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Plasma phase transition in hydrogen and electron-hole plasmas

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The plasma phase transition in dense hydrogen and in electron-hole plasmas is investigated by direct path integral Monte Carlo simulations. Hydrogen results for the internal energy at $T = 10,000$K show a deep minimum and strong fluctuations around the density $n = 10^{23}\text{cm}^{-3}$ indicating the existence of a phase transition. To verify this explanation, the analogous phenomenon is studied for an electron-hole plasma in Germanium. The calculated phase boundary of the electron-hole liquid is found to agree reasonably well with the available experimental data.

1 Introduction

Warm dense matter in general and high pressure hydrogen in particular have attracted inceased attention from experimentalists and theorists over the past decade. Among the phenomena of current interest are the high-pressure compressibility of deuterium, metallization of hydrogen, plasma phase transition etc., which occur in situations where both *interaction and quantum effects* are relevant [1, 2, 3, 4]. The path integral Monte Carlo (PIMC) method is particularly well suited to describe thermodynamic properties in the region of high density[5]. This is because it starts from the fundamental plasma particles - electrons and ions, (physical picture) and treats all interactions, including bound state formation, rigorously and selfconsistently. We apply direct PIMC simulations methods (DPIMC) to dense hydrogen in the region of the hypothetical plasma phase transition. New simulation results confirm the earlier observation of droplet formation and, at the same time, yield energies substantially above the previously found data [5, 6, 7, 8, 9]. This has been achieved by an improved treatment of many-particle exchange effects at high densities.

2 Summary of the path integral Monte Carlo simulations

First, we briefly outline the idea of our scheme. All thermodynamic properties of a two-component plasma are defined by the partition function Z which, for the case of N_e electrons and N_p protons, is given by $Z(N_e, N_p, V, \beta) = \frac{Q(N_e, N_p, \beta)}{N_e! N_p!}$ with $Q(N_e, N_p, \beta) = \sum_\sigma \int_V dq\, dr\, \rho(q, r, \sigma; \beta)$, where $\beta = 1/k_B T$. The exact density matrix is, for a quantum system, in general, not known but can be constructed using a path integral representation [5, 6, 7, 8, 9],
$\int_V dR^{(0)} \sum_\sigma \rho(R^{(0)}, \sigma; \beta) = \int_V dR^{(0)} \ldots dR^{(n)}\, \rho^{(1)} \cdot \rho^{(2)} \ldots \rho^{(n)} \times \sum_\sigma \sum_P (\pm 1)^{\kappa_P}\, \mathcal{S}(\sigma, \hat{P}\sigma')\, \hat{P} \rho^{(n+1)}$, where $\rho^{(i)} \equiv \rho\left(R^{(i-1)}, R^{(i)}; \Delta\beta\right) \equiv \langle R^{(i-1)} | e^{-\Delta\beta \hat{H}} | R^{(i)} \rangle$ and $\Delta\beta \equiv \beta/(n+1)$. $\hat{H}$ is the Hamilton operator, $\hat{H} =$

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$\hat{K}+\hat{U}_c$, containing kinetic and potential energy contributions, $\hat{K}$ and $\hat{U}_c$, respectively, with $\hat{U}_c = \hat{U}_c^p + \hat{U}_c^e + \hat{U}_c^{ep}$ being the sum of the Coulomb potentials between protons (p), electrons (e) and electrons and protons (ep). Further, σ comprises all particle spins, and the particle coordinates are denoted by $R^{(i)} = (q^{(i)}, r^{(i)}) \equiv (R_p^{(i)}, R_e^{(i)})$, for $i = 1, \ldots n+1$, $R^{(0)} \equiv (q, r) \equiv (R_p^{(0)}, R_e^{(0)})$, and $R^{(n+1)} \equiv R^{(0)}$ and $\sigma' = \sigma$. This means, the particles are represented by loops with the coordinates (beads) $[R] \equiv [R^{(0)}; R^{(1)}; \ldots; R^{(n)}; R^{(n+1)}]$, where q and r denote the electron and proton coordinates, respectively. The spin gives rise to the spin part of the density matrix $\mathcal{S}$, whereas exchange effects are accounted for by the permutation operator $\hat{P}$, which acts on the electron coordinates and spin projections, and the sum over the permutations with parity κ_P. In the fermionic case (minus sign), the sum contains $N_e!/2$ positive and negative terms leading to the notorious sign problem. Due to the large mass difference of electrons and ions, the exchange of the latter is not included. To describe interaction between beads of the two charged particles we use the effective quantum pair interaction potential Φ^{ab} immersed into a weakly degenerate plasma. It has been derived by Kelbg and co-workers [10, 11] who showed that it contains quantum effects exactly in first order in the coupling parameter Γ, $\Phi^{ab}(|\mathbf{r}_{ab}|, \Delta\beta) = \frac{e_a e_b}{\lambda_{ab} x_{ab}} \left\{1 - e^{-x_{ab}^2} + \sqrt{\pi}\, x_{ab}\, [1 - \mathrm{erf}(x_{ab})]\right\}$, where $x_{ab} = |\mathbf{r}_{ab}|/\lambda_{ab}$, and we underline that the Kelbg potential is finite at zero distance.

To compute thermodynamic functions, the logarithm of the partition function has to be differentiated with respect to thermodynamic variables. In particular, the internal energy E follows from Q by $\beta E = -\beta \partial \ln Q/\partial\beta$, This leads to the very complicated expression (for details, cf. [8]). Thus, the expressions for energy and pressure have been calculated by the standard Monte Carlo techniques.

3 Numerical results and discussion

Let us now come to the numerical results. The path integral representation for the N-particle density operator discussed above allows for *direct fermionic path integral Monte Carlo* (DPIMC) simulations of dense plasmas in a wide range of densities and temperatures. Using this concept, the pressure, energy and the pair distribution functions of a degenerated strongly coupled hydrogen plasma have been computed as well as in the region of partial ionization and dissociation [6, 7, 8, 9].

Before performing calculations in the region of the hypothetical plasma phase transition in hydrogen, we checked the correctness of our calculations in the region of strong electron degeneracy for two physical systems. The first system is a low-temperature 3D electron – hole plasma in Germanium, for which a lot of experimental data exists In particular, many measurements of the electron-hole liquid have been performed together with an extensive theoretical analysis, see e.g. [12] for an overview. Also, the phase boundary of the electron-hole liquid has been determined experimentally [13] and is reproduced in Fig. 1.

We have performed DPIMC simulations of the e-h plasma in Germanium in the region of the experimentally observed phase transition and present the calculated boundary in Fig. 1 as well. Inside this region, the homogeneous electron - hole plasma is unstable with respect to droplet formation which manifests itself, in the simulations, in strong fluctuations of pressure and energy. Fig. 1 shows reasonable agreement of the experimental data and our numerical results for Germanium. In the central part, the region of fluctuations extends significantly higher than in the experiments, indicating that there our curve provides rather an upper bound for the instability. Note that a possible source of the difference between our results and the experimental data is the very complicated band structure of Germanium, which in our model is approximated by an effective electron mass picture (parabolic dispersion). Evidently, this approximation is most accurate at the lowest temperature were all electrons and holes are residing in band regions close to the respective minimum. Such low temperatures occur at the wings of the phase boundary and, indeed, there we observe very good agreement with the experiment. We mention that the experiments directly observed the formation of e-h clusters (droplets) in the region of instability. Analogous electron-hole clusters have been found in our DPIMC simulations [14].

The second system which was used for preliminary tests is an ideal electron- proton plasma for which the energy and other thermodynamic quantities can be obtained analytically. From this comparison for the energy of an ideal Fermi gas we vierified that the Fermi statistics is well reproduced with a limited number of particles, $N \sim 100$ and beads, $n \sim 20$, up to the degeneracy parameter $n\lambda^3 \sim 100$. This comparison is included in Fig. 2, see the two curves labeled "ideal plasma".

This extension of the validity of our DPIMC simulations to such large values of the degneracy has been achieved by an improved numerical treatment of the electron exchange, see below.

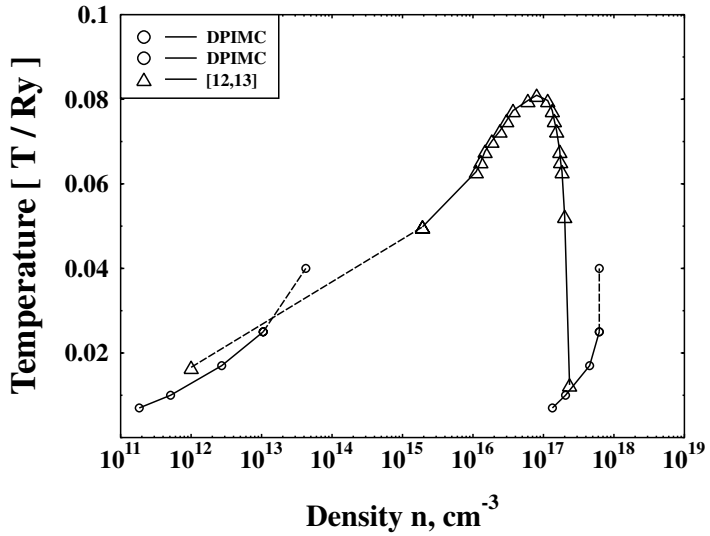

Fig. 1 Phase Boundary of the electron-hole liquid in Germanium. The "DPIMC" data mark the region were strong energy and pressure fluctuations are observed in the simulations and are an upper bound for the temperature of the phase transition.

Let us now turn to the results for dense *nonideal* hydrogen. in Fig. 2 we present new data for the isotherm $T = 10,000$K of the internal energy, together with results from various other theoretical approaches. The overall trend is an increase of the energy with density which is particularly rapid at high densities due to electron degeneracy effects; this is clearly seen from the analytical and numerical results for an *ideal plasma* (dash-dotted and dotted lines in of Fig. 2). The *nonideal plasma* results show an analogous trend. At intermediate densities, between 10^{22}cm^{-3} and 10^{23}cm^{-3}, the nonideal plasma energy is significantly lower than the ideal energy which is due to strong correlations and formation of bound states. In our previous calculations [14, 15], the energy around this minimum was unexpectedly low (below the molecular ground state). Here, we present new calculations where we increase the number of electrons taking part in the exchange interaction. In refs. [14, 15] the exchange interaction was taken into account only for electrons from one (basic) Monte Carlo cell, which becomes increasingly inaccurate at high densities. It is clear that with increasing density the ratio of the thermal electron wave length λ_e to the size of the Monte Carlo cell eventually exceeds one. Then it is essential to take into account also the exchange between electrons from the main cell with all electrons from the neighbor cells – first the $3^3 - 1$ nearest neighbor cells, then also the $5^3 - 1$ next to nearest neighbor and so on. Whith this improvement the exchange energy which contributes a positive (repulsive) term to the total energy is treated much more accurately yielding larger total energies than before: at the energy minimum we now observe a mean value of 0.6Ryd per $2N$ protons. As in our previous results, we observe strong fluctuations of the energy and other thermodynamic functions with an average magnitude of 0.4 Ryd per $2N$ protons (indicated by the points on the vertical line at $n = 10^{23}$cm^{-3}). These fluctuations are due to an instability of the homogeneous plasma state and indicate the existence of the plasma phase transition. This interpretation is supported by the observed plasma configuration which is characterized by formation of large droplets consisting of several atoms [9, 14]. The fact that this instability is related to a phase transition is confirmed by the analogous simulation results obtained for electron-hole plasmas in the region of the electron-hole liquid which were discussed above, see Fig. 1.

Let us briefly discuss the comparison of our results to other theoretical models. In Fig. 2. we also included data from a Padé approach within the chemical picture ("PACH", see e.g. [3, 15]), from an effective electron-ion potential model "EIIP" [15], from density functional theory ("DFT" [16]) and from restricted PIMC simulations "RPIMC".

[17, 18]. There is rather good agreement between the RPIMC, Padé and DFT results. At high densities where the correlation energy becomes comparatively small, the Padé and DFT data are rather close to each other which is not surprising, as the ideal Fermi gas limit is "built into" each of these three approaches. On the other hand, the EIIP and DPIMC data are significantly lower in the region of the energy minimum. This can be explained by the formation of atoms and molecules which are missing in this DFT approach, while the PACH results include

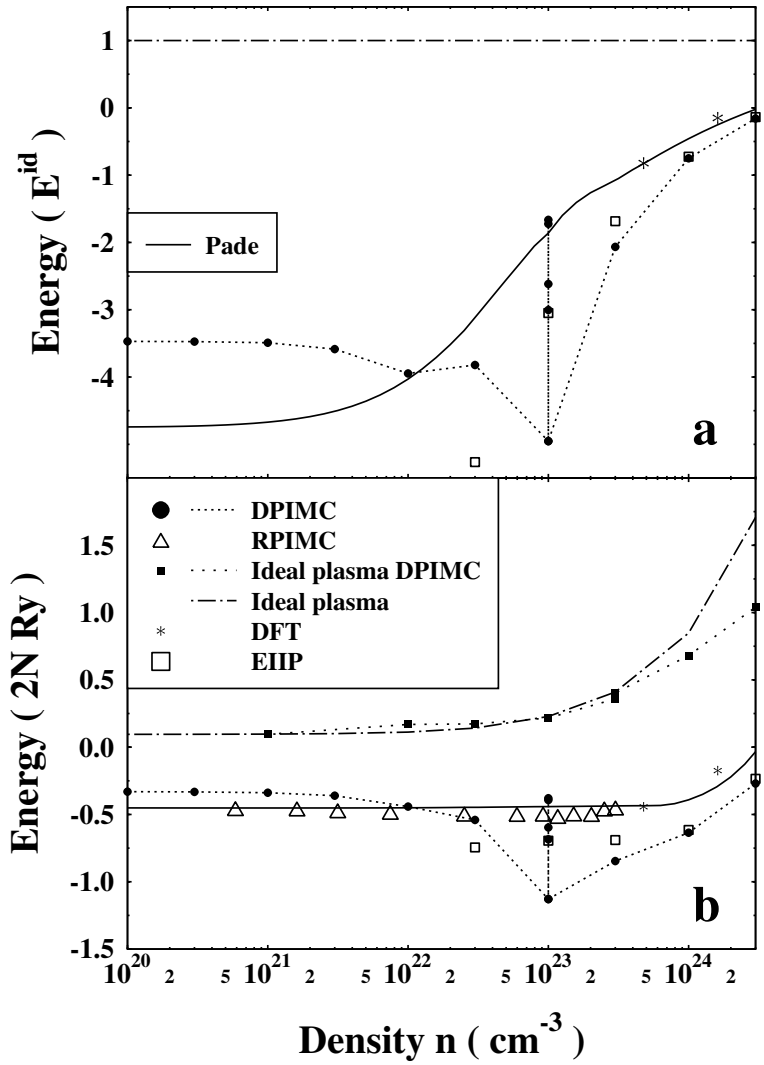

Fig. 2 Internal energy of hydrogen for $T = 10,000K$ in units of $2N$·Rydberg. The curves show results of PACH-calculations ("Pade"), our Monte Carlo simulations ("DPIMC"), density functional theory ("DFT") [16], the effective electron-ion interaction model (EIIP) and restricted PIMC data ("RPIMC") of Militzer et al. [17, 18]. Further, we compare DPIMC results for an ideal plasma ("Ideal plasma DPIMC") to the known analytical result ("Ideal plasma").

bound states only approximately. In contrast, the two quantum Monte Carlo simulations have no restrictions with respect to bound state formation. Our DPIMC data are still lower than the RPIMC results which is attributed to the choice of the nodes in the RPIMC simulations which, apparantly, do not allow for inhomogeneous plasma configurations.

Finally, we mention that the high-density asymptotics of our calculations which was substantially too low previously is now much improved as well. In the region beyond the instability (at densities exceeding $5 \cdot 10^{23}\mathrm{cm}^{-3}$) there is still a small off-set compared to the DFT and PACH data. This is not surprising since here the electron degeneracy exceeds 400 which is an enormous challenge for direct fermionic PIMC simulations. So we have to conclude that here the present treatment of the electron exchange is still not sufficiently accurate. This explanation is confirmed by the comparison of our ideal plasma simulations with the analytical results, see Fig 2. To further improve the simulation accuracy at high densities is subject of ongoing work.

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