

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

Tobias Dornheim, Tim Schoof, Simon Groth, Alexey Filinov, and Michael Bonitz

Citation: *The Journal of Chemical Physics* **143**, 204101 (2015); doi: 10.1063/1.4936145

View online: <http://dx.doi.org/10.1063/1.4936145>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/143/20?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Structural stability and defect energetics of ZnO from diffusion quantum Monte Carlo](#)

J. Chem. Phys. **142**, 164705 (2015); 10.1063/1.4919242

[Generalizing the self-healing diffusion Monte Carlo approach to finite temperature: A path for the optimization of low-energy many-body bases](#)

J. Chem. Phys. **140**, 074103 (2014); 10.1063/1.4861222

[Efficient methods for including quantum effects in Monte Carlo calculations of large systems: Extension of the displaced points path integral method and other effective potential methods to calculate properties and distributions](#)

J. Chem. Phys. **138**, 014110 (2013); 10.1063/1.4772667

[Quantum Monte Carlo Simulations](#)

AIP Conf. Proc. **1162**, 98 (2009); 10.1063/1.3225490

[Thermodynamic and structural properties of repulsive hard-core Yukawa fluid: Integral equation theory, perturbation theory and Monte Carlo simulations](#)

J. Chem. Phys. **121**, 1480 (2004); 10.1063/1.1759616



AIP | APL Photonics

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief



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

Tobias Dornheim,^{1,a)} Tim Schoof,¹ Simon Groth,¹ Alexey Filinov,^{1,2} and Michael Bonitz¹

¹*Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität, Leibnizstrasse 15, Kiel D-24098, Germany*

²*Joint Institute for High Temperatures RAS, Izhorskaya Str. 13, 125412 Moscow, Russia*

(Received 14 August 2015; accepted 6 November 2015; published online 23 November 2015)

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, $r_s = \bar{r}/a_B \gtrsim 1$. These data have been complemented by configuration path integral Monte Carlo (CPIMC) simulations for $r_s \leq 1$ 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.*, New J. Phys. **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. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936145>]

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 uniform electron gas (UEG), hitherto at zero temperature.^{13–17} 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., Ref. 18, is a powerful tool for the *ab initio* simulation of both distinguishable particles (often referred to as “boltzmannions,” e.g., Refs. 19 and 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., Ref. 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 ($r_s \rightarrow 0$).^{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) approach³⁴ 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 warm dense matter (WDM) parameters, would be highly desirable.

In this work we, therefore, investigate the applicability of the recently developed permutation blocking PIMC (PB-PIMC) approach³⁹ to the uniform electron gas. We note

^{a)}Electronic mail: dornheim@theo-physik.uni-kiel.de

that PB-PIMC is essentially standard PIMC but combines two well known concepts: (1) antisymmetric imaginary time propagators,^{40–42} i.e., determinants, between all “time slices” and (2) 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). (3) To efficiently sample this more complicated configuration space, PB-PIMC uses a novel Monte Carlo update scheme which combines the worm algorithm idea^{21,22} with the temporary construction of artificial trajectories, cf. Ref. 39. The application of determinants leads to a relieve 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. Therefore, it is the combination of the above three ingredients that allows us to significantly extend the range of applicability of standard PIMC towards stronger degeneracy, see also Fig. 1.

The details of our PB-PIMC scheme, for the UEG, are described in Section II B, after a brief introduction of the employed model in Section II 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 $N = 33$ spin-polarized electrons, which is a commonly used model system of the UEG, see Section III B. Interestingly, our PB-PIMC approach allows us to obtain accurate results over the entire density range and, therefore, to make a comparison with the pre-existing RPIMC and CPIMC results for the UEG. Finally, in Section III C we investigate the applicability of our method with respect to the temperature. We find that PB-PIMC, in combination with CPIMC, allows for the simulation of

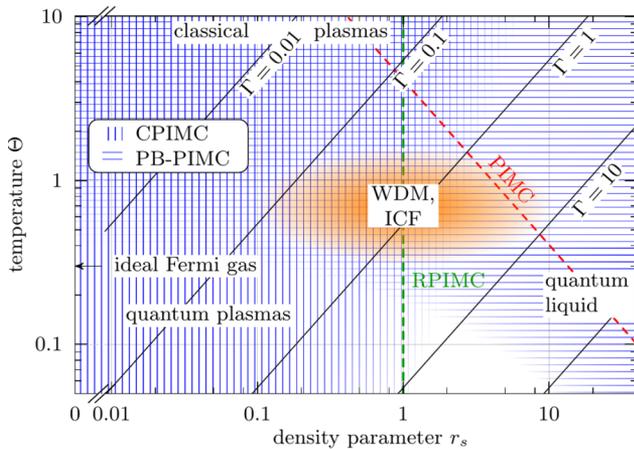


FIG. 1. Density-temperature plain around the warm dense matter (WDM) regime. PB-PIMC significantly extends the range of applicability of standard PIMC (qualitatively shown by the red dashed line, see also Figs. 5 and 7) towards lower temperature and higher density while CPIMC is applicable to the highly degenerate and weakly nonideal UEG.³³ RPIMC data²⁵ are available for $r_s \geq 1$. The orange area marks the conditions of WDM and inertial confinement fusion (ICF).⁵

the UEG over a broad parameter range, which includes the physically most interesting regime of warm dense matter, cf. Fig. 1.

II. THEORY

A. Model Hamiltonian

The uniform electron gas, often referred to as “Jellium,” is a model description of Coulomb interacting electrons with a neutralizing background of positive charges which are uncorrelated and homogeneously distributed. To describe an infinite system based on a finite number of particles, one implements periodic boundary conditions and includes the interaction of the N electrons in the main cell with all their images via Ewald summation. Following the notation from Ref. 47, we express the Hamiltonian of the N electron UEG (in atomic units) as

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N e^2 \Psi(\mathbf{r}_i, \mathbf{r}_j) + \frac{Ne^2}{2} \xi,$$

with ξ being the Madelung constant and the periodic Ewald pair potential

$$\Psi(\mathbf{r}, \mathbf{s}) = \frac{1}{V} \sum_{\mathbf{G} \neq 0} \frac{e^{-\pi^2 \mathbf{G}^2 / \kappa^2} e^{2\pi i \mathbf{G}(\mathbf{r}-\mathbf{s})}}{\pi \mathbf{G}^2} - \frac{\pi}{\kappa^2 V} + \sum_{\mathbf{R}} \frac{\text{erfc}(\kappa |\mathbf{r} - \mathbf{s} + \mathbf{R}|)}{|\mathbf{r} - \mathbf{s} + \mathbf{R}|}. \quad (1)$$

Here, $\mathbf{R} = \mathbf{n}_1 L$ and $\mathbf{G} = \mathbf{n}_2 / L$ 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 κ 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

$$\mathbf{F}_{ij} = -\nabla_i \Psi(\mathbf{r}_i, \mathbf{r}_j). \quad (2)$$

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

$$\mathbf{F}_{ij} = \frac{2}{V} \sum_{\mathbf{G} \neq 0} \left(\frac{\mathbf{G}}{G^2} \sin[2\pi \mathbf{G}(\mathbf{r}_i - \mathbf{r}_j)] e^{-\pi^2 \mathbf{G}^2 / \kappa^2} \right) + \sum_{\mathbf{R}} \frac{\mathbf{r}_i - \mathbf{r}_j + \mathbf{R}}{\alpha^3} \left(\text{erfc}(\kappa \alpha) + \frac{2\kappa \alpha}{\sqrt{\pi}} e^{-\kappa^2 \alpha^2} \right),$$

with the definition $\alpha = |\mathbf{r}_i - \mathbf{r}_j + \mathbf{R}|$.

B. Simulation method

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

$$Z = \frac{1}{N!} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \int d\mathbf{R} \langle \mathbf{R} | e^{-\beta \hat{H}} | \hat{\pi}_\sigma \mathbf{R} \rangle, \quad (3)$$

with $\mathbf{R} = \mathbf{r}_1, \dots, \mathbf{r}_N$ containing the coordinates of all electrons, $\hat{\pi}_\sigma$ denoting the exchange operator which corresponds to a specific element σ 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 $e^{-\epsilon\hat{H}} \approx e^{-\epsilon\hat{K}}e^{-\epsilon\hat{V}}$, with $\epsilon = \beta/P$ being the imaginary time step of a single propagator and the kinetic and potential contributions to the Hamiltonian \hat{K} and \hat{V} , respectively, we use the fourth order factorization,^{44,45}

$$e^{-\epsilon\hat{H}} \approx e^{-v_1\epsilon\hat{W}_{\alpha 1}}e^{-t_1\epsilon\hat{K}}e^{-v_2\epsilon\hat{W}_{1-2\alpha 1}}e^{-t_1\epsilon\hat{K}}e^{-v_1\epsilon\hat{W}_{\alpha 1}}e^{-2t_0\epsilon\hat{K}}. \quad (4)$$

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

$$[[\hat{V}, \hat{K}], \hat{V}] = \frac{\hbar^2}{m} \sum_{i=1}^N |\mathbf{F}_i|^2 \quad (5)$$

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

$$Z = \frac{1}{(N!)^{3P}} \int d\mathbf{X} \prod_{\alpha=0}^{P-1} e^{-\epsilon\tilde{V}_{\alpha}} e^{-\epsilon^3 u_0 \frac{\hbar^2}{m} \tilde{F}_{\alpha}} \times \det(\rho_{\alpha}) \det(\rho_{\alpha A}) \det(\rho_{\alpha B}), \quad (6)$$

with the definition of the potential and force terms

$$\begin{aligned} \tilde{V}_{\alpha} &= v_1 V(\mathbf{R}_{\alpha}) + v_2 V(\mathbf{R}_{\alpha A}) + v_1 V(\mathbf{R}_{\alpha B}), \\ \tilde{F}_{\alpha} &= \sum_{i=1}^N (a_1 |\mathbf{F}_{\alpha, i}|^2 + (1 - 2a_1) |\mathbf{F}_{\alpha A, i}|^2 + a_1 |\mathbf{F}_{\alpha B, i}|^2), \end{aligned} \quad (7)$$

and the diffusion matrices

$$\rho_{\alpha}(i, j) = \lambda_{t_1 \epsilon}^{-D} \sum_{\mathbf{n}} \exp\left(-\frac{\pi}{\lambda_{t_1 \epsilon}^2} (\mathbf{r}_{\alpha, j} - \mathbf{r}_{\alpha A, i} + \mathbf{n}L)^2\right),$$

with D being the dimensionality, see, e.g., Ref. 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, $d\mathbf{X} = d\mathbf{R}_0 \dots d\mathbf{R}_{P-1} d\mathbf{R}_{0A} \dots d\mathbf{R}_{P-1A} d\mathbf{R}_{0B} \dots d\mathbf{R}_{P-1B}$. Instead of explicitly sampling each permutation individually, as in standard PIMC, we combine configuration weights of both

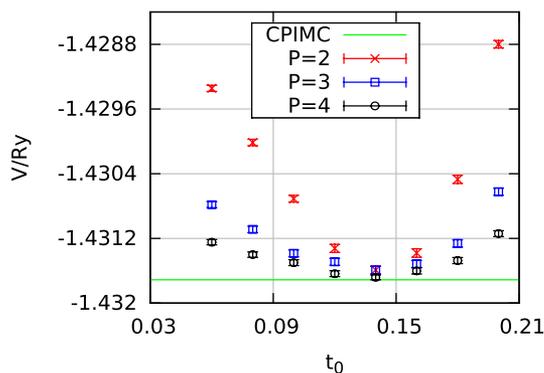


FIG. 2. Influence of the relative interslice spacing t_0 for $N = 4$, $r_s = 4$, and $\theta = 0.5$ on the convergence of the propagator. The exact result known from CPIMC (green line) is compared to the PB-PIMC results for $P = 2$, $P = 3$, and $P = 4$ for the fixed free parameter $a_1 = 0.33$ over the entire t_0 range. The optimal value is located around $t_0 = 0.14$.

positive and negative signs 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, $\lambda_{t_1 \epsilon} = \sqrt{2\pi\epsilon t_1 \hbar^2/m}$, 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 For this purpose, we have introduced a set of efficient Monte Carlo updates that combine the worm algorithm idea^{21,22} with the temporary construction of artificial trajectories, see Ref. 39 for a more detailed description.

C. Energy estimator

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

$$E = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}. \quad (8)$$

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

$$\begin{aligned} E &= \frac{1}{P} \sum_{k=0}^{P-1} \left(\tilde{V}_k + 3\epsilon^2 u_0 \frac{\hbar^2}{m} \tilde{F}_k \right) + \frac{3DN}{2\epsilon} \\ &\quad - \sum_{k=0}^{P-1} \sum_{\kappa=1}^N \sum_{\xi=1}^N \left(\frac{\pi \eta_{\kappa \xi}^k}{\epsilon P \lambda_{t_1 \epsilon}^2} + \frac{\pi \eta_{\kappa \xi}^{kA}}{\epsilon P \lambda_{t_1 \epsilon}^2} + \frac{\pi \eta_{\kappa \xi}^{kB}}{\epsilon P \lambda_{2t_0 \epsilon}^2} \right), \end{aligned}$$

with the definition

$$\eta_{\kappa \xi}^k = \frac{(\rho_{\kappa}^{-1})_{\kappa \xi}}{\lambda_{t_1 \epsilon}^D} \sum_{\mathbf{n}} \exp\left[-\frac{\pi}{\lambda_{t_1 \epsilon}^2} (\mathbf{r}_{k, \kappa} - \mathbf{r}_{kA, \xi} + \mathbf{L}\mathbf{n})^2\right] \times (\mathbf{r}_{k, \kappa} - \mathbf{r}_{kA, \xi} + \mathbf{L}\mathbf{n})^2. \quad (9)$$

For completeness, we note that the total energy E splits into the kinetic and potential contributions, K and 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 al.*⁴⁵ and the application of PB-PIMC to electrons in a quantum dot.³⁹ For completeness, we mention that the kinetic energy K exhibits the same behavior. Hence, we use the combination $a_1 = 0.33$ and $t_0 = 0.14$ for all presented simulations in this work. However, 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 , θ , and N , we investigate the convergence of both contributions separately. The top panel shows the potential energy versus the inverse number of propagators $P^{-1} \propto \epsilon$ 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 address the r_s -dependence of the time step error by comparing PB-PIMC results for V with $P = 2$

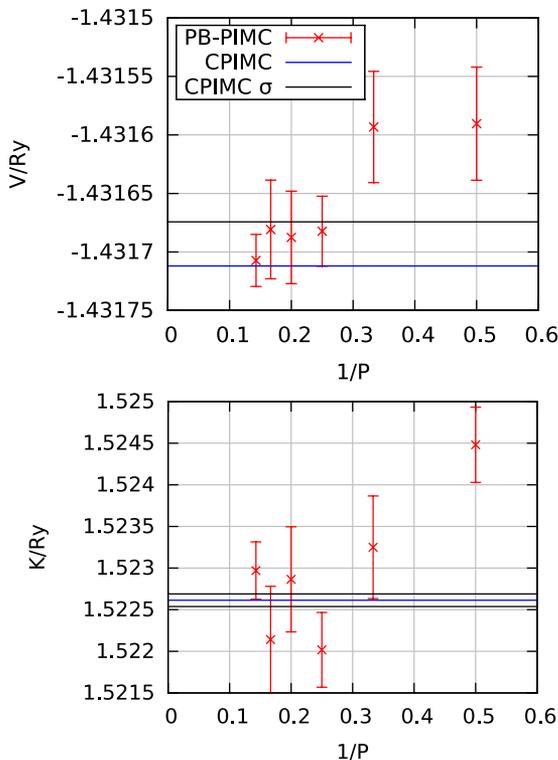


FIG. 3. Convergence of the potential (top) and kinetic (bottom) energy for $N = 4$, $r_s = 4$, and $\theta = 0.5$ with $t_0 = 0.14$ and $a_1 = 0.33$. In the top panel, the potential energy V is plotted versus the inverse number of propagators $P^{-1} \propto \epsilon$ and the PB-PIMC results are compared to the exact value known from CPIMC. The bottom panel shows the same information for the kinetic energy K .

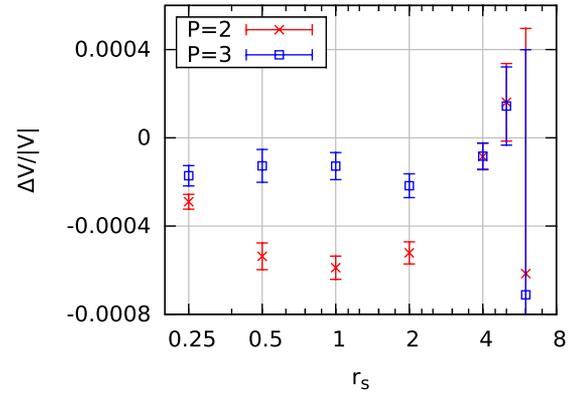


FIG. 4. Accuracy of two and three propagators over a broad r_s range for $N = 4$ and $\theta = 0.5$ with $t_0 = 0.14$ and $a_1 = 0.33$. We show the relative difference between the potential energy from PB-PIMC and CPIMC, $\Delta V/|V|$, for the optimal parameters from the fourth order propagator.

(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 errorbars 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 \hat{K} and \hat{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.

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 PB-PIMC data 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

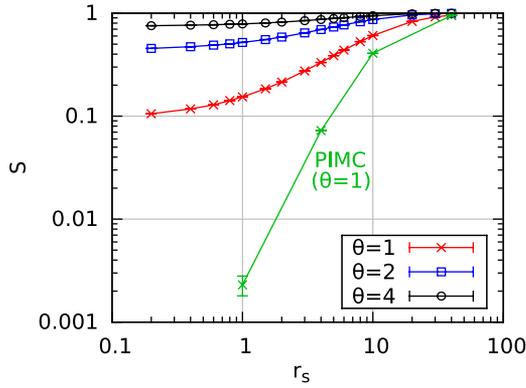


FIG. 5. The average sign of PB-PIMC is plotted versus the density parameter r_s for three different temperatures and $N = 33$ spin-polarized electrons with $P = 2$, $a_1 = 0.33$, and $t_0 = 0.14$. The standard PIMC data (green crosses) are taken from the supplement of Ref. 25.

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 (cf. the green curve), which exhibits a significantly smaller average sign and, for $\theta = 1$, is not feasible for $r_s \lesssim 3$. Nevertheless, with decreasing temperature the sign of PB-PIMC drops and the FSP makes the simulations more involved, cf. Section III C.

In Fig. 6, we compare the corresponding energies with RPIMC⁴⁹ 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

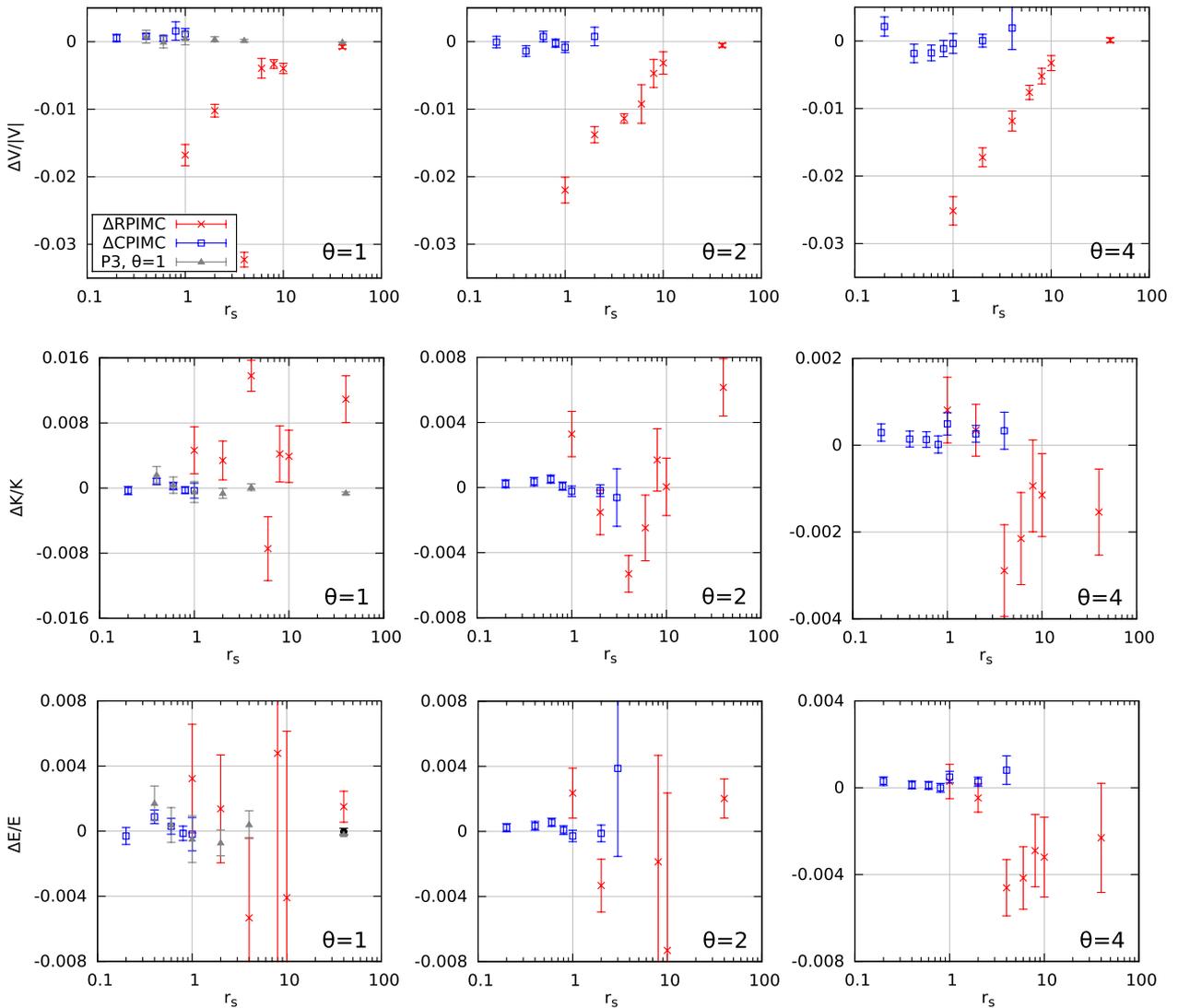


FIG. 6. Comparison of PB-PIMC with CPIMC and RPIMC for $N = 33$ spin-polarized electrons and three temperatures. In the top row, the relative deviation of the potential energy from PB-PIMC with $P = 2$, $t_0 = 0.14$ and $a_1 = 0.33$ is plotted versus r_s . The center and bottom rows display the same information for the kinetic and total energy, respectively. The black dot in the bottom left panel ($\Delta E/E$ for $\theta = 1$) corresponds to standard PIMC and is taken from the supplement of Ref. 25.

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 of PB-PIMC is plotted versus θ for $N = 33$ spin-polarized electrons at $r_s = 10$, $r_s = 1$, and $r_s = 0.1$. All three curves exhibit a similar behavior, that is, a large sign S at high temperature and a monotonous decay for $T \rightarrow 0$. However, for $r_s = 10$, the system is significantly less degenerate than for both other density parameters, and even at $\theta = 0.5$, the

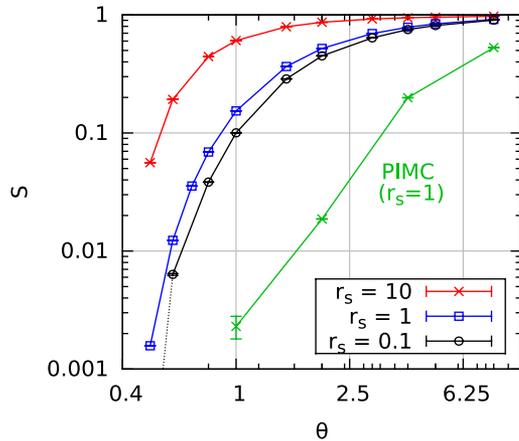


FIG. 7. The average sign of PB-PIMC is plotted versus the temperature θ for $r_s = 10$, $r_s = 1$, and $r_s = 0.1$ and $N = 33$ spin-polarized electrons with $P = 2$ and the free parameters $t_0 = 0.14$ and $\alpha_1 = 0.33$. The standard PIMC data (green crosses) are taken from the supplement of Ref. 25.

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. For completeness, we also show the average sign of standard PIMC for $r_s = 1$, cf. the green curve. Evidently, these simulations are significantly more severely affected by the FSP and simulations are feasible only for $\theta \gtrsim 2$. Finally, we note that the average signs of PB-PIMC 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, θ 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 RPIMC⁴⁹ and CPIMC. The top panel displays the relative difference in the potential energy versus θ . 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 independent of the temperature. In the bottom panel, the same information is shown for the kinetic energy and, again, PB-PIMC agrees with CPIMC over the entire

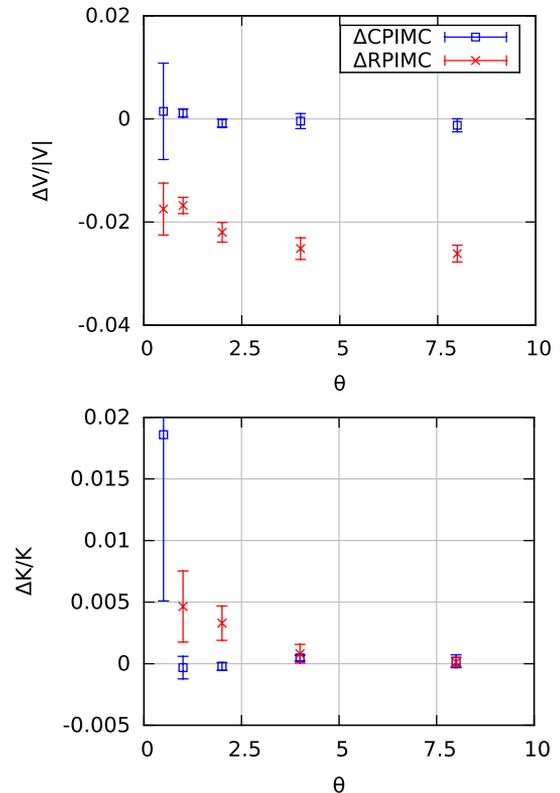


FIG. 8. Comparison with CPIMC and RPIMC as a function of temperature. In the top panel, the relative deviation of the potential energy from the PB-PIMC result is plotted versus θ for $N = 33$ spin-polarized electrons and $r_s = 1$. The bottom panel displays the same information for the kinetic contribution.

temperature range. The large statistical uncertainty at $\theta = 0.5$ is a manifestation of the FSP in PB-PIMC, which prevents us from obtaining more precise kinetic energies with feasible computational effort. The RPIMC data for K are slightly lower, at low temperature, which confirms the trend observed by Schoof *et al.*,³³ and seems to converge towards the other methods for large θ .

IV. DISCUSSION

In summary, we have successfully extended the PB-PIMC approach³⁹ to the uniform electron gas at finite temperature. We have started the discussion with a brief introduction of our simulation scheme, which combines a fourth-order factorization of the density matrix with the application of antisymmetric imaginary time propagators, i.e., determinants. This allows us to combine permutations, which appear as individual configurations with positive and negative sign in standard PIMC, into a single configuration weight (hence the label permutation blocking). Furthermore, we employ an efficient set of Monte Carlo updates which is based on the temporary construction of artificial trajectories. Due to the combination of these three concepts, the average sign in our simulations is significantly increased.

To assert the quality of our numerical results, we have investigated the optimization of the free parameters of our propagator and demonstrated the convergence of both the potential and kinetic energies with respect to the number of imaginary time steps. We have found that even for the lowest considered temperature, $\theta = 0.5$, as few as two propagators allow for a relative accuracy of 0.1% and 0.01% in the kinetic and potential energies, respectively. After this preparatory work, we have shown results for $N = 33$ spin-polarized electrons, which is a commonly used model system as it is well suited to be a starting point for the extrapolation to the macroscopic limit (finite size corrections). In striking contrast to previous implementations of standard PIMC, PB-PIMC is feasible over the entire density range and, therefore, allows us to compare our results to both CPIMC and RPIMC data, where they are available. Our PB-PIMC data exhibit a very good agreement with CPIMC, for both the potential and kinetic energies, for all three investigated temperatures. On the other hand, we observe deviations between PB-PIMC and RPIMC of up to 3% in the potential energy, which decrease towards strong coupling. For the kinetic energy, we find no systematic trend although, for $\theta = 1$, most of the RPIMC-values are smaller while, for $\theta = 4$, most are larger than the PB-PIMC results. However, for both temperatures this deviation hardly exceeds twice the RPIMC errorbars.

Finally, we have investigated the applicability of PB-PIMC to the $N = 33$ spin-polarized electrons with respect to the temperature. With decreasing θ , exchange effects lead to more negative determinants in the configuration weights and, therefore, a smaller average sign. For the physically most interesting density regime, $r_s \sim 1$, simulations are feasible above $\theta = 0.5$ while for larger r_s even lower temperatures are possible. Therefore, it has once more been demonstrated that the range of applicability of standard PIMC has been significantly extended. 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 θ -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 $0.5T_F$ 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., Ref. 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., Refs. 54 and 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.

ACKNOWLEDGMENTS

We acknowledge stimulating discussions with C. Hann (Kiel and Durham, North Carolina) and V. S. Filinov (Moscow). This work is supported by the Deutsche Forschungsgemeinschaft via SFB TR-24 Project A9 and via Project No. BO 1366/10 as well as by Grant Nos. SHP00006 and SHP00015 for CPU time at the Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen (HLRN).

¹L. B. Fletcher *et al.*, "Observations of continuum depression in warm dense matter with x-ray Thomson scattering," *Phys. Rev. Lett.* **112**, 145004 (2014).

²D. Kraus *et al.*, "Probing the complex ion structure in liquid carbon at 100 GPa," *Phys. Rev. Lett.* **111**, 255501 (2013).

³S. P. Regan *et al.*, "Inelastic x-ray scattering from shocked liquid deuterium," *Phys. Rev. Lett.* **109**, 265003 (2012).

⁴J. D. Lindl *et al.*, "The physics basis for ignition using indirect-drive targets on the National Ignition Facility," *Phys. Plasmas* **11**, 339 (2004).

⁵S. 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).

⁶O. A. Hurricane *et al.*, "Fuel gain exceeding unity in an inertially confined fusion implosion," *Nature* **506**, 343-348 (2014).

⁷R. Nora *et al.*, "Gigabar spherical shock generation on the OMEGA laser," *Phys. Rev. Lett.* **114**, 045001 (2015).

⁸M. R. Gomez *et al.*, "Experimental demonstration of fusion-relevant conditions in magnetized liner inertial fusion," *Phys. Rev. Lett.* **113**, 155003 (2014).

⁹P. F. Schmit *et al.*, "Understanding fuel magnetization and mix using secondary nuclear reactions in magneto-inertial fusion," *Phys. Rev. Lett.* **113**, 155004 (2014).

- ¹⁰M. D. Knudson *et al.*, “Probing the interiors of the ice giants: Shock compression of water to 700 GPa and 3.8 g/cm³,” *Phys. Rev. Lett.* **108**, 091102 (2012).
- ¹¹B. Militzer *et al.*, “A massive core in Jupiter predicted from first-principles simulations,” *Astrophys. J.* **688**, L45 (2008).
- ¹²N. Nettelmann, A. Becker, B. Holst, and R. Redmer, “Jupiter models with improved *ab initio* hydrogen equation of state (H-REOS.2),” *Astrophys. J.* **750**, 52 (2012).
- ¹³D. M. Ceperley and B. J. Alder, “Ground state of the electron gas by a stochastic method,” *Phys. Rev. Lett.* **45**, 566 (1980).
- ¹⁴For completeness, we mention that improved ground state methods have been developed, the most accurate apparently being the full configuration interaction QMC method.^{15–17}
- ¹⁵J. 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).
- ¹⁶J. 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).
- ¹⁷J. 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).
- ¹⁸D. M. Ceperley, “Path integrals in the theory of condensed helium,” *Rev. Mod. Phys.* **67**, 279-355 (1995).
- ¹⁹B. Militzer and E. L. Pollock, “Equilibrium contact probabilities in dense plasmas,” *Phys. Rev. B* **71**, 134303 (2005).
- ²⁰B. K. Clark, M. Casula, and D. M. Ceperley, “Hexatic and mesoscopic phases in a 2D quantum Coulomb system,” *Phys. Rev. Lett.* **103**, 055701 (2009).
- ²¹M. Boninsegni, N. Prokof’ev, and B. Svistunov, “Worm algorithm for continuous-space path integral Monte Carlo simulations,” *Phys. Rev. Lett.* **96**, 070601 (2006).
- ²²M. 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).
- ²³E. 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).
- ²⁴M. Troyer and U. J. Wiese, “Computational complexity and fundamental limitations to fermionic quantum Monte Carlo simulations,” *Phys. Rev. Lett.* **94**, 170201 (2005).
- ²⁵E. 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).
- ²⁶D. M. Ceperley, “Fermion nodes,” *J. Stat. Phys.* **63**, 1237-1267 (1991).
- ²⁷B. Militzer and E. L. Pollock, “Variational density matrix method for warm, condensed matter: Application to dense hydrogen,” *Phys. Rev. E* **61**, 3470-3482 (2000).
- ²⁸B. Militzer, Ph.D. dissertation, University of Illinois at Urbana-Champaign (2000).
- ²⁹V. S. Filinov, “Cluster expansion for ideal Fermi systems in the ‘fixed-node approximation,’” *J. Phys. A: Math. Gen.* **34**, 1665-1677 (2001).
- ³⁰V. S. Filinov, “Analytical contradictions of the fixed-node density matrix,” *High Temp.* **52**, 615-620 (2014).
- ³¹T. Schoof, M. Bonitz, A. V. Filinov, D. Hochstuhl, and J. W. Dufty, “Configuration path integral Monte Carlo,” *Contrib. Plasma Phys.* **51**, 687-697 (2011).
- ³²T. Schoof, S. Groth, and M. Bonitz, “Towards *ab initio* thermodynamics of the electron gas at strong degeneracy,” *Contrib. Plasma Phys.* **55**, 136-143 (2015).
- ³³T. Schoof, S. Groth, J. Vorberger, and M. Bonitz, “*Ab initio* thermodynamic results for the degenerate electron gas at finite temperature,” *Phys. Rev. Lett.* **115**, 130402 (2015).
- ³⁴N. S. Blunt, T. W. Rogers, J. S. Spencer, and W. M. Foulkes, “Density-matrix quantum Monte Carlo method,” *Phys. Rev. B* **89**, 245124 (2014).
- ³⁵F. D. Malone *et al.*, “Interaction picture density matrix quantum Monte Carlo,” *J. Chem. Phys.* **143**, 044116 (2015).
- ³⁶V. S. Filinov, V. E. Fortov, M. Bonitz, and Zh. Moldabekov, “Fermionic path integral Monte Carlo results for the uniform electron gas at finite temperature,” *Phys. Rev. E* **91**, 033108 (2015).
- ³⁷E. 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).
- ³⁸E. 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).
- ³⁹T. 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).
- ⁴⁰M. Takahashi and M. Imada, “Monte Carlo calculation of quantum systems,” *J. Phys. Soc. Jpn.* **53**, 963-974 (1984).
- ⁴¹V. S. Filinov *et al.*, “Thermodynamic properties and plasma phase transition in dense hydrogen,” *Contrib. Plasma Phys.* **44**, 388-394 (2004).
- ⁴²A. P. Lyubartsev, “Simulation of excited states and the sign problem in the path integral Monte Carlo method,” *J. Phys. A: Math. Gen.* **38**, 6659-6674 (2005).
- ⁴³M. Takahashi and M. Imada, “Monte Carlo of quantum systems. II. Higher order correction,” *J. Phys. Soc. Jpn.* **53**, 3765-3769 (1984).
- ⁴⁴S. A. Chin and C. R. Chen, “Gradient symplectic algorithms for solving the Schrödinger equation with time-dependent potentials,” *J. Chem. Phys.* **117**, 1409 (2002).
- ⁴⁵K. Sakkos, J. Casulleras, and J. Boronat, “High order Chin actions in path integral Monte Carlo,” *J. Chem. Phys.* **130**, 204109 (2009).
- ⁴⁶S. A. Chin, “High-order path integral Monte Carlo methods for solving quantum dot problems,” *Phys. Rev. E* **91**, 031301(R) (2015).
- ⁴⁷L. 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).
- ⁴⁸N. 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).
- ⁴⁹We take the energy values from the supplement of Ref. 25 and subtract the finite size corrections. This allows for a meaningful comparison with the same model system of $N = 33$ spin-polarized electrons.
- ⁵⁰J. L. DuBois, B. J. Alder, and E. W. Brown, “Overcoming the fermion sign problem in homogeneous systems,” e-print [arXiv:1409.3262](https://arxiv.org/abs/1409.3262) (2014).
- ⁵¹E. W. Brown, Ph.D. dissertation, University of Illinois at Urbana-Champaign (2014).
- ⁵²N. D. Drummond, R. J. Needs, A. Sorouri, and W. M. C. Foulkes, “Finite-size errors in continuum quantum Monte Carlo calculations,” *Phys. Rev. B* **78**, 125106 (2008).
- ⁵³C. Lin, F. H. Zong, and D. M. Ceperley, “Twist-averaged boundary conditions in continuum quantum Monte Carlo algorithms,” *Phys. Rev. E* **64**, 016702 (2001).
- ⁵⁴E. 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* **88**, 081102(R) (2013).
- ⁵⁵V. V. Karasiev, T. Sjöström, 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).
- ⁵⁶M. 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).
- ⁵⁷M. A. Morales, C. Pierleoni, and D. Ceperley, “Equation of state of metallic hydrogen from coupled electron-ion Monte Carlo simulations,” *Phys. Rev. E* **81**, 021202 (2010).
- ⁵⁸V. 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).