

# Phase Transition in Strongly Degenerate Hydrogen Plasma<sup>1</sup>

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Direct fermionic path-integral Monte Carlo simulations of strongly coupled hydrogen are presented. Our results show evidence for the hypothetical plasma phase transition. Its most remarkable manifestation is the appearance of metallic droplets, which are predicted to be crucial for the electrical conductivity and allow one to explain the rapid increase found in recent shock compression measurements. © 2001 MAIK “Nauka/Interperiodica”.

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Hydrogen at high pressures remains the subject of many investigations (see, e.g., [1, 2] for an overview). Many interesting phenomena, such as the metal–insulator transition (MIT), the Mott effect and the plasma phase transition (PPT) have been predicted. They occur in situations where both quantum and Coulomb effects are important, making a theoretical analysis difficult. Among the most promising theoretical approaches to such systems is the path-integral quantum Monte Carlo (PIMC) method [3, 4], which has seen remarkable progress recently (e.g., [4, 5]). However, for Fermi systems, these simulations are substantially hampered by the so-called fermion sign problem. Additional assumptions, such as fixed node and restricted path concepts, have been introduced to overcome this difficulty [4]. It can be shown, however, that such assumptions do not reproduce the correct ideal Fermi gas limit [6].

Recently, we presented a new path-integral representation which avoids additional approximations, (direct path-integral Monte Carlo, DPIMC) which has successfully been applied to strongly coupled hydrogen [7–9] (see below). In this work, we apply the DPIMC method to the analysis of dense liquid hydrogen in the region of the hypothetical plasma phase transition [1, 10, 11, 12]. Computing the equation of state and the internal energy, we find clear indications for the existence of the PPT—its first confirmation by a *first-principle* method. It is shown that the PPT manifests itself by the formation of large metallic droplets, which are crucial for plasma transport properties.

It is well known that the thermodynamic properties of a quantum system are fully determined by the partition function  $Z$ . For a binary mixture of  $N_e$  electrons and

$N_i$  protons,  $Z$  can be written as

$$Z(N_e, N_i, V, \beta) = Q(N_e, N_i, \beta) / N_e! N_i!, \quad (1)$$

$$Q(N_e, N_i, \beta) = \sum_{\sigma} \int d\mathbf{q} d\mathbf{r} \rho(\mathbf{q}, \mathbf{r}, \sigma; \beta).$$

Here,  $\mathbf{q} \equiv \{\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_i}\}$  are the coordinates of the protons;  $\sigma \equiv \{\sigma_1, \dots, \sigma_{N_e}\}$  and  $\mathbf{r} \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_{N_e}\}$  are the electron spins and coordinates, respectively; and  $\beta \equiv 1/k_B T$ . The density matrix  $\rho$  in Eq. (1) is represented in the common way by a path integral [13]:

$$\rho(\mathbf{q}, \mathbf{r}, \sigma; \beta) = \frac{1}{\lambda_i^{3N_i} \lambda_{\Delta}^{3N_e}} \sum_P (\pm 1)^{\kappa_P} \times \int_V d\mathbf{r}^{(1)} \dots d\mathbf{r}^{(n)} \rho(\mathbf{q}, \mathbf{r}, \mathbf{r}^{(1)}; \Delta\beta) \dots \rho(\mathbf{q}, \mathbf{r}^{(n)}, \hat{P}\mathbf{r}^{(n+1)}; \Delta\beta) \mathcal{S}(\sigma, \hat{P}\sigma'), \quad (2)$$

where  $\Delta\beta \equiv \beta/(n+1)$  and  $\lambda_{\Delta}^2 = 2\pi\hbar^2\Delta\beta/m_e$ . Further,  $\mathbf{r}^{n+1} \equiv \mathbf{r}^n$ ,  $\sigma' = \sigma$ ; i.e., electrons are represented by fermionic loops with the coordinates (beads)  $[\mathbf{r}] \equiv [\mathbf{r}, \mathbf{r}^{(1)}, \dots, \mathbf{r}^{(n)}, \mathbf{r}]$ . The electron spin gives rise to the spin part of the density matrix  $\mathcal{S}$ , whereas exchange effects are accounted for by the permutation operator  $\hat{P}$  and the sum over the permutations with parity  $\kappa_P$ .

Following [3], we use a modified representation (3) of the high-temperature density matrices on the right-hand side of Eq. (2), which is suitable for the efficient direct fermionic PIMC simulation of plasmas. With the error of the order  $\epsilon \sim (\beta Ry)^2 \chi/(n+1)$ , which vanishes

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with a growing number of beads, we obtain the approximation

$$\begin{aligned} \sum_{\sigma} \rho(q, r, \sigma; \beta) &= \frac{1}{\lambda_i^{3N_i} \lambda_{\Delta}^{3N_e}} \sum_{s=0}^{N_e} \rho_s(q, [r], \beta), \\ \rho_s(q, [r], \beta) &= \frac{C_{N_e}^s}{2^{N_e}} e^{-\beta U(q, [r], \beta)} \prod_{l=1}^n \prod_{p=1}^{N_e} \phi_{pp}^l \det |\Psi_{ab}^{n,1}|_s, \\ U(q, [r], \beta) &= U^i(q) + \sum_{l=0}^n \frac{U_l^e([r], \beta) + U_l^{ei}(q, [r], \beta)}{n+1}, \end{aligned} \quad (3)$$

where  $\chi$  is the degeneracy parameter and  $U^i$ ,  $U_l^e$ , and  $U_l^{ei}$  denote the sum of the binary Kelbg potentials  $\Phi^{ab}$  [14, 15] between protons, electrons at vertex “ $l$ ,” and electrons (vertex “ $l$ ”) and protons, respectively.

In Eq. (3),  $\phi_{pp}^l \equiv \exp[-\pi |\xi_p^{(l)}|^2]$  arises from the kinetic-energy part of the density matrix of the electron with index  $p$ , and we introduced dimensionless distances between the neighboring vertices on the loop,  $\xi^{(1)}, \dots, \xi^{(n)}$ . Finally, the exchange matrix is given by

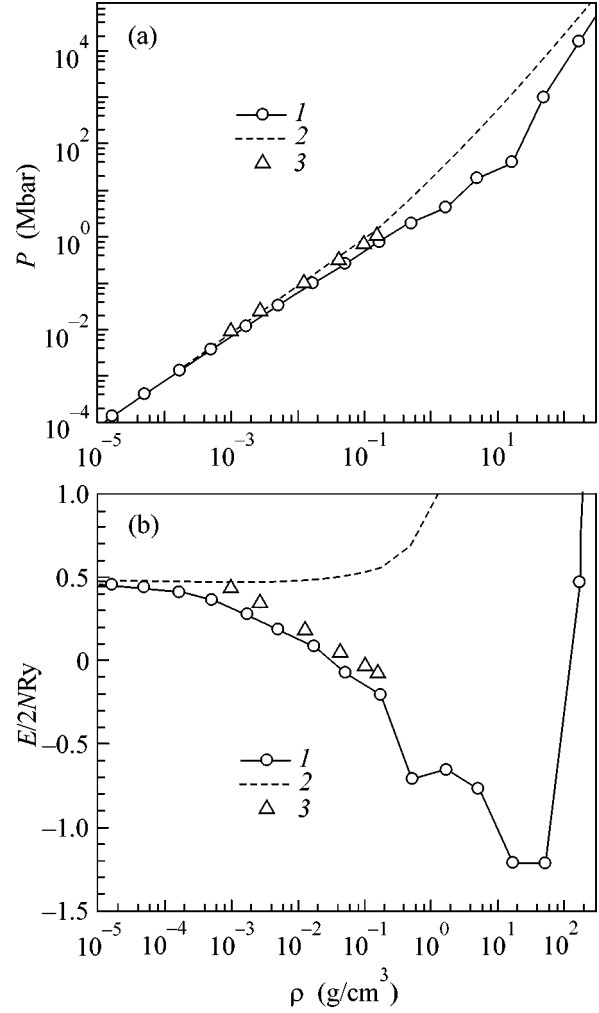
$$\begin{aligned} \|\Psi_{ab}^{n,1}\|_s &\equiv \left\| \exp \left\{ -\frac{\pi}{\lambda_{\Delta}^2} |(r_a - r_b) + y_a^n|^2 \right\} \right\|_s, \\ \text{with } y_a^n &= \lambda_{\Delta} \sum_{k=1}^n \xi_a^{(k)}, \end{aligned}$$

where the subscript  $s$  denotes the number of electrons having the same spin projection. From the above Eqs. (1)–(3), one readily computes the internal energy and the equation of state:

$$\beta E = \frac{3}{2}(N_e + N_i) - \beta \frac{\partial \ln Q}{\partial \beta}, \quad (4)$$

$$\beta p = \frac{\partial \ln Q}{\partial V} = \left[ \frac{\alpha}{3V} \frac{\partial \ln Q}{\partial \alpha} \right]_{\alpha=1}. \quad (5)$$

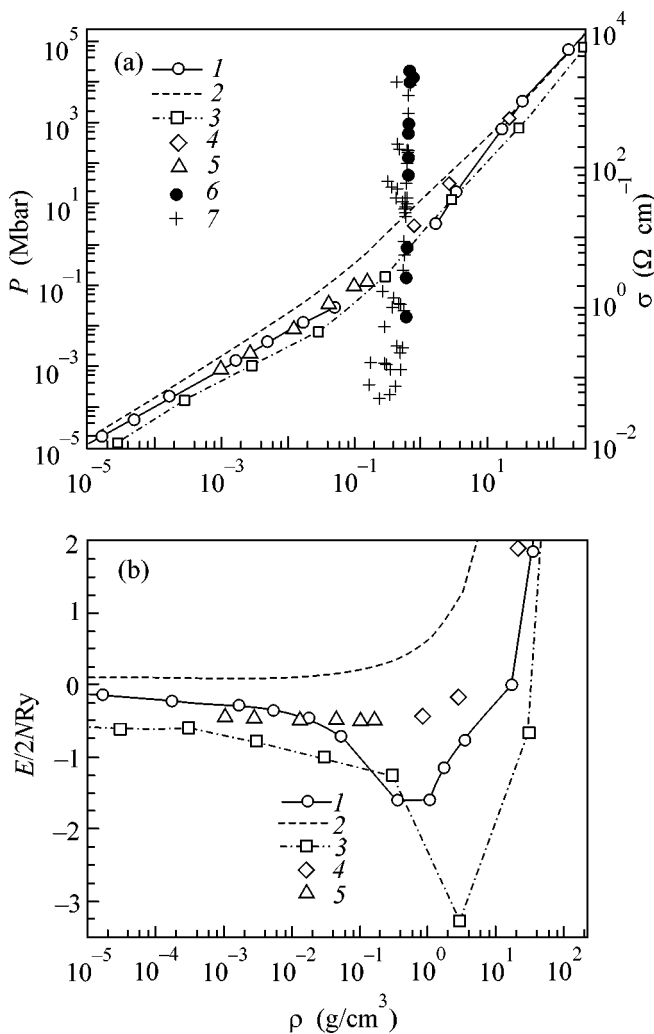
In our simulations, we used  $N_e = N_i = 50$  and  $n = 20$ . To test the MC procedure, we considered a mixture of *ideal* degenerate electrons and classical protons, for which the thermodynamic quantities are known analytically. The agreement, up to the degeneracy parameter  $\chi$  as large as 10, was very good and improved with increasing number of particles [7]. Further, the method was successfully tested in applications to electrons in a harmonic trap [16]. For the case of *interacting* electrons and protons in dense hydrogen, we previously performed a series of calculations over a wide range of the classical coupling parameter  $\Gamma$  and degeneracy  $\chi$  for temperatures  $T \geq 10000$  K. The analysis of the results clearly showed a number of interesting phenomena,



**Fig. 1.** (a) Pressure and (b) internal energy for hydrogen plasma at  $T = 5 \times 10^4$  K vs. density. (1) Direct PIMC simulation of this work, (2) ideal plasma, and (3) restricted PIMC computations at  $T = 6.25 \times 10^4$  K [17].

such as formation and decay of hydrogen bound states [8, 9, 15], including hydrogen atoms, molecules, molecular ions, clusters and, further, at high densities, pairing of electrons and ordering of protons into a Wigner crystal [9].

In this work, we present new results which concentrate on the hypothetical plasma phase transition [10]. For this purpose, we analyze the plasma properties and compute the equation of state (5) and internal energy (4) of dense hydrogen along two isotherms,  $T = 10^4$  K and  $5 \times 10^4$  K. Figure 1 shows pressure and energy vs. density at  $T = 5 \times 10^4$  K. For comparison, we also include the results for an ideal plasma. As expected, due to Coulomb interaction and bound-state formation, the nonideal plasma results are below the ideal ones. We mention that our results are in good agreement with the restricted path-integral calculations of Militzer and Ceperley (Fig. 1a contains available data points for a



**Fig. 2.** (a) (1–5) Pressure and (6, 7) electrical conductivity and (b) internal energy for hydrogen at  $T = 10^4$  K vs. density. (1) Direct PIMC simulation of this work, (2) ideal plasma, (3) direct PIMC simulation of a mixture consisting of 25% helium and 75% hydrogen, (4) density functional theory [20], (5) restricted PIMC computations [17], (6, 7) electrical conductivity of hydrogen (right axis), (6) [18], and (7) [19].

slightly higher temperature of  $6.25 \times 10^4$  K [17]). For higher temperatures, agreement is very good [15]. More importantly, at this temperature, pressure increases monotonically with density, and, at high densities, a continuous increase in the degree of ionization (Mott effect) is found.

However, at  $T = 10^4$  K, the properties of the hydrogen plasma change qualitatively (cf. Figs. 2, 3). While the overall trend of the pressure (Fig. 2a) is still a monotonic increase, in the density region of  $0.1 \dots 1.5 \text{ g/cm}^3$  the plasma exhibits unusual behavior. Inside this region, the Monte Carlo simulations do not converge to an equilibrium state; the pressure strongly fluctuated

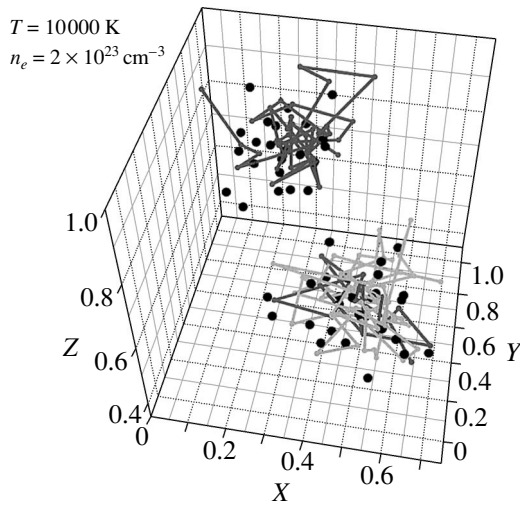
and reached even negative values. Such behavior is typical for Monte Carlo simulations of metastable systems.

Note that no such peculiarities appear for densities below and above this interval, as well as for the isotherm  $T = 5 \times 10^4$  K and for higher temperatures.

These facts suggest that our simulations encountered the plasma phase transition predicted by many chemical models of partially ionized hydrogen, e.g., in [1, 10, 11, 12]. According to these models, this is a first-order transition with two coexisting phases of different degrees of ionization. While canonical Monte Carlo simulations do not yield the coexisting phases and the coexistence pressure directly, they allow one to analyze in detail the actual microscopic particle configurations. A typical particle arrangement inside the instability region,  $T = 10^4$  K and  $\rho = 0.3346 \text{ g/cm}^3$ , is shown in Fig. 3. Obviously, the protons arrange themselves into large clusters (droplets), with the electrons (the piecewise linear lines show their closed fermionic path) being fairly delocalized over the cluster. This is a clear precursor of the metal-like state, which is found in the simulations for densities above the instability region.

As mentioned above, the plasma phase transition appears in many chemical models in the same density–temperature range. However, these simple approaches become questionable in the region of pressure ionization and dissociation, where the consistent treatment of all possible pair interactions, including charge–charge, neutral–neutral, and charge–neutral, is crucial. Furthermore, these approaches neglect larger bound aggregates such as clusters, which our simulations reveal to be crucial in the metastable region. We mention that indirect indications for a phase transition have been found in recent density-functional studies [20]. In this work, the thermodynamic properties of hydrogen in the metallic phase were computed (see data points in Fig. 2), and enhanced long-wavelength ion density fluctuations were observed as the density was reduced to  $\rho = 0.799 \text{ g/cm}^3$  (the lowest density explored). This led to unusual behavior of the ion–ion structure factor and the effective potential, which the authors of [20] interpreted as a possible precursor to an incipient metal-to-insulator transition.

Our simulations suggest that the existence of the PPT should have a noticeable influence on the transport properties. In fact, when the density changes from  $0.1 \dots 1.5 \text{ g/cm}^3$ , hydrogen transforms from a neutral into a metallic fluid. Accordingly, electrical conductivity should increase rapidly. Indeed, shock compression experiments have revealed a dramatic increase in the electrical conductivity by 4–5 orders of magnitude in a very narrow density range of  $0.3 \text{--} 0.5 \text{ g/cm}^3$  [18, 19]. So far, theoretical models cannot reproduce this behavior correctly, predicting either a too early (hopping conductivity in the molecular fluid) or too late (free electron conductivity) increase [21]. But, seeing as the experimental data (black circles and crosses in Fig. 2a) are located right inside the PPT region, one has to take



**Fig. 3.** Snapshot of a Monte Carlo cell at  $T = 10^4$  K and  $\rho = 0.3346$  g/cm<sup>3</sup>. Black circles are protons, and dark and light broken lines are representations of electrons as fermionic loops with different spin projections.

into account a third conductivity mechanism—charge transport via electron hopping between individual metal-like droplets. Obviously, this mechanism will be effective in between the regions where the two other effects dominate and thus should allow for a much better agreement with the experiments.

Finally, we mention that our simulations predict a PPT for pure hydrogen plasma only. In contrast, no PPT was found for a binary mixture of 25% of helium and 75% of hydrogen atoms (cf. Fig. 2).

In summary, we have presented direct path-integral Monte Carlo simulations of dense fluid hydrogen in the region of the MIT. Our results give evidence for the plasma phase transition, which, to the best of our knowledge, is its first prediction by a *first principle* theory. Most importantly, we found clear evidence for the formation of large metallic droplets which are predicted to play a crucial role in transport and optics in the region of the MIT at low temperatures. In further investigations, we will focus on a more precise analysis of the MIT and the plasma phase transition, including determination of its critical point and the transport and optical properties of the droplets.

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