Thermodynamics of hot dense H-plasmas: Path integral Monte Carlo simulations and analytical approximations

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Abstract

This work is devoted to the thermodynamics of high-temperature dense hydrogen plasmas in the pressure region between $10^{-1}$ and $10^2$ Mbar. In particular we present for this region results of extensive calculations based on a recently developed path integral Monte Carlo scheme (direct PIMC). This method allows for a correct treatment of the thermodynamic properties of hot dense Coulomb systems. Calculations were performed in a broad region of the nonideality parameter $\Gamma \lesssim 3$ and degeneracy parameter $n_e A^3 \lesssim 10$. We give a comparison with a few available results from other path integral calculations (restricted PIMC) and with analytical calculations based on Padé approximations for strongly ionized plasmas. Good agreement between the results obtained from the three independent methods is found.
I. INTRODUCTION

The thermodynamics of strongly correlated Fermi systems at high pressures are of growing importance in many fields, including shock and laser plasmas, astrophysics, solids and nuclear matter, see Refs. [1-4] for an overview. In particular the thermodynamical properties of hot dense plasmas under high pressure are of importance for the description of plasmas relevant for laser fusion [5]. Further among the phenomena of current interest are Fermi liquids, metallic hydrogen [6], plasma phase transition, e.g. [7] and references therein, bound states etc., which occur in situations where both Coulomb and quantum effects are relevant. There has been significant progress in recent years to study these systems analytically and numerically, see e.g. [6-10,13-15]. Due to the enormous difficulties to develop analytical descriptions for hydrogen plasmas with strong coupling, e.g. [1-3], there is still an urgent need to test the analytical theory by an independent numerical approach.

An approach which is particularly well suited to describe thermodynamic properties in the region of high pressure, characterized by strong coupling and strong degeneracy, is the path integral quantum Monte Carlo (PIMC) method. There has been remarkable recent progress in applying these techniques to Fermi systems, for an overview see e.g. Refs. [1,2,16-18]. However, these simulations are essentially hampered by the fermion sign problem. To overcome this difficulty, several strategies have been developed to simulate macroscopic Coulomb systems [8,19,20]: the first is the restricted PIMC concept where additional assumptions on the density operator $\hat{\rho}$ are introduced which reduce the sum over permutations to even (positive) contributions only. This requires knowledge of the nodes of the density matrix which is available only in a few special cases, e.g. [19,20]. However, for interacting macroscopic systems, these nodes are known only approximately, e.g. [21], and the accuracy of the results is difficult to assess from within this scheme. An alternative are direct fermionic PIMC simulations which have occasionally been attempted by various groups [22] but which were not sufficiently precise and efficient for practical purposes. Recently, three of us have proposed a new path integral representation for the N-particle density operator [23,24] which allows for direct fermionic path integral Monte Carlo simulations of dense plasmas in a broad range of densities and temperatures. Using this concept we computed the pressure and energy of a degenerate strongly coupled hydrogen plasma [24,26] and the pair distribution functions in the region of partial ionization and dissociation [26,27]. This scheme is rather efficient when the number of time slices (beads) in the path integral is less or equal 50 and was found to work well for temperatures $k_B T \gtrsim 0.1 R_y$. In this paper we derive further improved formulas for the pressure and energy and give, for the first time, a detailed derivation of all main results and rigorously justify the use of the effective quantum pair potential (Kelbg potential) in direct PIMC simulations. Further, in the present work this method will be applied to high-pressure plasmas ($p \approx 10^{-1} - 10^2$ Mbar) in such temperature regions were considerable deviations from the ideal behavior are observed.

One difficulty of PIMC simulations is that reliable error estimates are often not available, in particular for strongly coupled degenerate systems. Moreover, in this region no reliable data from other theories such as density functional theory or quantum statistics, e.g. [3,15], are available which would allow for an unambiguous test. Furthermore, results from classical molecular dynamics simulations exist, but they apply only to fully ionized and weakly
degenerate plasmas, e.g. [28–30], which is outside the range of interest for this work. Also, new quantum molecular dynamics approaches are being developed, e.g. [10–12], but they are only beginning to produce accurate results.

Therefore, it is of high interest to perform quantitative comparisons of independent simulations, such as restricted and direct fermionic PIMC, and to develop improved analytical approximations, which is the aim of this paper. We compare recent results of Militzer et al. [32] for pressure and energy isochors \((n \approx 2.5 \times 10^{23} \text{cm}^{-3})\) of dense hydrogen to our own direct PIMC results. This is a non-trivial comparison since the two approaches employ independent sets of approximations. Nevertheless, we find very good agreement for temperatures ranging from \(10^6\) K to as low as \(50,000\) K. This is remarkable since there the coupling and degeneracy parameters reach rather large values, \(\Gamma \approx 3\) and \(n_e \Lambda^3 \approx 10\), and the plasma contains a substantial fraction of bound states.

Further, we use the new data to make a comparison with analytical estimates which are based on Padé approximations for strongly ionized plasmas. These formulae were constructed on the basis of the known analytical results for the limiting cases of low density [3,33] and high density [3]. These Padé approximations are exact up to quadratic terms in the density and interpolate between the virial expansions and the high-density asymptotics [34–36]. We find that the results for the internal energy and for the pressure agree well with the PIMC results in the region of the density temperature plane, where \(\Gamma \lesssim 1.6\) and \(n \Lambda^3 \lesssim 5\).

II. PATH INTEGRAL REPRESENTATION OF THERMODYNAMIC QUANTITIES

We now our direct PIMC 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 [37],

\[
\int_V dR^{(0)} \sum_\sigma \rho(R^{(0)}, \sigma; \beta) = \int_V dR^{(0)} \cdots dR^{(n)} \rho^{(1)} \cdots \rho^{(n)} \times \sum_\sigma \sum_P (\pm 1)^{e_F} S(\sigma, \hat{P}_\sigma') \hat{P} \rho^{(n+1)},
\]

where \(\rho^{(i)} \equiv \rho(R^{(i-1)}, R^{(i)}; \Delta \beta) \equiv \langle R^{(i-1)} | e^{-\Delta \beta \hat{H}} | R^{(i)} \rangle\), whereas \(\Delta \beta \equiv \beta/(n + 1)\) and \(\Delta \lambda_a^2 = 2\pi \hbar^2 \Delta \beta / m_a\), \(a = p, e\). \(\hat{H}\) is the Hamilton operator, \(\hat{H} = \hat{K} + \hat{U}_c\), 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, \( R^{(i)} = (q^{(i)}, r^{(i)}) \equiv (R_{p}^{(i)}, R_{e}^{(i)}) \), 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 fermionic 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 \( S \), 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 \( \kappa_{p} \). 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. The matrix elements \( \rho^{(i)} \) can be rewritten identically as

\[
\langle R^{(i-1)} | e^{-\Delta \hat{H}} | R^{(i)} \rangle = \int d\hat{p}^{(i)} d\hat{p}^{(i)} \langle R^{(i-1)} | e^{-\beta \hat{U}_{c}} | \hat{p}^{(i)} \rangle \langle \hat{p}^{(i)} | e^{-\beta \hat{U}_{c}} | \hat{p}^{(i)} \rangle \langle \hat{p}^{(i)} | e^{-\Delta \hat{R}} | R^{(i)} \rangle.
\]

To compute thermodynamic functions, the logarithm of the partition function has to be differentiated with respect to thermodynamic variables. In particular, for the equation of state \( p \) and internal energy \( E \) follows,

\[
\begin{align*}
\beta p &= \partial \ln Q / \partial V = [\alpha / 3V \partial \ln Q / \partial \alpha]_{\alpha = 1}, \\
\beta E &= -\beta \partial \ln Q / \partial \beta ,
\end{align*}
\]

where \( \alpha \) is a length scaling parameter \( \alpha = L / L_{0} \). This means, in the path integral representation (2), each high-temperature density matrix has to be differentiated in turn. For example, the result for the energy will have the form

\[
\beta E = -\frac{1}{Q} \int_{V} dR^{(0)} \ldots dR^{(n)} \times \sum_{k=1}^{n+1} \rho^{(1)} \ldots \rho^{(k-1)} . \left[ \beta \frac{\partial \rho^{(k)}}{\partial \beta} \right] \cdot \rho^{(k+1)} \ldots \rho^{(n)} \sum_{\sigma} \sum_{p} (\pm 1)^{\kappa_{p}} S(\sigma, \hat{P} \sigma') \hat{P} \rho^{(n+1)},
\]

and, analogously for other thermodynamic functions.

There are two different approaches to evaluate this expression. One is to first choose an approximation for the high-temperature density matrices \( \rho^{(i)} \) and then to perform the differentiation. The other way is to first differentiate the operator expression for \( \rho^{(k)} \) and use an approximation for the matrix elements only in the final result. As we checked, the second method is more accurate and will be used in the following.

To evaluate the derivatives in Eq. (3), it is convenient to introduce dimensionless integration variables \( \eta^{(k)} = (\eta_{p}^{(k)}, \eta_{e}^{(k)}) \), where \( \eta_{a}^{(k)} = \kappa_{a} (R_{a}^{(k)} - R_{a}^{(k-1)}) \) for \( k = 1, \ldots , n \) and \( a = p, e \), and \( \kappa_{a}^{2} \equiv m_{a} k_{B} T / (2 \pi \hbar^{2}) = 1 / \lambda_{a}^{2} \). This has the advantage that now the differentiation of the density matrix affects only the interaction terms. Indeed, one can show that

\[
\beta \frac{\partial \rho^{(k)}}{\partial \beta} = -\beta \frac{\partial \Delta \rho_{c} \cdot U_{c}(X^{(k-1)})}{\partial \beta} \rho^{(k)} + \beta \rho_{\beta}^{(k)},
\]
where \( X^{(0)} \equiv (\kappa_p R_p^{(0)}, \kappa_e R_e^{(0)}) \), \( X^{(k)} \equiv (X_p^{(k)}, X_e^{(k)}) \), with \( X_a^{(k)} = \kappa_a R_a^{(0)} + \sum_{i=1}^{k} \eta_a^{(i)} \), and \( k \) runs from 1 to \( n \). Further, \( X^{(n+1)} \equiv (\kappa_p R_p^{(n+1)}, \kappa_e R_e^{(n+1)}) = X^{(0)} \), and we denoted

\[
\tilde{\rho}_\beta^{(k)} = \int dp^{(k)} \langle X^{(k-1)}| e^{-\Delta \beta \hat{U}_c} |p^{(k)}\rangle e^{-\beta_\beta (p^{(k)}|p^{(k)})} \langle p^{(k)}| \frac{\partial}{\partial \beta} e^{-\frac{1}{2} (\Delta \beta \hat{U}_c)} \cdots |X^{(k)}\rangle,
\]

where \( p_a^{(k)} = \tilde{p}_a^{(k)}/(\kappa_a \hbar) \), \( p(k) \equiv (p_p^{(k)}, p_e^{(k)}) \) and use has been made of Eq. (3). For \( k = n+1 \), we have

\[
\beta \frac{\partial}{\partial \beta} \sum_\sigma \sum_P \langle \pm 1 \rangle^{\kappa_P} S(\sigma, \hat{P} \hat{\sigma}') \hat{P} \rho^{(n+1)} = \sum_\sigma \sum_P \langle \pm 1 \rangle^{\kappa_P} S(\sigma, \hat{P} \hat{\sigma}') \times
\]

\[
\times \left\{ -\beta \frac{\partial \Delta \beta \cdot U_c(X^{(n)})}{\partial \beta} \hat{P} \rho^{(n+1)} + \hat{P} \left[ \beta \tilde{\rho}_\beta^{(n+1)} \right] \right\}.
\]

Further, \( U_c(X^{(k-1)}) \equiv U_c^{(1)}(X^{(k-1)}) + U_c^{(2)}(X^{(k-1)}) \), with \( U_c^{(1)} \) and \( U_c^{(2)} \) denoting the interaction between identical and different particle species, respectively, \( U_c^{(1)}(X) = U_c(X) + U_p(X) \) and \( U_c^{(2)}(X) = U_c^{ep}(X) \).

Using these results and Eq. (3), we obtain for the energy

\[
\beta E = \frac{3}{2} (N_e + N_p) - \frac{1}{Q} \chi_p^{3N_p} \chi_e^{3N_e} \int dR^{(0)} d\eta^{(1)} \cdots d\eta^{(n)} \sum_\sigma \sum_P \langle \pm 1 \rangle^{\kappa_P} S(\sigma, \hat{P} \hat{\sigma}') \times
\]

\[
\times \left\{ \sum_{k=1}^{n+1} \rho^{(1)} \cdots \rho^{(k-1)} \left[ -\beta \frac{\partial \Delta \beta \cdot U_c^{(1)}(X^{(k-1)})}{\partial \beta} - \beta \frac{\partial \Delta \beta \cdot U_c^{(2)}(X^{(k-1)})}{\partial \beta} + \beta \tilde{\rho}_\beta^{(n+1)} \right] \right\} \bigg|_{X^{(n+1)} = X^{(0)}, \sigma' = \sigma}.
\]

This way, the derivative of the density matrix has been calculated, and we turn to the next point - to find approximations for the high-temperature density matrix.

**III. HIGH-TEMPERATURE ASYMPTOTICS OF THE DENSITY MATRIX IN THE PATH INTEGRAL APPROACH. KELBG POTENTIAL**

In this section we derive an approximation for the high-temperature density matrix which is suitable for direct PIMC simulations. Further, we demonstrate that the proper choice of the effective quantum pair potential is given by the Kelbg potential. Following Refs. [16,38,39], we derive a modified representation for the density matrix. The main steps are:

1. The N-particle density matrix is expanded in terms of 2-particle, 3-particle etc. contributions from which only the first, \( \rho_{ab} \), is retained [16,38,39];

2. In the high-temperature limit, \( \rho_{ab} \) factorizes into a kinetic \( (\rho^0) \) and an interaction term \( (\rho^I_{ab}) \), \( \rho_{ab} \approx \rho_0 \rho^0_{ab} \), because it can be shown that [40,41]

\[
e^{-\frac{1}{2} (\Delta \beta \hat{U}_c)} = \hat{I} + O \left( \frac{1}{(n+1)^2} \right),
\]

\( (\Delta \beta \hat{U}_c) \) represents the kinetic and interaction terms.

This completes the derivation of the high-temperature density matrix approach.
where $\hat{I}$ is the unity operator. In this way we get the following representation for the two-particle density matrix

$$\rho_{ab} = \left( \frac{(m_a m_b)^{3/2}}{(2\pi\hbar^3)} \right) \exp[-\frac{m_a}{2\hbar^2 \beta}(r_a - r_a')^2] \exp[-\frac{m_b}{2\hbar^2 \beta}(r_b - r_b')^2] \exp[-\beta \Phi_{ab}] \tag{12}$$

where $\Phi_{ab}(r_a, r_a', r_b, r_b')$ is the off-diagonal two-particle effective potential.

3. In the following, the off-diagonal matrix elements of the effective binary potentials will be approximated by the diagonal ones by taking the Kelbg potential at the center coordinate, $\Phi^{ab}(r, r'; \Delta \beta) \approx \Phi^{ab}(\frac{r + r'}{2}; \Delta \beta)$.

4. For the plasma parameter region of interest, the protons can be treated classically, and $\Phi^{ii}$ may be approximated by the Coulomb potential.

We will now comment on these steps in some more detail. We calculated the effective potential by solving a Bloch equation by first order perturbation theory. The method has been described in detail in [11]. This procedure defines an effective off-diagonal quantum pair potential for Coulomb systems, which depends on the inter-particle distances $r_{ab}, r'_{ab}$. As a result of first-order perturbation theory we get explicitly

$$\Phi^{ab}(r_{ab}, r'_{ab}, \Delta \beta) \equiv e_a e_b \int_0^1 \frac{d\alpha}{d_{ab}(\alpha)} \text{erf} \left( \frac{d_{ab}(\alpha)}{2\lambda_{ab}\sqrt{\alpha(1-\alpha)}} \right) \tag{13}$$

where $d_{ab}(\alpha) = |\alpha r_{ab} + (1-\alpha)r'_{ab}|$, $\text{erf}(x)$ is the error function $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dt e^{-t^2}$, and $\lambda_{ab}^2 = \frac{\hbar^2 \Delta \beta}{2\mu_{ab}}$ with $\mu_{ab}^{-1} = m_a^{-1} + m_b^{-1}$. It is interesting to note, that a simple approximation of the complicated integral over $\alpha$ by the length of the interval multiplied with the integrand in the center (Mittelwertsatz) leads us to the so-called KTR-potential due to Klakov, Toepffer and Reinhard which (in the diagonal approximation) is often used in quasi-classical MD simulations [10,13]

$$\Phi^{ab}(r_{ab}, r'_{ab}, \Delta \beta) \equiv \frac{e_a e_b}{d_{ab}(1/2)} \text{erf} \left( \frac{d_{ab}(1/2)}{\lambda_{ab}} \right) \tag{14}$$

In our direct PIMC calculations we used the full expression for the interaction potential, keeping the $\alpha$-integration but, in order to save computer time, we approximated the two-particle interaction potential by its diagonal elements. The diagonal element ($r'_{ab} = r_{ab}$) of $\Phi^{ab}$ is just the familiar Kelbg potential, given by (we will use the same notation for the potential)

$$\Phi^{ab}(|r_{ab}|, \Delta \beta) \equiv \Phi^{ab}(r_{ab}, r_{ab}, \Delta \beta) = \frac{e_a e_b}{\lambda_{ab} x_{ab}} \left[ 1 - e^{-x_{ab}^2} + \sqrt{\pi} x_{ab} \left( 1 - \text{erf}(x_{ab}) \right) \right] \tag{15}$$

where $x_{ab} = |r_{ab}|/\lambda_{ab}$, and we underline that the Kelbg potential is finite at zero distance. The error of the above approximations, for each of the high-temperature factors on the r.h.s. of Eq. (2), is of the order $1/(n+1)^2$.

With these approximations, we obtain the result $\rho^{(k)} = \rho_0^{(k)} \rho_U^{(k)} + O[1/(n+1)^2]$, where $\rho_0^{(k)}$ is the kinetic density matrix, while $\rho_U^{(k)} = e^{-\Delta \beta U(X^{(k-1)})} \delta(X^{(k-1)} - X^{(k)})$, where $U$ denotes
the following sum of Coulomb and Kelbg potentials, $U(X^{(k)}) = U^p(X_p^{(k)}) + U^e(X_e^{(k)}) + U^{ep}(X_p^{(k)}, X_e^{(k)})$. Notice that special care has to be taken in performing the derivatives with respect to $\beta$ of the Coulomb potentials which appear in Eq. (10). Indeed, products $\rho^{(1)} \ldots \rho^{(n+1)} \beta \frac{\partial \Delta \beta U_c(X^{(k-1)})}{\partial \beta}$ have a singularity at zero interparticle distance which is integrable but leads to difficulties in the simulations. Due to the Kelbg potential, for the e-e and p-p interaction, this singularity is weakened, but it is enhanced for the e-p interaction. In order to assure efficient simulations we, therefore, further transform the e-p contribution in the following way:

$$\int_0^1 d\alpha \int dR^{(k-1)} \langle R^{(k-2)} | e^{-\Delta \beta K} | R^{(k-1)} \rangle \left[ -\beta \frac{\partial}{\partial \beta} (\Delta \beta U_c^{(2)}(R^{(k-1)})) \right]$$

$$\times \langle R^{(k-1)} | e^{-\Delta \beta K} | R^{(k)} \rangle$$

$$\approx \langle R^{(k-1)} | e^{-\Delta \beta K} | R^{(k)} \rangle \left[ -\beta \frac{\partial}{\partial \beta} (\Delta \beta U_c^{(2)}(R^{(k-1)})) \right] + O \left( \frac{1}{n^2} \right). \quad (16)$$

This means, within the standard error of our approximation $O \left( \Delta \beta^2 \right)$, we have replaced the e-p Coulomb potential $U_c^{(2)}$ by the corresponding Kelbg potential $U^{(2)}$, which is much better suited for MC simulations.

Thus, using $\lambda_p \ll \lambda_e$, we finally obtain for the energy:

$$\beta E = \frac{3}{2} (N_e + N_p) + \frac{1}{Q} \lambda_p^{3N_p} \Delta \lambda_e^{3N_e} \sum_{s=0}^{N_e} \int dq \, dr \xi \rho_s(q, |r|, \beta) \times$$

$$\left\{ \sum_{p<t} N_p \beta e^2 |q_{pt}| + \sum_{l=0}^{n} \left[ \sum_{p<t} N_p \Delta \beta e^2 |r_l^{pt}| + \sum_{p=1}^{N_p} \sum_{t=1}^{N_e} \Psi_l^{ep} \right] \right.$$  

$$+ \sum_{l=1}^{n} \left[ - \sum_{p<t} C_l^{pt} \frac{\Delta \beta e^2}{|r_l^{pt}|^2} + \sum_{p=1}^{N_p} \sum_{t=1}^{N_e} D_l^{pt} \frac{\partial \Delta \beta \Phi^{ep}}{\partial |x_l^{pt}|} \right]$$

$$- \frac{1}{\det |\psi_{ab}^{n+1}|} \frac{\partial \det |\psi_{ab}^{n+1}|}{\partial \beta} \right\}, \quad (17)$$

and $\Psi_l^{ep} = \Delta \beta \partial [\beta' \Phi^{ep}(|x_l^{pt}|, \beta')]/\partial \beta'|_{\beta=\Delta \beta}$ contains the electron-proton Kelbg potential $\Phi^{ep}$. Here, $\langle \ldots | \ldots \rangle$ denotes the scalar product, and $q_{pt}$, $r_{pt}$ and $x_{pt}$ are differences of two coordinate vectors: $q_{pt} \equiv q_p - q_t$, $r_{pt} \equiv r_p - r_t$, $x_{pt} \equiv x_p - q_t$, $r_{pt}^{l} = r_p + y^{l}_{pt}$, $x_{pt}^{l} \equiv x_p + y^{l}_{pt}$, with $y^{l}_{pt} \equiv y^{l}_{p} - y^{l}_{t}$, with $y^{l}_{a} = \Delta \lambda_e \sum_{k=1}^{n} \xi^{(k)}._{a}$. Here we introduced dimensionless distances between neighboring vertices on the loop, $\xi^{(1)}, \ldots, \xi^{(n)}$, thus, explicitly, $|r| \equiv |r; y_e^{(1)}; y_e^{(2)}; \ldots |$. Further, the density matrix $\rho_s$ in Eq. (17) is given by

$$\rho_s(q, |r|, \beta) = C^{eS}_{N_e} e^{-\beta U(q, |r|, \beta)} \prod_{l=1}^{n} \prod_{p=1}^{N_e} \phi^{l}_{pp} \det |\psi_{ab}^{n+1}|_{s}, \quad (18)$$
where \( U(q, [r], \beta) = U_p(q) + \{ U^e([r], \Delta \beta) + U^{ep}(q, [r], \Delta \beta) \} / (n + 1) \) and \( \phi_{pp}^l \equiv \exp[-\pi |\xi_p^{(l)}|^2] \).

We underline that the density matrix (18) does not contain an explicit sum over the permutations and thus no sum of terms with alternating sign. Instead, the whole exchange problem is contained in a single exchange matrix given by

\[
||\psi_{ab}^{n,1}||_s \equiv ||e^{-\frac{n}{2\Delta \xi}((r_a - r_b) + y_n^a)}||_s.
\]

(19)

As a result of the spin summation, the matrix carries a subscript \( s \) denoting the number of electrons having the same spin projection. For more details, we refer to Refs. [23, 24].

In similar way, we obtain the result for the equation of state,

\[
\frac{\beta p V}{N_e + N_p} = 1 + \frac{1}{N_e + N_p} \frac{(3Q)^{-1}}{\lambda_p^3 N_p^3 \lambda_e^3 N_e^3} \sum_{s=0}^{N_e} \int dq dr d\xi \rho_s(q, [r], \beta) \times
\]

\[
\left\{ \sum_{p<t} \beta e^2 \frac{x_{pt}}{|q_{pt}|} + \sum_{p<t} \Delta \beta e^2 \frac{x_{pt}}{|r_{pt}|} - \sum_{p=1}^{N_p} \sum_{t=1}^{N_e} \frac{\partial \Delta \beta \Phi^{ep}}{\partial |x_{pt}|} \right\}
\]

\[
+ \sum_{l=1}^n \left[ \sum_{p<t} A_{pt}^l \frac{\Delta \beta e^2}{|r_{pt}^l|^2} - \sum_{p=1}^{N_p} \sum_{t=1}^{N_e} B_{pt}^l \frac{\partial \Delta \beta \Phi^{ep}}{\partial |x_{pt}^l|} \right]
\]

\[
+ \frac{\alpha}{\det|\psi_{ab}^{n,1}|_s} \frac{\partial \det|\psi_{ab}^{n,1}|_s}{\partial \alpha}
\}
\]

with \( A_{pt}^l = \frac{\langle r_{pt}^l | r_{pt} \rangle}{|r_{pt}|^2}, \quad B_{pt}^l = \frac{\langle x_{pt}^l | x_{pt} \rangle}{|x_{pt}|^2}. \)

(20)

The structure of Eqs. (17, 20) is obvious: we have separated the classical ideal gas part (first term). The ideal quantum part in excess of the classical one and the correlation contributions are contained in the integral term, where the second line results from the ionic correlations (first term) and the e-e and e-i interaction at the first vertex (second and third terms respectively). The third and fourth lines are due to the further electronic vertices and the explicit temperature dependence [in Eq. (17) and volume dependence in Eq. (20)] of the exchange matrix, respectively. The main advantage of Eqs. (17, 20) is that the explicit sum over permutations has been converted into the spin determinant which can be computed very efficiently using standard linear algebra methods. Furthermore, each of the sums in curly brackets in Eqs. (17, 20) is bounded as the number of vertices increases, \( n \to \infty \), and is thus well suited for efficient Monte Carlo simulations. Notice also that Eqs. (17, 20) contain the important limit of an ideal quantum plasma in a natural way [42].

**IV. COMPARISON OF DIRECT AND RESTRICTED PIMC SIMULATIONS**

Expressions (17, 20) are well suited for numerical evaluation using Monte Carlo techniques, e.g. [16,17]. In our Monte Carlo scheme we used three types of steps, where either electron or proton coordinates, \( r_i \) or \( q_i \) or individual electronic beads \( \xi_i^{(k)} \) were moved until convergence of the calculated values was reached. Our procedure has been extensively tested. In particular, we found from comparison with the known analytical expressions for
pressure and energy of an ideal Fermi gas that the Fermi statistics is very well reproduced \[26\]. Further, we performed extensive tests for few–electron systems in a harmonic trap where, again, the analytically known limiting behavior (e.g. energies) is well reproduced \[43,44\]. For the present simulations of dense hydrogen, we varied both the particle number and the number of time slices (beads). As a result of these tests, we found that to obtain convergent results for the thermodynamic properties of dense hydrogen, particle numbers \(N_e = N_p = 50\) and beads numbers in the range of \(n = 6 \ldots 20\) are adequate \[24,26\].
FIG. 1. Density-temperature plane showing the parameter region for which calculations are performed. The data of Fig. 2 are along the dashed line (isochor $r_s = 1.86$). The data of Figs. 3 and 4 are inside the bold rhomb, along lines of constant $\Gamma$ between the lines $n\Lambda^3 = 2$ and $n\Lambda^3 = 5$, respectively. Data for the vertical line (isotherm $T = 50,000 K$) are given in Fig. 5.

We will now compare our results with some available results obtained by the Monte Carlo technique developed by the Urbana group [19,32]. We may first state that both Monte Carlo techniques differ in several fundamental points, so that they are essentially independent approaches. Let us briefly outline the main differences between the technique developed in Urbana, known as the restricted PIMC scheme [32] and references therein, and the approach described here. These authors performed simulations with 32 electrons and protons; their restricted PIMC scheme required to use a rather small time step assuring $1/\Delta\beta \sim 2 \times 10^6 K$. Also, the treatment of the interactions differs from our scheme: the authors of Ref. [32] perform a numerical solution of the Bloch equation for the two-particle density matrix whereas we use an analytical approximation for the effective pair interaction (based on the Kelbg potential, see above). Finally, Ref. [32] approximately computes the nodal surface of the density matrix using a variational ansatz which is then used to restrict the integrations to the region of positive density matrix. For more details regarding the restricted PIMC simulations, see Refs. [19,32].
FIG. 2. Comparison of direct and restricted PIMC results and analytical results (PADE) for the pressure and total energy of dense hydrogen as a function of temperature for $r_s = 1.86$, corresponding to $n = 2.5 \cdot 10^{23} \text{cm}^{-3}$. For illustration, also the coupling and degeneracy parameters $\Gamma$ and $n_e \Lambda^3$ are shown in the upper figure.

Let us now turn to a comparison of the numerical results. The restricted PIMC simulation data for dense hydrogen are taken from Ref. [32]. A comparison of results for the pressure and the internal energy for a fixed value of the density ($r_s = 1.86$) is shown in Fig. 1 and TABLE I. At high temperatures, above 50,000 K, where only a small fraction of atoms is expected, the agreement is rather good. This is remarkable since the nonideality and the degeneracy reach values of 3 and 10, respectively. This result demonstrates that, at least for $r_s \simeq 1$ and for $T \geq 50,000 K$ both methods yield results which are more or less equivalent. At $T < 50,000 K$, where partial ionization is expected, we still observe a reasonable agreement of both approaches, however, we see also that the differences start to grow. The reasons for that are manyfold. From our results we conclude that the main problem is not the bound state formation - atoms and molecules are well described by the two PIMC simulations which use a physical picture which does not involve any artificial distinction between free and bound electrons, e.g. [26]. On the other hand, with growing degeneracy $n \Lambda^3$, both PIMC methods become less reliable, and a detailed analysis, although being very desirable, will have to be based on more extensive calculations in the future.
Further we present in TAB. I also Padé results for the weakly nonideal region. We find good agreement with the PIMC results for \( T > 10^5 \) K. Details on the method of these analytical calculations will be discussed in the next section.

V. COMPARISON WITH ANALYTICAL APPROXIMATIONS FOR THE THERMODYNAMIC FUNCTIONS OF STRONGLY IONIZED DENSE PLASMAS

In this section we give a comparison of the available data points from direct PIMC calculations with analytical estimates based on Padé approximations for strongly ionized plasmas [34–36]. The comparison concentrates on H-plasmas in a region in the density-temperature plane with the following borders

\[
0.2 \leq \Gamma \leq 1.6, \\
0.2 \leq n_e\Lambda_e^3 \leq 5, 
\]

which will be called “rhomb of moderate nonideality and moderate degeneracy” (see bold rhomb in Fig. 1). With respect to analytical treatment, this rhombic region is of particular difficulty since none of the known analytic limiting expressions is valid. Further we calculated several points for \( r_s = 1.86 \) and \( \Gamma \lesssim 2 \) which correspond to the PIMC data discussed in the previous section and also an isotherm at \( T = 50,000K \) including some data at higher density, outside the rhomb, cf. Fig. 1 for an overview.

We demonstrate below that the Padé approximations which interpolate between the limits where theoretical results are available are a useful tool for the description of the available data points, at least for the case of moderate nonideality \( \Gamma \lesssim 1.6 \) and moderate degeneracy \( n_e\Lambda_e^3 \lesssim 5 \). The Padé approximations which we use here were constructed in earlier work, [34–36], from the known analytical results for limiting cases of low density [3–33] and high density [3]. The structure of the Padé approximations was devised in such a way that they are analytically exact up to quadratic terms in the density (up to the second virial coefficient) and interpolate between the virial expansions and the high-density asymptotic expressions [34–36]. The formation of bound states was taken into account by using a chemical picture. This means the plasma is considered as a mixture of free electrons, free ions, atoms and molecules which are in chemical equilibrium, being described by mass action laws or minimization of the free energy [36].

We follow in large here this cited work, only the contribution of the ion-ion interaction which is, in most cases, the largest one, was substantially improved following recent work of Kahlbaum, who succeeded in describing the available classical Monte Carlo data for the ions by accurate Padé approximations [46]. By using Kahlbaum’s formulas we achieve a rather accurate description of the thermodynamics in the region where the plasma behaves like a classical one-component ion plasma imbedded into a sea of nearly ideal electrons. This is the region where the electrons are strongly degenerate

\[
n_e\Lambda_e^3 \gg 1 \quad \text{and} \quad r_s \ll 1, \tag{22}
\]

and the ions are still classical but nonideal

\[
\Gamma \gg 1 \quad \text{and} \quad n_i\Lambda_i^3 \ll 1. \tag{23}
\]
This region lies in the upper left corner of Fig. 1.

With respect to the chemical picture we restrict ourselves to the region of strong ionization where the number of atoms is still relatively low and where the fraction of molecules is small as well, see below. We will discuss here only the general structure of the Padé formulae. For example, the internal energy density of the plasma is given by

\[ u = u_{id} + u_{int}. \] (24)

Here \( u_{id} \) is the internal energy of an ideal plasma consisting of Fermi electrons, classical protons and classical atoms, and \( u_{int} \) is the interaction energy

\[ u_{int} = u_{ii} + u_{ee} + u_{ie} + u_{vdW}. \] (25)

The interaction contribution to the internal energy consists of four terms:

- **Ion-ion interaction contribution**: this term which, in general, yields the largest contribution is generated by the OCP subsystem of the protons. For the OCP energy of protons many expressions are available, e.g. [45]. We have used here the most precise formula due to Kahlbaum [46] which interpolates between the Debye region, \( u_{ii} \sim \Gamma^{3/2} \), and the high density fluid, \( u_{ii} \sim \Gamma \).

- **Electron-electron interaction**: This term corresponds to the OCP energy of the electron subsystem. We used the rather simple expressions used in earlier work [34,35].

- **Electron-proton interaction**: This term corresponds to the interaction between the two OCP subsystems which is mostly due to polarization effects. Again, we used the rather simple expressions proposed in earlier work [34,35].

- **Van der Waals contribution**: In the region of densities and temperatures defined above this contribution gives only a small correction. Therefore, this term was approximated here in the simplest way by a second virial contribution. The neutral particles were treated as hard spheres.

In the region of densities which are studied here, molecules do not play a role, therefore, the formation of molecules was taken into account only in a very rough approximation according to Ref. [34]. The number density of the neutrals was calculated on the basis of a nonideal Saha equation. We restricted this comparison to a region where the number density of neutrals is relatively small, the degree of ionization being larger than 75%.

The contributions to the pressure were calculated, in part, from scaling relations e.g. we used \( p_{ii} = u_{ii}/3 \), and, for the other (smaller) contributions, by numerical differentiation of the free energy given earlier [34,35]. In a similar way, the chemical potential which appears in the nonideal Saha equation was obtained. For the partition function in the Saha equation we used the Brillouin-Planck-Larkin expression [3,36]. The solution of the nonideal Saha equation which determines the degree of ionization (the density of the atoms) was solved by up to 100 iterations starting from the ideal Saha equation.
FIG. 3. Comparison of Padé calculations (lines without symbols) for the internal energy with the direct PIMC results (lines with full circles).

Since all the expression described so far are given in analytic form, the calculation of about 1000 data points for energy and pressure takes less than a minute on a PC. The result of our calculations for density-temperature points in the “rhomb of moderate nonideality and moderate degeneracy” are given in Figs. 2,3. Further, we give in TAB. I several data points obtained from the Padé formulas. Since the Padé formulas used here do not apply to low temperatures, we included in TAB. I only Padé data for $T > 10^5 K$. 
Summarizing the results for the internal energy and for the pressure we find that the Padé results, with a few exceptions, agree well with the PIMC data in the region of the density temperature plane, where $\Gamma \leq 1.6$ and $n\Lambda^3 \leq 5$. The agreement is particularly good for the energies. [The larger deviations for the pressure may be due to the numerical differentiation.] In fact, the Padé formulas used here in combination with the chemical picture works only in the case that the plasma is strongly ionized, i.e. the degree of ionization is larger than 75%. The description of the region where a higher percentage of atoms and, due to this, also molecules is present needs a more refined chemical picture.
FIG. 5. Comparison of Padé calculations (lines without symbols) of the pressure (in units of the Boltzmann pressure) with direct PIMC simulation results (lines with full circles) for an isotherm $T = 50,000K$.

Finally, we compare the Padé and PIMC data along the isotherm $T = 50,000K$ which is given in Fig. 5. This figure shows the transition from a classical ideal gas (low density) to a nearly ideal quantum gas (limit of high density). In the central part, $n \lesssim 10^{19}\text{cm}^{-3} \lesssim 10^{25}\text{cm}^{-3}$, Coulomb interaction leads to strong deviations from the behavior of an ideal plasma. The strong increase of the energy at high density is due to the Mott effect and to the increase of the ideal quantum contribution to the electron energy. Comparing the Padé and PIMC results, we find good agreement up to electron densities $n = 10^{22}\text{cm}^3$. For higher densities, the deviations are growing. For intermediate densities, $n \lesssim 10^{22}\text{cm}^{-3} \lesssim 10^{24}\text{cm}^{-3}$, the PIMC data are more reliable. On the other hand, in the limit of very high density, $r_s \ll 1$, 

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the Padé results are known to correctly approach the ideal quantum plasma limit whereas the PIMC data should be regarded as preliminary due to the extremely high electron degeneracy. Interestingly, we find that at high density the Padé data approaches the ideal curves earlier than the PIMC data which is important for further improvement of the presented Monte Carlo approach.

VI. DISCUSSION

This work is devoted to the investigation of the thermodynamic properties of hot dense partially ionized plasmas in the pressure range between 0.1 and 100 Mbar. Most of the new results are based on a Quantum Monte Carlo study of a correlated proton-electron system with degenerate electrons and classical protons. In this paper, we gave a detailed derivation of improved estimators for the internal energy and the equation of state for use in direct fermionic path integral simulations. Also, we gave a rigorous justification for the use of an effective quantum pair potential (Kelbg potential) in PIMC simulations.

Further, we compared our direct PIMC results with independent restricted PIMC data of Militzer and Ceperley for one isochor corresponding to \( r_s = 1.86 \), Fig. 2. We found very good quantitative agreement between the two PIMC methods for temperatures in the range of \( 50,000K \leq T \leq 10^6K \), where \( \Gamma \lesssim 3 \) and \( n_e^3 \lesssim 10 \). This region is particularly complicated as here pressure and temperature ionization occur and, therefore, an accurate and consistent treatment of scattering and bound states is crucial. This agreement is remarkable because the two simulation methods are completely independent and use essentially different approximations. We, therefore, expect that the results for the thermodynamic properties of high pressure hydrogen plasmas in this temperature-density range are reliable within the limits of the simulation accuracy. This is the main result of the present paper.

In future work, it will be important to extend the range of agreement. To analyze the deviations between the simulation methods, we also included some data for \( r_s = 1.86 \) and lower temperatures, \( 10,000K \leq T \leq 50,000K \), Fig. 2. At this point, no conclusive answer about the reasons of the deviations can be given. For these parameters, the electron degeneracy is growing rapidly and, therefore, each of the simulation methods is becoming less reliable. So these data should be regarded as preliminary results which will be useful for future improvements of the simulations.

Furthermore, the Monte Carlo results allowed us to develop and test analytical approximations of Padé-type which are improvements of earlier approximations \([34,36]\) in a region in the density-temperature plane bounded by \( \Gamma \leq 1.6 \) and \( n_e^3 \leq 5 \). This is a region of moderate nonideality and degeneracy and high degree of ionization. We have shown that for these parameters, the Padé approximations which interpolate between the limits where theoretical results are available agree well with the Monte Carlo data, cf. Figs. 2-4 and Table I. Thus, these approximations provide a useful tool for the description of these plasmas which include hydrogen at a pressure between 0.1 and 100 Mbar. At lower temperature, deviations from the Monte Carlo data are growing, cf. Fig. 2. This is mostly due to the growing role of bound states. Whether the Padé approximations, in combination with an improved chemical picture (mass action law), continue to work at lower temperatures, has still to be explored, first steps are under way \([48]\).
Also, we showed some data for $T = 50,000\, K$ and higher pressure, up to $p \sim 10^6 \, \text{Mbar}$, Fig. 5. Here the Monte Carlo simulations are particularly difficult due to the high electron degeneracy, and they can benefit from the Pade simulations, as the latter correctly reproduce the high-density limit, $r_s \ll 1$.

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TABLE I. Direct versus restricted PIMC [23] simulation results (upper and middle lines, respectively) and results of Padé calculations (numbers in the lowest lines) for the pressure $p$(Mbar) and energy $E$(2NRy) for dense hydrogen (deuterium [23]) for $r_s = 1.86$.

| $T$, 1000K | $n\Lambda^3$ | $\Gamma$ | $p$, Mbar | $E$, 2NRy |
|------------|--------------|---------|-----------|-----------|
| 1000       | 0.10         | 0.169   | 67.74 ± 0.02 | 9.050 ± 0.005 |
|            |              |         | 66.86 ± 0.08 | 9.018 ± 0.015 |
|            |              |         | 67.38      | 9.063      |
| 500        | 0.29         | 0.339   | 32.85 ± 0.03 | 4.169 ± 0.003 |
|            |              |         | 32.13 ± 0.05 | 4.114 ± 0.007 |
|            |              |         | 31.91      | 4.162      |
| 250        | 0.83         | 0.679   | 15.37 ± 0.01 | 1.654 ± 0.005 |
|            |              |         | 14.91 ± 0.03 | 1.629 ± 0.007 |
|            |              |         | 14.40      | 1.679      |
| 125        | 2.33         | 1.350   | 6.98 ± 0.01  | 0.412 ± 0.005 |
|            |              |         | 6.66 ± 0.02  | 0.404 ± 0.004 |
|            |              |         | 6.47       | 0.471      |
| 62.5       | 6.58         | 2.701   | 3.07 ± 0.02  | -0.248 ± 0.005 |
|            |              |         | 2.99 ± 0.04  | -0.140 ± 0.007 |
| 31.25      | 18.48        | 5.376   | 2.20 ± 0.01  | -2.377 ± 0.005 |
|            |              |         | 1.58 ± 0.07  | -0.360 ± 0.010 |