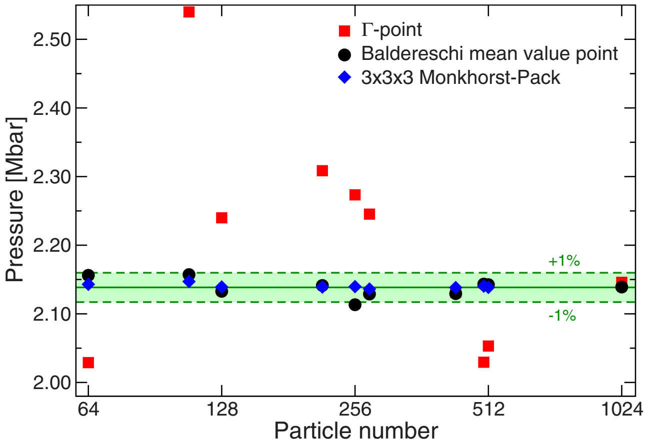

FIG. 1. (Color online) Convergence with respect to particle number at 1000 K and 1 g/cm^3 for calculations at the Γ point, the Baldereschi mean value point, and a $3\times3\times3$ Monkhorst-Pack grid. Each symbol corresponds to a full FT-DFT-MD simulation. The solid line corresponds to the pressure calculated with 512 atoms and a $3\times3\times3$ Monkhorst-Pack grid, assumed to be the most accurate result. The dashed lines indicate the region of 1% accuracy with respect to this value.

III. RESULTS

A. Equation of state

We have performed FT-DFT-MD simulations for liquid hydrogen in the density-temperature plane above the predicted high-pressure melting line,[4] i.e., for $500\text{ K}\leq T\leq1500\text{ K}$ and $0.7\text{ g/cm}^3\leq\varrho\leq1.1\text{ g/cm}^3$; the respective pressure range is 1–3 Mbar. Results for the thermal EOS $p(\varrho,T)$ are shown in Fig. 2, along with the results by Morales *et al.*[40] The pressure isotherms are only weakly dependent on temperature, in good agreement with previous results.[52] We can identify a first-order phase transition as in Ref. 40 by inspecting the thermodynamic stability condition $(\partial p/\partial\rho)_T\geq0$. A Maxwell construction yields constant pressures in the coexistence region along the isotherms below 1500 K. The respective density discontinuity amounts up to 3% which can only be resolved using a very fine mesh along the isotherms. Therefore, numerous large-scale FT-DFT-MD simulations have been performed (each symbol in Fig. 2 represents a full FT-DFT-MD simulation). This phase transition shifts to lower densities with higher temperatures and becomes continuous above a temperature of 1500 K. The transition pressures are in good agreement with the results of

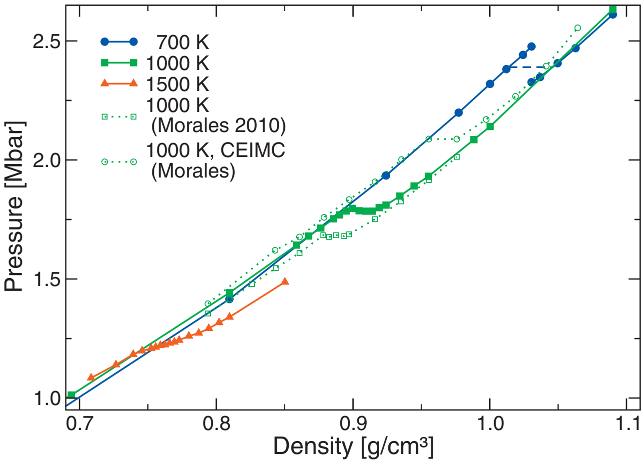

FIG. 2. (Color) Thermal EOS of dense hydrogen. A first-order phase transition is observed for temperatures below 1500 K and a Maxwell construction is performed (dashed line). The results are in good agreement with DFT and CEIMC calculations (Ref. 40).

Morales *et al.*,[40] lying between their DFT and coupled electron-ion Monte Carlo (CEIMC) results.

B. Electrical conductivity

The nature of this first-order phase transition requires further attention. Based on earlier work on dense hydrogen we expect an important influence of the transformation from a molecular to an atomic fluid at high pressures which is connected with a simultaneous transition from insulating or semiconducting behavior to a conducting fluid as experimentally verified.[30,31,33] Therefore, we have performed extensive calculations of the electrical conductivity by evaluating the Kubo-Greenwood formula, see Refs. 37, 53, and 54 for details.

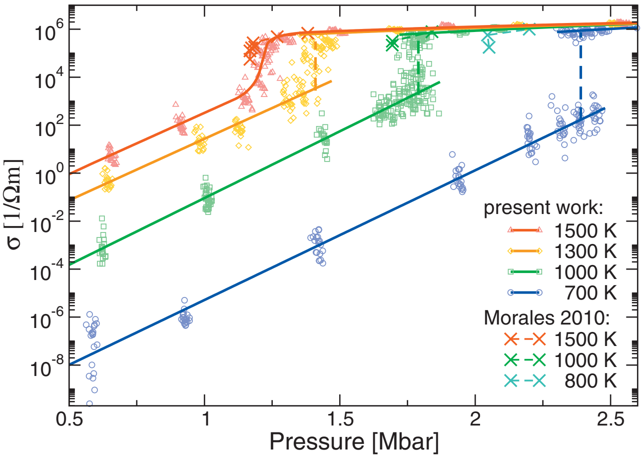

FIG. 3. (Color) Isotherms of the electrical conductivity in dense liquid hydrogen as function of pressure. Each point in the diagram corresponds to one snapshot of the simulation. The solid lines are fits to these points. For temperatures below 1500 K pronounced jumps (dashed lines) indicate the discontinuous nonmetal-to-metal transition. Also shown are the results from Ref. 40.

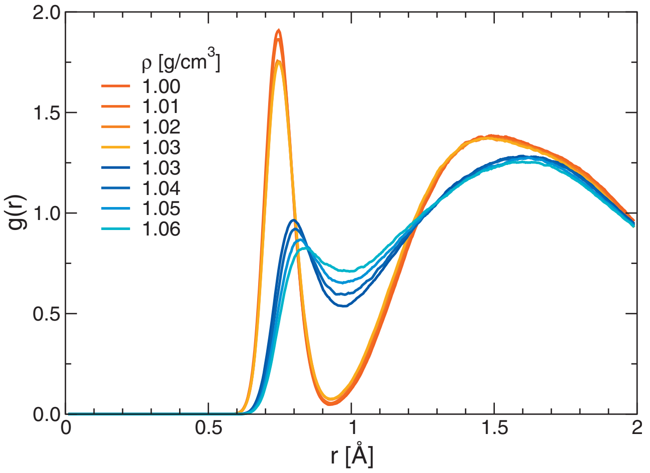

FIG. 4. (Color) Variation in the proton-proton pair-correlation function $g(r)$ in liquid hydrogen in the coexistence region as function of the density along the 700 K isotherm. The abrupt transition from the nonmetallic phase with a pronounced molecular peak to a metalliclike liquid occurs at 1.03 $\mathrm{g/cm^3}$.

The isotherms of the electrical conductivity displayed in Fig. 3 (shown are results for each snapshot, lines are fits to these data) exhibit a characteristic dependence on pressure and temperature. For temperatures below 1500 K, the conductivity increases strongly with the pressure and shows a pronounced jump in the coexistence region which amounts up to three to four orders of magnitude. This jump indicates that the phase transition occurs between a nonmetallic liquid and a liquid with typical metalliclike conductivity. For higher temperatures the increase in the conductivity with the pressure is continuous but still very steep. This supercritical region has been probed with quasi-isentropic shock-compression experiments,[33] their continuous slope (see also Fig. 6) is in agreement with our results. The present results are also in agreement with the calculations of Morales *et al.*[40] but extend to lower pressures where a behavior as typical for semiconductors is found. Note that we were able to determine the conductivity within the FT-DFT-MD schema for values as low as $1\times10^{-8}/\Omega$ m, i.e., many orders of magnitude below the usual metallic conductivity.

The electrical conductivity becomes almost independent of temperature in the high-pressure region. We attribute this

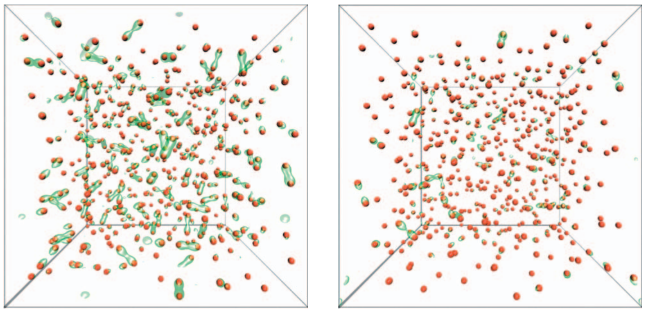

FIG. 5. (Color) Snapshots of the simulation box at 700 K and 1.03 $\mathrm{g/cm^3}$, visualized with the VMD program (Ref. 56). Shown are the ions (red spheres) and the isosurfaces of the electron density (n_e=2/Å^3) (green) in (a) the molecular phase and (b) the metallic phase.

behavior to the formation of a degenerate electron liquid[55] as a result of purely pressure-driven band-gap closure (or ionization in chemical models) at low temperatures as considered here. At higher temperatures, thermal effects lead to an earlier occupation of states in the conduction band (or thermal ionization) and a less pronounced increase in the conductivity occurs. These results confirm the interplay between pressure and thermal effects during the nonmetal-to-metal transition in dense liquid hydrogen at finite temperatures which can be treated consistently within the present FT-DFT-MD approach.

C. Pair-correlation functions

The transition from a nonmetallic to a conducting liquid is accompanied by rapid dissociation of molecules as can be seen from the proton-proton pair-correlation functions displayed in Fig. 4 for the 700 K isotherm. The molecular peak vanishes abruptly at 1.03 $\mathrm{g/cm^3}$ in the coexistence region.

To illustrate this behavior further we show in Fig. 5 isosurfaces of the electron density at this specific condition for one snapshot in the molecular and one snapshot in the metallic phase. One can clearly see in (a) that the electronic density is pronounced between pairs of protons, indicating still a molecular structure, while for (b) the electron density is more homogeneous, as characteristic for a degenerate electron liquid, see above. This behavior is similar for the other temperatures, although the transition becomes less sharp with increasing temperature.

D. Phase diagram

Finally, we show the resulting high-pressure phase diagram for hydrogen in Fig. 6 with the new coexistence line; the melting line taken from Ref. 4 represents experimental data as well as *ab initio* calculations while the melting line from Ref. 40 is based purely on *ab initio* data. Interestingly, the slope of our coexistence line, although systematically a bit lower, is in very good agreement with the transition line between a molecular and an atomic fluid as predicted by Tamblyn and Bonev[38] recently. Their first-principles molecular-dynamics study is also based on DFT in GGA but uses the CPMD code within the Born-Oppenheimer approximation. They concluded from their data that the molecular-to-atomic transition in the liquid might be of first order below 1000 K but a very fine sampling of the phase diagram would be necessary to confirm their prediction—as we have done in the present work. Although we find a very similar coexistence line to the results by Morales *et al.*,[40] our results indicate a continuous transition already at 1500 K, in agreement with earlier Quantum Monte Carlo simulations by Delaney *et al.*[41]

Our extensive FT-DFT-MD simulations have confirmed the discontinuous nature of that transition and enable us to give an estimate for the critical point which we locate at $T_c = (1400 \pm 100)$ K, $P_c = (1.32 \pm 0.1)$ Mbar, and $\varrho_c = (0.79 \pm 0.05)$ $\mathrm{g/cm^3}$, i.e., at lower temperatures than predicted in Ref. 40. The shock-wave experiments[33,58] have indicated a continuous transition to metalliclike conductivities, in agreement with our results which locate their path in the supercritical region, see Fig. 6. We can also give a rough estimate for the intersection of the coexistence line with the extrapolated melting line. The new triple point should be located below 500 K and above 3.5 Mbar if using the extrapolation of Ref. 4 for the high-pressure melting line, or at 685 K and 2.75 Mbar in the case of the new melting line given in Ref. 40. Evaluation of the Clausius-Clapeyron equation with our EOS data gives the same slope of the coexistence line shown in Fig. 6.

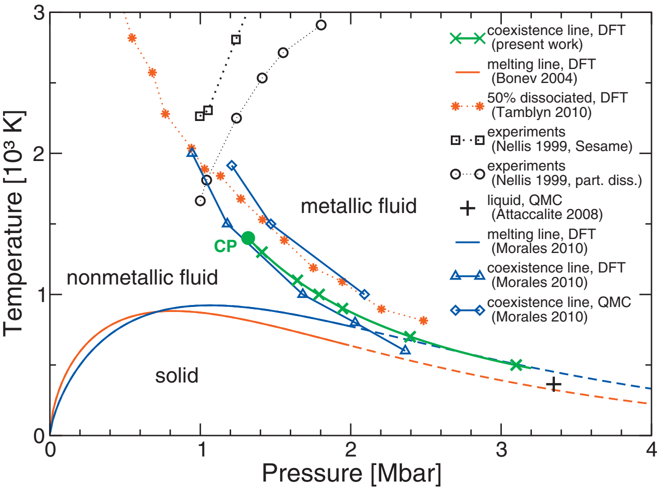

FIG. 6. (Color) High-pressure phase diagram of hydrogen with the predicted first-order liquid-liquid phase transition (solid line with crosses), including an estimate for the critical point. The results are in agreement with the DFT results by Morales *et al.* (Ref. 40). The CEIMC results have a similar slope but are located at slightly higher temperatures, coinciding with the molecular-to-atomic transition line given in Ref. 38. The melting lines are taken from Refs. 4 and 40. The extrapolation given in Ref. 4 is consistent with QMC calculations for the liquid (Ref. 57). Also shown are possible paths of the shock-wave experiments (Ref. 33), depending on the EOS (partial dissociation model and Sesame tables) used to derive the temperatures (Ref. 58).

E. Conclusions

In summary, we have performed extensive FT-DFT-MD simulations for the EOS of dense hydrogen which show clear evidence for the existence of a first-order phase transition between a nonmetallic and conducting liquid. The convergence of the *ab initio* simulations is sensitive with respect to the **k**-point sampling, especially in the transition region. The two phases are also identified by a simultaneous calculation of the electrical conductivity and the pair-correlation functions. Both physical quantities exhibit dramatic changes during the transition. We were able to resolve the semiconducting behavior in the molecular fluid. The fine mesh of *ab initio* EOS data allows us to locate the coexistence line in the usual pressure-temperature phase diagram, see Fig. 6. We give an estimate for the location of the critical point of this liquid-liquid transition as well as an approximate value for the triple point between the solid and the two liquid phases. These results let us conclude that the existence of another first-order phase transition, i.e., the controversially discussed *plasma phase transition* above 10 000 K, is highly unlikely. Furthermore, our results show no evidence for an intermediate semiconducting atomic phase between the nonmetallic molecular phase and the conducting (plasma) phase. The behavior at even higher pressures and low temperatures, for example, the existence and location of the triple point, remains subject of further work. The experimental verification of the proposed new phase diagram is a great challenge since high pressures have to be probed at low temperatures.

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