Permutation blocking path integral Monte Carlo approach to the uniform electron gas at finite temperature

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The uniform electron gas (UEG) at finite temperature is of high current interest due to its key relevance for many applications including dense plasmas and laser excited solids. In particular, density functional theory heavily relies on accurate thermodynamic data for the UEG. Until recently, the only existing first-principle results had been obtained for $N = 33$ electrons with restricted path integral Monte Carlo (RPIMC), for low to moderate density, $r_s = \tau/a_B \gtrsim 1$. This data has been complemented by Configuration path integral Monte Carlo (CPIMC) simulations for $r_s \lesssim 1$ that substantially deviate from RPIMC towards smaller $r_s$ and low temperature. In this work, we present results from an independent third method—the recently developed permutation blocking path integral Monte Carlo (PB-PIMC) approach [T. Dornheim et al., NJP 17, 073017 (2015)] which we extend to the UEG. Interestingly, PB-PIMC allows us to perform simulations over the entire density range down to half the Fermi temperature ($\theta = k_B T / E_F = 0.5$) and, therefore, to compare our results to both aforementioned methods. While we find excellent agreement with CPIMC, where results are available, we observe deviations from RPIMC that are beyond the statistical errors and increase with density.

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I. INTRODUCTION

Over the last years, there has been an increasing interest in the thermodynamic properties of degenerate electrons in the quantum mechanical regime. Such information is vital for the description of highly compressed matter [1–3], including plasmas in laser fusion experiments [4–9] and in compact stars and planet cores [10–12]. In addition, the widespread density functional theory (DFT) approach crucially depends on the availability of accurate quantum Monte Carlo (QMC) data for the exchange correlation energy of the UEG, hitherto at zero temperature [13, 14]. However, in recent years more and more applications with highly excited electrons have emerged, which require to go beyond ground state DFT. Hence, there exists a high current need for an ab-initio thermodynamic description of the UEG at finite $T$.

The widely used path integral Monte Carlo (PIMC) method, e.g. [18], is a powerful tool for the ab-initio simulation of both distinguishable particles (often referred to as “boltzmannons”, e.g. [19, 20]) and bosons and allows for quasi exact results for up to $N \sim 10^3$ particles at finite temperature [21, 22]. However, the application of PIMC to fermions is hampered by the notorious fermion sign problem (FSP), e.g. [23], which might render even small systems unfeasible for state of the art QMC methods and is known to be NP-hard for a given representation [24]. With increasing degeneracy effects, permutation cycles with opposite signs nearly cancel each other and the statistical uncertainty grows exponentially. Hence, standard PIMC cannot provide the desired results without further improvement. Brown et al. [25] have presented the first finite temperature results for the UEG down to $r_s = 1$ using restricted PIMC (RPIMC) [26], a popular approach to extend PIMC to higher degeneracy, that is, lower temperature and higher density. To avoid the FSP, this method requires explicit knowledge of the nodal surface of the density matrix, which is, in general, unknown and one has to rely on approximations. The use of the ideal nodes for a nonideal system appears to be problematic, as has been shown for the case of hydrogen [27, 28]. In addition, it has been shown analytically that RPIMC does not reproduce the exact limit of the ideal Fermi gas ($r_s \to 0$) [29, 30]. Therefore, the quality of the RPIMC data remains unclear. Indeed, recent configuration PIMC (CPIMC) [31, 32] results for the highly degenerate UEG by Schoof et al. [33] have revealed a significant disagreement between the two methods at small $r_s$ and low temperature. While the first application of a novel density matrix QMC (DMQMC) approach [34] to the UEG for four particles reports excellent agreement with CPIMC [35], additional simulations of larger systems are needed to resolve the discrepancy towards RPIMC. For completeness, we mention that QMC results by Filinov et al. [36] cannot be used as a benchmark due to the different treatment of the homogeneous positive background and a different account of the long-range Coulomb interaction [37, 38] than the usual Ewald summation. In this situation an independent third first-principle method, capable to treat WDM parameters, would be highly desirable.

In this work we, therefore, investigate the applicability of the recently developed permutation blocking PIMC (PB-PIMC) approach [39] to the uniform electron gas. The basic idea behind PB-PIMC is to combine antisymmetric imaginary time propagators [40–42], i.e., determinants, between all “time slices” with a higher order
factorization of the density matrix \([43–46]\). This means that each particle is represented by a “path” consisting of \(3 \times P\) coordinates (“beads”), where \(P\) is the number of high-temperature factors (or propagators). The application of determinants leads to a relief of the FSP by an effective cancellation of positive and negative terms in the partition function, which belong to permutation cycles of different parity in standard PIMC. However, since the blocking is most effective if the thermal wavelength of a single propagator is of the same order as the mean interparticle distance, it is crucial to employ a higher order factorization scheme which allows for sufficient accuracy with only a few time slices.

The details of our PB-PIMC scheme are described in section II B, after a brief introduction of the employed model I A. In section III A, we present our simulation results starting with a detailed investigation of the convergence behavior with respect to the factorization of the density matrix. We proceed by simulating a single propagator is of the same order as the mean interaction of determinants leads to a relieve of the FSP by an effective cancellation of positive and negative terms in the density matrix. We proceed by simulating a system of the UEG, see section III B. Interestingly, our spin-polarized electrons, which is a commonly used model for high-temperature factors (or propagators). The application of determinants leads to a relieve of the FSP by a broad parameter range, which includes the physically most interesting regime of warm dense matter, cf. Fig. 1.

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} e^2 \Psi(r_i, r_j) + \frac{N e^2}{2} \xi ,
\]

with \(\xi\) being the Madelung constant and the periodic Ewald pair potential

\[
\Psi(r, s) = \frac{1}{V} \sum_{G \neq 0} e^{-\pi^2 G^2 / \kappa^2} e^{2 \pi G (r-s)}
\]

\[
- \frac{\pi}{\kappa^2 V} \sum_{\mathbf{R}} \frac{\text{erfc} (\kappa | \mathbf{r} - \mathbf{s} + \mathbf{R} |)}{| \mathbf{r} - \mathbf{s} + \mathbf{R} |} . \tag{1}
\]

Here \(\mathbf{R} = n_1 L\) and \(\mathbf{G} = n_2 / L\) denote the real and reciprocal space lattice vectors, respectively, with the box length \(L\) and volume \(V = L^3\). The specific choice of the Ewald parameter \(\kappa\) does not influence the outcome of Eq. (1) and, therefore, can be used to optimize the convergence. PB-PIMC requires explicit knowledge of all forces in the system, and the force between the electrons \(i\) and \(j\) can be obtained from

\[
F_{ij} = -\nabla_i \Psi(r_i, r_j) . \tag{2}
\]

The evaluation of Eq. (2) is relatively straightforward and we find

\[
F_{ij} = \frac{2}{V} \sum_{G \neq 0} \left( \frac{G}{G^2} \sin 2\pi G (r_i - r_j) \right) e^{-\pi^2 G^2 / \kappa^2}
\]

\[
+ \sum_{\mathbf{R}} \frac{r_i - r_j + \mathbf{R}}{\alpha \beta^3} \left( \text{erfc} (\kappa \alpha) + \frac{2\kappa \alpha}{\sqrt{\pi}} e^{-\kappa^2 \beta^2} \right) ,
\]

with the definition \(\alpha = |r_i - r_j + \mathbf{R}|\).

B. Simulation method

To calculate canonical expectation values with the PB-PIMC approach \([39]\), we write the partition function in coordinate representation as

\[
Z = \frac{1}{N!} \sum_{\sigma \in S_N} \text{sgn} (\sigma) \int d\mathbf{R} \langle \mathbf{R} | e^{-\beta \hat{H}} | \hat{\sigma} \mathbf{R} \rangle \tag{3}
\]
with $\mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$ containing the coordinates of all electrons, $\hat{\pi}_\sigma$ denoting the exchange operator which corresponds to a specific element $\sigma$ from the permutation group $S_N$, and $\beta = 1/k_B T$. For the next step, we make use of the usual group property of the density matrix in Eq. (3) and arrive at an expression for $Z$ which requires the evaluation of $P$ density matrices at $P$ times higher temperature. However, instead of the primitive approximation $e^{-\mathcal{H}} \approx e^{-\mathcal{K}} e^{-\mathcal{V}}$, with $\epsilon = \beta/P$ being the imaginary time step of a single propagator and the kinetic and potential contributions to the Hamiltonian $\mathcal{K}$ and $\mathcal{V}$, respectively, we use the fourth order factorization

$$e^{-\mathcal{H}} \approx e^{-\nu_1 \mathcal{W}_1} e^{-t_1 \mathcal{K}} e^{-\nu_2 \mathcal{W}_1 - 2a_1} \times e^{-t_1 \mathcal{K}} e^{-\nu_1 \mathcal{W}_1} e^{-2t_0 \mathcal{K}} \ .$$

(4)

The $\mathcal{W}$ operators in Eq. (4) denote a modified potential, which combines $\mathcal{V}$ with double commutator terms of the form

$$\{[\hat{\pi}, \hat{K}], \hat{V} \} = \frac{\hbar^2}{m} \sum_{i=1}^{N} |\mathbf{F}_i|^2 \ ,$$

(5)

and, therefore, requires the evaluation of all forces on each particle, $\mathbf{F}_i = -\nabla_i \mathcal{V} (\mathbf{R})$. Our final result for the partition function is given by

$$Z = \frac{1}{(N!)^{3P}} \int d\mathbf{X} \prod_{a=0}^{P-1} e^{-\nu_a \mathcal{W}_a - \epsilon u_0 \frac{\hbar^2}{2m} \mathcal{F}_a} \ ,$$

(6)

with the definition of the potential and force terms

$$\hat{V}_a = \nu_1 \mathcal{V} (\mathbf{R}_a) + \nu_2 \mathcal{V} (\mathbf{R}_{aA}) + \nu_1 \mathcal{V} (\mathbf{R}_{aB}) \ ,$$

(7)

and

$$\mathcal{F}_a = \sum_{i=1}^{N} \left( a_1 |\mathbf{F}_{a,i}|^2 + (1 - 2a_1) |\mathbf{F}_{aA,i}|^2 + a_1 |\mathbf{F}_{aB,i}|^2 \right) \ ,$$

and the diffusion matrices

$$\rho_\alpha (i,j) = \frac{\lambda_{t_1 \epsilon}}{\eta_{i,j}^D} \sum_n \exp \left(-\frac{\pi}{\lambda_{t_1 \epsilon}} (\mathbf{r}_{a,j} - \mathbf{r}_{a,A,i} + \mathbf{nL})^2 \right) \ .$$

with $D$ being the dimensionality, see e.g. [40]. Eq. (6) contains two free coefficients, $t_0$ and $a_1$, which can be used for optimization, cf. Fig. 2, and the integration is carried out over $3P$ sets of coordinates, $d\mathbf{X} = d\mathbf{R}_0 \ldots d\mathbf{R}_{P-1,0} d\mathbf{R}_{0A} \ldots d\mathbf{R}_{P-1,4} d\mathbf{R}_{0B} \ldots d\mathbf{R}_{P-1,1B}$. Instead of explicitly sampling each permutation individually, as in standard PIMC, we combine configuration weights of both positive and negative sign in the determinants, which leads to a cancellation of terms and, therefore, an effective blocking of permutations. When the thermal wavelength of a single time slice, $\lambda_{t_1 \epsilon} = \sqrt{2 \pi t_1 \epsilon / m}$, is comparable to the mean interparticle distance, the effect of the blocking is most pronounced and the average sign in our simulations is significantly increased. However, with an increasing number of propagators $P$, $\lambda_{t_1 \epsilon}$ decreases and, eventually, the blocking will have no effect and the sign converges towards the sign from standard PIMC. Hence, it is crucial to employ the high order factorization from Eq. (4), which allows for reasonable accuracy even for only two or three propagators. We simulate the canonical probability distribution defined by Eq. (6) using the Metropolis algorithm [48] and refer to [39] for a more detailed description of the PB-PIMC method.

C. Energy estimator

The consideration of periodicity in the diffusion matrices requires minor modifications in the energy estimator presented in [39], which can be derived from the partition function via the familiar relation

$$E = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \ .$$

(8)

Inserting the expression from Eq. (6) into (8) and performing a lengthy but straightforward calculation leads to

$$E = \frac{1}{P} \sum_{k=0}^{P-1} \left( \nu_k 3 \epsilon^2 u_0 \frac{\hbar^2}{m} \mathcal{F}_k \right) + \frac{3DN}{2\epsilon}$$

$$- \sum_{k=0}^{P-1} \sum_{\xi=1}^{N} \left( \frac{\pi \eta_{k\xi}^D}{\lambda_{t_1 \epsilon}^D} + \frac{\pi \eta_{kA}^D}{\lambda_{t_1 \epsilon}^{A,-}} + \frac{\pi \eta_{kB}^D}{\lambda_{t_1 \epsilon}^{B,-}} \right) \ ,$$

with the definition

$$\eta_{k\xi}^D = \left( \frac{\rho_\xi}{\lambda_{t_1 \epsilon}^D} \right) \sum_n \exp \left[-\frac{\pi}{\lambda_{t_1 \epsilon}^D} (\mathbf{r}_{k,\kappa} - \mathbf{r}_{kA,\xi} + \mathbf{nL})^2 \right].$$

(9)

For completeness, we note that the total energy $E$ splits into the kinetic and potential contribution, $\mathcal{K}$ and $\mathcal{V}$, in precisely the same way as before [39].

III. RESULTS

A. Convergence

We begin the discussion of our simulation results by investigating the convergence of the energy with the number of imaginary time propagators $P$. To enhance the performance, the free parameters from the propagator, $a_1$ and $t_0$, can be optimized. In Fig. 2, we choose $a_1 = 0.33$, which corresponds to equally weighted forces on all time slices, and plot the potential energy $V$, calculated with $P = 2, P = 3$ and $P = 4$, versus $t_0$ over the entire possible range for a benchmark system of $N = 4$ spin-polarized electrons with $\theta = 0.5$ and $r_s = 4$. To assess the accuracy, we compare these results with the exact energy known from CPIMC (green line). Evidently, the optimal choice for this free parameter is located around $t_0 = 0.14$, which is consistent with previous findings by Sakkos et
agators allow for a relative accuracy $\Delta V$ (time step interval) from CPIMC. We find that as few as two propagators, we find the relative time step error $\Delta V$ of magnitude larger than that of $P = 3$. In the bottom panel, we show the same information with $P = 4$. For completeness, we mention that our method converges for all possible choices presented simulations in this work. Hence, it should be noted that our method converges for all possible choices of the free parameters. In Fig. 3, we demonstrate the convergence of the energy with respect to the number of propagators for the same system as in Fig. 2. However, since $V$ and $K$ nearly cancel for this particular combination of $r_s$, $\theta$, and $N$, we investigate the convergence of both contributions separately. The top panel shows the potential energy versus the inverse number of propagators $1/P$, and we compare the PB-PIMC results to the exact value (with the corresponding confidence interval) from CPIMC. We find that as few as two propagators allow for a relative accuracy $\Delta V/|V| \sim 10^{-4}$ and with $P = 4$ the potential energy is converged within error bars. In the bottom panel, we show the same information for the kinetic energy $K$. The variance of $K$ is one order of magnitude larger than that of $V$ and, for two propagators, we find the relative time step error $\Delta K/K \sim 10^{-3}$. With increasing $P$, the PB-PIMC results are fluctuating around the exact value, within error bars.

Finally, we adress the $r_s$-dependence of the time step error by comparing PB-PIMC results for $V$ with $P = 2$ (red crosses) and $P = 3$ (blue squares) to the exact values from CPIMC. In Fig. 4, the relative error of the potential energy $\Delta V/|V|$ is plotted versus $r_s$ for $N = 4$ spin-polarized electrons at $\theta = 0.5$. The increased error-bars for larger $r_s$ are a manifestation of the sign problem from CPIMC [32], while for the rest the statistical uncertainty from PB-PIMC predominates. The time step error is smaller for three propagators over the entire $r_s$-range, as it is expected, and adopts a maximum around $r_s = 1$. This can be understood by recalling the source of the systematic error in PB-PIMC. For $r_s \rightarrow 0$, the UEG approaches an ideal system and the commutator error from $K$ and $V$ vanishes. For $r_s \rightarrow \infty$, on the other hand, the particles are more separated and the system becomes more classical. Therefore, the neglected commutator terms are most important at intermediate $r_s$, which is the case for the results in Fig. 4.

We conclude that as few as two or three propagators provide sufficient accuracy to assess the discrepancy between CPIMC and RPIMC observed in previous studies [33]. In particular, the selected benchmark temperature, $\theta = 0.5$, is even lower than for all other simulations to be presented in this work. Hence, the observed time step error constitutes an upper bound for the accuracy of our results in the remainder of the paper.
Among the most interesting questions regarding the implementation of PB-PIMC for the UEG is the range of applicability with respect to the density parameter $r_s$. To address this issue, we simulate $N = 33$ spin-polarized electrons with $P = 2$, $a_1 = 0.33$ and $t_0 = 0.14$, for the optimal parameters from the fourth order propagator. 

FIG. 4. Accuracy of two and three propagators over a broad $r_s$ range for $N = 4$ and $\theta = 0.5$ with $t_0 = 0.14$ and $a_1 = 0.33$. We show the relative difference between the potential energy from PB-PIMC and CPIMC, $\Delta V/|V|$, for the optimal

B. Density parameter dependence

Among the most interesting questions regarding the implementation of PB-PIMC for the UEG is the range of applicability with respect to the density parameter $r_s$. To address this issue, we simulate $N = 33$ spin-polarized electrons, which corresponds to a closed momentum shell and is often used as a starting point for finite size corrections. In Fig. 5, we show the average sign $S$ versus $r_s$ for three different temperatures over a broad density range. All curves exhibit a qualitatively similar behavior, that is, a smooth decrease of $S$ towards smaller $r_s$ until it saturates. At large $r_s$, the coupling induced particle separation mostly exceeds the extension of the single particle wavefunctions and quantum exchange effects do not play a dominant role. With decreasing $r_s$, the UEG approaches an ideal system and the particles begin to overlap, which leads to sign changes in the determinants. However, due to the blocking, the average sign, instead of dropping exponentially, remains finite which implies that, for the three depicted temperatures, PB-PIMC is applicable over the entire density range. This is in stark contrast to standard PIMC, see e.g. supplement of [25]. Nevertheless, with decreasing temperature the sign drops and the FSP makes the simulations more involved, cf. section III C.

In Fig. 6, we compare the corresponding energies with RPIMC [49] and CPIMC [33], where they are available. The top row displays the relative difference in the potential energy towards PB-PIMC with two propagators. For $\theta = 4$ and $\theta = 2$, we find excellent agreement with CPIMC. For the lowest temperature, $\theta = 1$, the CPIMC values are systematically lower by $\Delta V/|V| \lesssim 10^{-3}$. However, this discrepancy can be explained by the convergence behavior of the propagator, cf. Fig. 4, since the potential (and kinetic) energy is expected to converge from above towards the exact result. To confirm this assumption, we also plot results for $P = 3$ and $\theta = 1$, visualized by the grey triangles. Evidently, these points coincide with the CPIMC data everywhere within the errorbars and, thus, can be regarded as quasi-exact. The RPIMC data for $V$, on the other hand, exhibit a systematic discrepancy with respect to PB-PIMC and CPIMC [33]. At $r_s = 1$, the energies approximately differ by $\Delta V/|V| \sim 0.02$, but the difference decreases with increasing $r_s$. In the center row, we display the relative difference in the kinetic energy. Again, all PB-PIMC results are in good agreement with CPIMC. On the other hand, there is no clear systematic deviation between the PB-PIMC and RPIMC data, although most RPIMC-values for $\theta = 1$ are lower while the opposite holds for most values for $\theta = 4$. Finally, the bottom row displays the relative difference in the total energy. Interestingly, for $\theta = 1$ the difference of RPIMC in $V$ and $K$ towards PB-PIMC nearly cancels, so that $E$ appears to be in good agreement. In particular, even the value for $\theta = 1$ and $r_s = 4$, where the potential energy is an outlier, and both $V$ and $K$ exhibit a maximum deviation, is almost within single error bars. For completeness, we have also included the total energy for $\theta = 1$ and $r_s = 40$ from standard PIMC [49], cf. the black circle, which is in excellent agreement with PB-PIMC as well. For $\theta = 2$ and $\theta = 4$, most RPIMC values for $E$ are higher than PB-PIMC, although the deviation hardly exceeds twice the error bars.

C. Temperature dependence

Finally, we investigate the performance of PB-PIMC with respect to the temperature. In Fig. 7, the average sign is plotted versus $\theta$ for $N = 33$ spin-polarized electrons at $r_s = 10$, $r_s = 1$ and $r_s = 0.1$. All three curves
FIG. 6. Comparison of PB-PIMC with CPIMC and RPIMC for \( N = 33 \) spin-polarized electrons and three temperatures. In the top row, the relative deviation of the potential energy towards PB-PIMC with \( P = 2 \), \( t_0 = 0.14 \) and \( a_1 = 0.33 \) is plotted versus \( r_s \). The center and bottom rows display the same information for the kinetic and total energy, respectively.

exhibit a similar behavior, that is, a large sign \( S \) at high temperature and a monotonous decay for \( T \to 0 \). However, for \( r_s = 10 \), the system is significantly less degenerate than for both other density parameters, and even at \( \theta = 0.5 \), the average sign of \( S \approx 0.056 \) indicates that the simulations are feasible. For \( r_s = 1 \) and \( r_s = 0.1 \), the decay of \( S \) is more rapid and, at low temperature, the simulations are more involved. In particular, half the Fermi temperature seems to constitute the current limit down to which reasonable results can be achieved for such \( r_s \)–values (and this particle number) and, for \( r_s = 0.1 \), the sign is zero within error bars, cf. the dashed line. Finally, we note that the average signs for the two smaller depicted \( r_s \) parameters are more similar to each other than to \( r_s = 10 \). We characterize the temperature in units of the ideal Fermi temperature, which is appropriate for weak coupling. However, for large \( r_s \), the system becomes increasingly nonideal and, therefore, \( \theta \) does not constitute an adequate measure for the degeneracy.

In Fig. 8, we compare the energies of the \( N = 33 \) electrons at \( r_s = 1 \) from PB-PIMC both to RPIMC \([49]\) and CPIMC. The top panel displays the relative difference in the potential energy versus \( \theta \). The CPIMC results for \( V \) are in good agreement with PB-PIMC, while the RPIMC data are systematically higher, by about 2%. Interestingly, this behavior appears to be almost indepen-
FIG. 7. The average sign is plotted versus the temperature $\theta$ for $r_s = 10$, $r_s = 1$ and $r_s = 0.1$ and $N = 33$ spin-polarized electrons with $P = 2$ and the free parameters $t_0 = 0.14$ and $a_1 = 0.33$.

FIG. 8. Comparison with CPIMC and RPIMC as a function of temperature. In the top panel, the relative deviation of the potential energy from the PB-PIMC result is plotted versus $\theta$ for $N = 33$ spin-polarized electrons with $r_s = 1$. The bottom panel displays the same information for the kinetic contribution.
simulations are feasible above $\theta = 0.5$ while for larger $r_s$ even lower temperatures are possible. A comparison of the energies for $r_s = 1$ over the entire applicable temperature range has again revealed an excellent agreement with CPIMC. On the other hand, we observe a nearly $\theta$-independent relative deviation between PB-PIMC and RPIMC in the potential energy of approximately 2%, whereas differences in the kinetic energy are observed only towards low temperature.

We conclude that our permutation blocking PIMC approach is capable to provide accurate results for the UEG over a broad parameter range. This approach is efficient above a minimum temperature of about $0.5 T_F$ and, thus, complements CPIMC. Even though PB-PIMC carries a small systematic error (which is controllable and depends only on the number of time slices), we expect it to be useful for the development and test of other new techniques such as DMQMC [34, 35] and other novel versions of fermionic PIMC, such as the approximate treatment of exchange cycles by DuBois et al. [50] or a variational approach to the RPIMC nodes, e.g. [51].

A natural follow-up of this work will be the extension of PB-PIMC to unpolarized systems which, in combination with CPIMC, should allow for a nearly complete description of the finite temperature UEG over the entire density range. In addition, we aim for the application or derivation of finite size corrections in order to extrapolate our results to the macroscopic limit [47, 52, 53] which could be followed by the construction of a new analytical fit formula for the UEG at finite temperature, e.g. [54, 55]. Finally, since PB-PIMC allows for efficient simulations in the warm dense matter regime, applications to two-component plasmas, such as dense hydrogen [56–58], are within reach.

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REFERENCES

[1] L.B. Fletcher et al., Observations of Continuum Depres- sion in Warm Dense Matter with X-Ray Thomson Scat- tering, Phys. Rev. Lett. 112, 145004 (2014)
[2] D. Kraus et al., Probing the Complex Ion Structure in Liquid Carbon at 100 GPa, Phys. Rev. Lett. 111, 255501 (2013)
[3] S.P. Regan et al., Inelastic X-Ray Scattering from Shocked Liquid Deuterium, Phys. Rev. Lett. 109, 265003 (2012)
[4] J.D. Lindl et al., The physics basis for ignition using indirect-drive targets on the National Ignition Facility, Phys. Plasmas 11, 339 (2004)
[5] S.X. Hu, B. Militzer, V.N. Goncharov, and S. Skupsky, First-principles equation-of-state table of deuterium for inertial confinement fusion applications, Phys. Rev. B 84, 224109 (2011)
[6] O.A. Hurricane et al., Fuel gain exceeding unity in an inertially confined fusion implosion Nature 506, 343-348 (2014)
[7] R. Nora et al., Gigabar Spherical Shock Generation on the OMEGA Laser Phys. Rev. Lett. 114, 045001 (2015)
[8] M.R. Gomez et al., Experimental Demonstration of Fusion-Relevant Conditions in Magnetized Liner Inertial Fusion Phys. Rev. Lett. 113, 155003 (2014)
[9] P.F. Schmit et al., Understanding Fuel Magnetization and Mix Using Secondary Nuclear Reactions in Magnetized Inertial Fusion Phys. Rev. Lett. 113, 155004 (2014)
[10] M.D. Knudson et al., Probing the Interiors of the Ice Giants: Shock Compression of Water to 700 GPa and 3.8 g/cm$^3$, Phys. Rev. Lett. 108, 091102 (2012)
[11] B. Militzer et al., A Massive Core in Jupiter Predicted from First-Principles Simulations, Astrophys. J. 688, L45 (2008)
[12] N. Nettelmann, A. Becker, B. Holst and R. Redmer, Jupiter Models with Improved Ab Initio Hydrogen Equation of State (II-REOS.2), Astrophys. J. 750, 52 (2012)
[13] D.M. Ceperley and B.J. Alder, Ground State of the Electron Gas by a Stochastic Method, Phys. Rev. Lett. 45, 566 (1980)
[14] For completeness, we mention that improved ground state methods have been developed, the most accurate apparently being the full configuration interaction QMC method [15–17]
[15] J.J. Shepherd, G. Booth, A. Grüneis and A. Alavi, Full configuration interaction perspective on the homogeneous electron gas, Phys. Rev. B 85, 081103(R) (2012)
[16] J.J. Shepherd, G.H. Booth and A. Alavi, Investigation of the full configuration interaction quantum Monte Carlo method using homogeneous electron gas models, J. Chem. Phys. 136, 244101 (2012)
[17] J.J. Shepherd, A. Grüneis, G.H. Booth, G. Kresse and A. Alavi, Convergence of many-body wave-function expansions using a plane-wave basis: From homogeneous electron gas to solid state systems, Phys. Rev. B 86, 035111 (2012)
[18] D.M. Ceperley, Path integrals in the theory of condensed helium, Rev. Mod. Phys. 67, 279-355 (1995)
[19] B. Militzer and E.L. Pollock, Equilibrium contact probabilities in dense plasmas, Phys. Rev. B 71, 134303 (2005)
[20] B.K. Clark, M. Casula and D.M. Ceperley, Hexatic and Mesoscopic Phases in a 2D Quantum Coulomb System, Phys. Rev. Lett. 103, 055701 (2009)
[21] M. Boninsegni, N. Prokof’ev and B. Svistunov, Worm Algorithm for Continuous-Space Path Integral Monte Carlo Simulations, *Phys. Rev. Lett.* **96**, 070601 (2006)

[22] M. Boninsegni, N.V. Prokof’ev and B.V. Svistunov, Worm algorithm and diagrammatic Monte Carlo: A new approach to continuous-space path integral Monte Carlo simulations *Phys. Rev. E* **74**, 036701 (2006)

[23] E.Y. Loh, J.E. Gubernatis, R.T. Scalettar, S.R. White, D.J. Scalapino and R.L. Sugar, Sign problem in the numerical simulation of many-electron systems, *Phys. Rev. B* **41**, 9301-9307 (1990)

[24] M. Troyer and U.J. Wiese, Computational Complexity and Fundamental Limitations to Fermionic Quantum Monte Carlo Simulations, *Phys. Rev. Lett.* **94**, 170201 (2005)

[25] E.W. Brown, B.K. Clark, J.L. DuBois and D.M. Ceperley, Path-Integral Monte Carlo Simulation of the Warm Dense Homogeneous Electron Gas, *Phys. Rev. Lett.* **110**, 146405 (2013)

[26] D.M. Ceperley, Fermion Nodes, *J. Stat. Phys.* **63**, 1237-1267 (1991)

[27] B. Militzer and E.L. Pollock, Variational density matrix method for warm, condensed matter: Application to dense hydrogen, *Phys. Rev. E* **61**, 3470-3482 (2000)

[28] B. Militzer, Ph.D. dissertation, University of Illinois at Urbana-Champaign (2000)

[29] V.S. Filinov, Cluster expansion for ideal Fermi systems in the ‘fixed-node approximation’, *J. Phys. A: Math. Gen.* **34**, 1665-1677 (2001)

[30] V.S. Filinov, Analytical contradictions of the fixed-node density matrix, *High Temp.**52**, 615-620 (2014)

[31] T. Schoof, M. Bonitz, A.V. Filinov, D. Hochstuhl and J.W. Dufty, Configuration Path Integral Monte Carlo, *Contrib. Plasma Phys.* **51**, 687-697 (2011)

[32] T. Schoof, S. Groth and M. Bonitz, Towards ab Initio Thermodynamics of the Electron Gas at Strong Degeneracy, *Contrib. Plasma Phys.* **55**, 136-143 (2015)

[33] T. Schoof, S. Groth, J. Vorberger and M. Bonitz, Ab initio thermodynamic results for the degenerate electron gas at finite temperature, *Arxiv e-prints* 1502.04616 (2015)

[34] N.S. Blunt, T.W. Rogers, J.S. Spencer and W.M. Foulkes, Density-matrix quantum Monte Carlo method, *Phys. Rev. B* **89**, 245124 (2014)

[35] F.D. Malone et al., Interaction Picture Density Matrix Quantum Monte Carlo, *Arxiv e-prints* 1506.03057 (2015)

[36] V.S. Filinov, V.E. Fortov, M. Bonitz and Zh. Moldabeov, Fermionic path integral Monte Carlo results for the uniform electron gas at finite temperature, *Phys. Rev. E* **91**, 033108 (2015)

[37] E. Yakub and C. Ronchi, An efficient method for computation of long-ranged Coulomb forces in computer simulation of ionic fluids, *J. Chem. Phys.* **119**, 11556-11560 (2003)

[38] E. Yakub and C. Ronchi, A New Method for Computation of Long Ranged Coulomb Forces in Computer Simulation of Disordered Systems, *J. Low. Temp. Phys.* **139**, 633-643 (2005)

[39] T. Dornheim, S. Groth, A. Filinov and M. Bonitz, Permutation blocking path integral Monte Carlo: A highly efficient approach to the simulation of strongly degenerate non-ideal fermions, *New J. Phys.* **17**, 073017 (2015)

[40] M. Takahashi and M. Imada, Monte Carlo Calculation of Quantum Systems, *J. Phys. Soc. Jpn.* **53**, 963-974 (1984)

[41] V.S. Filinov et al., Thermodynamic Properties and Plasma Phase Transition in dense Hydrogen, *Contrib. Plasma Phys.* **44**, 388-394 (2004)

[42] A.P. Lyubartsev, Simulation of excited states and the sign problem in the path integral Monte Carlo method, *J. Phys. A: Math. Gen.* **38**, 66596674 (2005)

[43] M. Takahashi and M. Imada, Monte Carlo of Quantum Systems. II. Higher Order Correction, *J. Phys. Soc. Jpn.* **53**, 3765-3769 (1984)

[44] S.A. Chin and C.R. Chen, Gradient symplectic algorithms for solving the Schrödinger equation with time-dependent potentials, *J. Chem. Phys.* **117**, 1409 (2002)

[45] K. Sakkos, J. Casulleras and J. Boronat, High order Chin actions in path integral Monte Carlo, *J. Chem. Phys.* **130**, 204109 (2009)

[46] S.A. Chin, High-order Path Integral Monte Carlo methods for solving quantum dot problems, *Phys. Rev. E* **91**, 031301(R) (2015)

[47] L.M. Fraser et al., Finite-size effects and Coulomb interactions in quantum Monte Carlo calculations for homogeneous systems with periodic boundary conditions, *Phys. Rev. B* **53**, 1814 (1996)

[48] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, Equation of State Calculations by Fast Computing Machines, *J. Chem. Phys.* **21**, 1087 (1953)

[49] We take the energy values from the supplement of [25] and subtract the finite size corrections. This allows for a meaningful comparison with the same model system of N = 33 spin-polarized electrons.

[50] J.L. DuBois, B.J. Alder and E.W. Brown, Overcoming the fermion sign problem in homogeneous systems, *Arxiv e-prints* 1409.3262 (2014)

[51] E.W. Brown, Ph.D. dissertation, University of Illinois at Urbana-Champaign (2014)

[52] N.D. Drummond, R.J. Needs, A. Soro and W.M.C. Foulkes, Finite-size errors in continuum quantum Monte Carlo calculations, *Phys. Rev. B* **78**, 125106 (2008)

[53] C. Lin, F.H. Zong and D.M. Ceperley, Twist-averaged boundary conditions in continuum quantum Monte Carlo algorithms, *Phys. Rev. E* **64**, 016702 (2001)

[54] E.W. Brown, J.L. DuBois, M. Holzmann and D.M. Ceperley, Exchange-correlation energy for the three-dimensional homogeneous electron gas at arbitrary temperature, *Phys. Rev. B* **85**, 081102(R) (2013)

[55] V.V. Karasiev, T. Sjostrom, J. Dufty and S.B. Trickey, Accurate Homogeneous Electron Gas Exchange-Correlation Free Energy for Local Spin-Density Calculations, *Phys. Rev. Lett.* **112**, 076403 (2014)

[56] M. Bonitz, V.S. Filinov, V.E. Fortov, P.R. Levashov and H. Fehske, Crystallization in Two-Component Coulomb Systems, *Phys. Rev. Lett.* **95**, 235006 (2005)

[57] M.A. Morales, C. Pierleoni and D. Ceperley, Equation of state of metallic hydrogen from coupled electron-ion Monte Carlo simulations, *Phys. Rev. E* **81**, 022102 (2010)

[58] V.S. Filinov, M. Bonitz, H. Fehske, V.E. Fortov and P.R. Levashov, Proton Crystallization in a Dense Hydrogen Plasma, *Contrib. Plasma Phys.* **52**, 224-228 (2012)