Thermodynamic properties of the nonideal hydrogen plasmas: Comparison of different simulation techniques

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Abstract. In this paper, we review the following simulation techniques for studying nonideal electron–ion plasmas: classical molecular dynamics, wave packet molecular dynamics and Monte Carlo and path integral Monte Carlo. As example the hydrogen nonideal plasma is considered for a wide range of densities and temperatures. The results for the thermodynamic properties such as the internal energy and pressure are compared. The area of applicability of the classical molecular dynamics and fundamental problems of the wave packet Monte Carlo are discussed.

1. Introduction

Atomistic simulations play essential role in studies of strongly coupled (nonideal) systems of charged particles where analytical approaches usually give only approximate results. In this paper we focus on the hydrogen plasma (warm dense matter) with electron number densities in the range of \( n_e = 10^{20} - 10^{24} \) cm\(^{-3} \) and the temperature range of \( T = 10 - 50 \) kK. It corresponds to the nonideality parameter values of \( \Gamma = e^2/(4\pi\varepsilon_0 k_B T)(4\pi n_e/3)^{1/3} = 0.025 - 18 \) and the quantum degeneracy parameter \( \Theta = \hbar^2(3\pi^2 n_e)^{2/3}/(2m_e k_B T) = 0.02 - 19 \). These conditions are related to the states of matter in astrophysical objects, strong laser and particle beam experiments where hydrogen can be found at megabar pressures and the above given temperatures. The equation of state for such a dense hydrogen is still an open question \cite{1, 2}. Moreover, the atomistic simulations with electron dynamics allow to study electron–ion relaxation processes which is required for higher lever simulation techniques \cite{3}.

In the classical molecular dynamics (MD) both electrons and ions are represented as point-like particles that interact via the Coulomb potential at large distance and a pseudopotential at short distances that accounts for quantum effects to a certain extent \cite{4–9}. Due to an ambiguity in choosing a correct pseudopotential at short distances the area of applicability of the classical MD is formally restricted to high temperatures and high ionization degrees. The critical parameter here is the fraction of bound states of electrons and ions where classical electrons fail to reproduce quantum properties of low energy atomic states. However, calculation of the ionization degree of nonideal plasmas is a complicated problem itself that often requires numerical approaches. Therefore the area of applicability of the classical MD needs quantification. In this work we...
address this question by comparing the results for general thermodynamical properties such as the internal energy and pressure with other simulation approaches.

With respect to the classical MD with pseudopotentials, the next step towards the quantum description can be done by replacing point-like electrons by a parametrized wave function of a certain form. This approach is used in the wave packet molecular dynamics (WPMD) and wave packet Monte Carlo (WPMC) methods where the wave function of a single electron is represented by a Gaussian wave packet with changing width [10–13]. In the simplest case the total wave function is defined as a Hartree product of the single electron wave functions. This version of the method describes atomic-like bound states more correctly than the classical molecular dynamics. In the Hartree–Fock limit the exchange interaction between electrons of the same spin can be taken into account using antisymmetrized wave function [14]. The antisymmetrized version may in principle describe both quantum uncertainty and Pauli exclusion principle, thus the atomic and molecule bound states are tractable together with the highly degenerate warm dense matter with large $\Theta > 1$.

The area of very high plasma densities (over $10^{23}$ cm$^{-3}$ for hydrogen plasma) and low temperatures (less than $10^4$ K) is well described by the WPMD and WPMC methods [12] including the version with antisymmetrized wave functions (AWPMD) [14]. These methods, however, were not directly applicable to higher temperatures due to the model breakdown caused by spreading of the wave packets for weakly bound electrons [15,16]. As proposed in [17] we use a confinement potential to solve this problem.

As the fully ab-initio benchmark for the classical and wave packet electron dynamics we consider the method of path integral Monte Carlo (PIMC) [18] which was successfully applied for *ab-initio* simulation of hydrogen plasmas [19–22], although the it is not capable to handle the dynamics of electrons. The main idea of PIMC simulations is to perform first-principle calculations without additional assumptions. The Feynman’s path integral concept and the Monte Carlo technique provide correct treatment of bound state formation, ionization and dissociation processes. Furthermore no restrictions on the type of chemical species are made and the appearance of complex aggregates such as molecular ions or clusters of several atoms can be reproduced. On the other hand, the simulations are expected to become increasingly difficult at high densities where the electron gas is highly degenerate and the Fermion sign problem arises [20]. The sign problem has different approximate solution presented in the following modifications of the PIMC method: restricted path integral Monte Carlo (RPIMC) [23, 24], coupled electron–ion Monte Carlo (CEIMC) [25–27] and direct path integral Monte Carlo (DPIMC) [20]. The difference between these methods was described in details in [19,20]. In this work we compare our results with the results of DPIMC and RPIMC methods.

In the present work we focus on the study of the computationally efficient simulation methods that may track the electron dynamics for large systems. Therefore we leave other approximate quantum simulation methods such as Born–Oppenheimer molecular dynamics (DFT-MD), which may also be applied to plasma simulations out of scope of this work. The DFT methods are much more computationally demanding [28], however in their applicability domain they are successfully used to describe warm dense matter [2].

2. Simulation methods

2.1. Classical molecular dynamics with pseudopotentials

As stated above in the classical MD simulations we consider a system of $N_e$ electron and $N_i$ ions with the general Hamiltonian form

$$H = U_{ee} + U_{ei} + U_{ii} + K_e + K_i,$$

(1)

where $K_e = \sum_{k}^{N_e} \frac{p_k^2}{2m_e}$ and $K_i = \sum_{j}^{N_i} \frac{p_j^2}{2m_i}$ are the electron and ion kinetic energies, $U_{\alpha\beta} = \sum_{k,j}^{N_e,N_i} V_{\alpha\beta}(|r_k - r_j|)$ represents the interaction energy between species $\alpha$ and $\beta$; $r_k$, $r_j$
\( p \) and \( m_\alpha \) are the coordinates, momenta and masses of the corresponding particles. Due to a relatively large mass of ions, their quantum properties are neglected and the ion–ion (i–i) interaction potential has the Coulomb form

\[
V_{ii}(r) = \frac{Z^2 e^2}{4\pi\varepsilon_0 r}.
\]

In this work we consider only the case of \( Z = 1 \).

There are various electron–ion (e–i) and electron–electron (e–e) interaction models that account for quantum properties of electrons. Generally the effect of the pseudopotential contains in smearing the Coulomb interaction at small separation between particles by taking into account the quantum uncertainty principle and in some cases a certain amount of low-energy bound states. Electrons and ions remain in this description the classical particles described by their positions and momenta, but the potentials become temperature dependent because they partly include the ensemble properties. Let us consider two of the pseudopotentials skipping their derivation and corresponding discussions. First of them has the form [9, 29]

\[
V_{\alpha\beta}^{\text{Kellbg}}(r) = \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r} \text{erf} \left( \frac{r}{\lambda_{\alpha\beta}} \right),
\]

where the parameter \( \lambda_{\alpha\beta} \) can be set to the mean de Broglie wavelength for electrons

\[
\lambda_{\alpha\beta} = \frac{\hbar}{\sqrt{2\mu_{\alpha\beta}k_B T}}, \quad \mu_{\alpha\beta}^{-1} = m_\alpha^{-1} + m_\beta^{-1}.
\]

In this case the temperature \( T \) is a constant parameter used in the thermostat to equilibrate the system rather than a dynamical quantity derived from an instantaneous kinetic energy. Therefore the potential energy is not a function of particle velocities so that the MD system is conservative.

In fact the potential (3) describes interaction of the electrons with point-like ions or between each other, as if they were represented by the Gaussian-like wave function where the width of the Gaussian profile is fixed.

A more complicated approach based on fitting the classical partition function to an approximate result of quantum statistics of bound and free states of a hydrogen atom at certain temperature is given by the so-called “Corrected Kellbg” pseudopotential [30]

\[
V_{\alpha\beta}^{\text{Kellbg}}(r) = \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r} \left[ F \left( \frac{r}{\lambda_{\alpha\beta}} \right) - \frac{k_B T}{q_\alpha q_\beta} A_{\alpha\beta}(\xi_{\alpha\beta}) \exp \left( -\frac{r^2}{2\lambda_{\alpha\beta}} \right) \right],
\]

where

\[
\xi_{\alpha\beta} = -\frac{q_\alpha q_\beta}{k_B T\lambda_{\alpha\beta}}, \quad F(x) = 1 - \exp(-x^2) + \sqrt{\pi}x[1 - \text{erf}(x)],
\]

\[
A_{\alpha\beta}(\xi_{\alpha\beta}) = \sqrt{p_\alpha p_\beta} |\xi_{\alpha\beta}| + \ln \left[ 2\sqrt{\pi} |\xi_{\alpha\beta}| \int_0^\infty \frac{y \exp(-y^2)dy}{\exp(\pi |\xi_{\alpha\beta}/y|) - 1} \right],
\]

\[
A_{\alpha\beta}(\xi_{\alpha\beta}) = -\sqrt{\pi} \xi_{\alpha\beta} + \ln \left[ \sqrt{\pi} \xi_{\alpha\beta}^3 \left( \zeta(3) + \frac{1}{4} \zeta(5) \xi_{\alpha\beta}^2 \right) + 4\sqrt{\pi} \xi_{\alpha\beta} \int_0^\infty \frac{y \exp(-y^2)dy}{1 - \exp(-\pi |\xi_{\alpha\beta}/y|)} \right].
\]

Here an approximate account for electron degeneracy is made. The forms of different interaction potentials are shown in figure 1. The table 2.1 summarizes the models used in the present work.

The setup of our classical MD simulations is as follows. The system of \( N_e = 4096 \) electrons and \( N_i = 4096 \) protons is considered. We use a reduced proton to electron mass ratio ratio of \( m_i/m_e = 100 \) to speed up electron–ion equilibration. As shown before [6] such a reduced mass ratio does not affect the results for the thermodynamical properties.

It should be noted, that in the both MD and WPMD simulations we do not account for neutral atoms and molecules as extra particles in addition to electrons and ions. The hydrogen
atoms and molecules such as H$_2$, H$_2^+$ and others can be seen in MD or WPMD simulations as transient complexes of electrons and ions. It is proved that the excited atoms can be considered within the classical MD approach as stable pairs of electrons and ions [31, 32]. However, this consideration is limited for highly excited bound states only.

The WPMD method can handle atoms starting from the ground state [33] and we believe that it reproduces the interaction between the molecules and other species in a more accurate way than the classical MD. Nevertheless both approaches miss the effect of generalization of electrons so they can hardly reproduce, for instance, covalent chemical bonds.

Since the classical MD cannot correctly predict the plasma ionization degree, the electrons forming the bound states should be taken out of consideration, thus a correction for the electron density should be applied for the MD model. However, some contribution from the excited bound states is still present in the model as noted above. This complicates the comparison of the MD model results with the energies and pressures predicted by chemical models like [34,35] because the actual correction of the electron density is unknown. In the following we will refer to the density as the density of free electrons.

Thermodynamical properties discussed below are related to the “Coulomb” part of the media under consideration. The chemical model [34,35] for the considered electron number densities

**Table 1.** Interaction models between different sorts of particles used for MD simulations of the cluster nano-plasmas.

| Label    | ion–ion potential | electron–ion potential | electron–electron potential |
|----------|-------------------|------------------------|-----------------------------|
| MD-Erf   | $V^{\text{Coul}}$, equation (2) | $V^{\text{erf}}$, equation (3) | $V^{\text{erf}}$, equation (3) |
| MD-Coul  | $V^{\text{Coul}}$, equation (2) | $V^{\text{erf}}$, equation (3) | $V^{\text{Coul}}$, equation (2) |
| MD-Kelbg | $V^{\text{Kelbg}}$, equation (5) | $V^{\text{Kelbg}}$, equation (5) | $V^{\text{Kelbg}}$, equation (5) |

**Figure 1.** Interaction potentials for the temperatures of $T = 10000 \ (a)$ and $30000 \ K \ (b)$: the Coulomb potential (2) (black line), the error function potential (3) (red line for e–i and blue line for e–e), the Kelbg potential (5) (green lines for e–e and e–i interactions).
\(10^{20}\text{–}10^{24} \text{ cm}^{-3}\) results in the following ionization degrees: 0.001–0.09 for \(T = 10^4\) K, 0.15–0.5 for \(T = 3 \times 10^4\) K and 0.3–0.9 for \(T = 5 \times 10^4\) K.

The nearest image method (periodical boundaries) is used. See [17] for discussion about the influence of the particle number and boundary conditions on the results for thermodynamical properties in MD simulations. We start from a random particle distribution and apply the Langevin thermostat to equilibrate the system with a given temperature \(T\). A special procedure is used to check if the equilibrium is established. Then the thermostat is switched off and the main MD run is performed for an adiabatic system. Our equilibrium trajectory length ranges from 160 fs to 4 ps depending on the electron density. The results are averaged over 3 statistically independent trajectories. The GPU accelerated code is used to speed up simulations and increase the accuracy.

### 2.2. Wave packet molecular dynamics

The details of WPMD and WPMC methods are described in [10,13,14], here we briefly mention their main principles. In these methods single electron wave functions are expanded in a set of normalized floating Gaussian wave packets (WP) [36]. Each of the wave packets is fully described by a set of 8 scalar parameters (components of the mean position \(\mathbf{r}\), components of the mean momentum \(\mathbf{p}\), width \(s\) and width momentum \(p_s\))

\[
\varphi(\mathbf{x}) = \left(\frac{3}{2\pi s^2}\right)^{3/4} \exp\left\{- \frac{3}{4s^2} - \frac{ip_s}{2\hbar s}\right\} (\mathbf{x} - \mathbf{r})^2 + \frac{i}{\hbar} \mathbf{p} \cdot (\mathbf{x} - \mathbf{r})\right\}.
\]

A trial many-body wave function \(\Psi(\{\mathbf{x}_k\})\) is constructed depending on the quantum statistical properties of the simulated ensemble, for example for fermions (electrons) a single Slater determinant antisymmetrized product is usually used for each spin projection. The resulting equations of motion for the parameters of all wave packets follow from the variational principle. They resemble the classical equations of motion in the fact that they may be derived from the generalized Hamiltonian function, which is the quantum expectation value of the system energy

\[
H = \langle \Psi | \mathbf{\hat{H}} | \Psi \rangle,
\]

\[
\mathbf{\hat{H}} = \sum_k \frac{\mathbf{p}_k^2}{2m_e} - \sum_{k,j} \frac{Z_j e^2}{|\mathbf{r}_k - \mathbf{r}_j|} + \sum_{k<l} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_l|} + K_i + U_{ii}.
\]

Analogously to a simulation of the classical system, the equilibrium properties of the WPMD system may be obtained either by solving the equations of motion (temporal evolution) or by sampling the phase space using Monte Carlo method. In the first case ergodicity of the system is implied.

The WPMD and WPMC methods are the candidates for fast numerical description of warm dense matter and nonideal plasmas taking quantum uncertainty and degeneration effects into account. However, there are several issues that have to be taken into account when using these methods. Here we briefly list these issues and specify how we address them in the present work.

(i) The unlimited broadening of the Gaussian wave packets and underestimation of the electron–electron and electron–ion collision frequencies is known to be the major problems of the WPMD method when applied to many-particle systems with homogeneous density, for example plasma systems. In our earlier work [17] we proposed to use a 3D confinement potential to properly limit the wave packet broadening without applying any other unphysical restrictions on the wave packet localization

\[
U_{\text{wall}}(x) = \begin{cases} 
a(|x| - L/2)^2, & |x| > L/2, 
0, & |x| \leq L/2,
\end{cases}
\]

where \(L = n_e^{-1/3} N_e\) is the simulation box edge. The infinite WP broadening is directly related to the infinite statistical sum in an unconstrained system and does not appear in the confined
system. In this work, such a confinement is used for plasma model instead of periodic boundary conditions, which we found hard to implement for localized wave packets.

(ii) The original quantum system in WPMD is mapped to the classical one with extra degrees of freedom compared to the original system. These degrees of freedom are related to the variable width parameters $s$ and $p_s$. As shown in [37] for a harmonic confinement, the WPMD system, specially equilibrated by a collisional thermostat, serves as a good model of a quantum NVT ensemble and demonstrates proper distribution of the system among quantum states, whereas the WPMC method samples a classical ensemble of states and “overheats” the system. This generally means that a dynamical thermalization should be preferred over the Monte Carlo sampling, provided that the proper collisional thermostat is used. Development of such a thermostat for electron–ion systems is a subject of our future work. Despite this deficiency, the Monte Carlo method for a plasma system currently remains the only available method allowing to explicitly set up the system temperature.

In the present work we used Monte Carlo equilibration, correcting the system energy for an excess energy related to the wave packet width degree of freedom. To calculate the correction we assume that in the thermal equilibrium the motion of the wave packet widths (extra degrees of freedom) is governed by harmonic oscillations around some equilibrium values. This implies that the wave packet widths, unlike particle positions, rarely change their mean values which happens only in transitions from free to bound states and vice versa. Let us rewrite the effective Hamiltonian function (7) as

$$H = \sum_{k=1}^{N_e} \left( \frac{p_k^2}{2m_e} + \frac{p_s^2}{2m_e} + \frac{9h^2}{8m_e s_k^2} - E_{0k} \right) + U_{\text{wpmd}}^{\text{ew}} + U_{\text{wpmd}}^{\text{ee}} + U_{\text{ext}} + K_i + U_{ij},$$

where the effective potential energies are

$$U_{\text{wpmd}}^{\text{ew}} + U_{\text{wpmd}}^{\text{ee}} + U_{\text{ext}} = \sum_{k=1}^{N_e} E_{0k} + \sum_{k} U_{\text{wall}}(r_k) - \frac{N_e}{\sum_{j=1}^{N_e}} \frac{e^2 Z_i}{r_k - r_j} \frac{\text{erf} \left( \sqrt{3} |r_k - r_j| / \sqrt{2s_k} \right)}{\sqrt{2s_k}} + \sum_{m<k}^{N_e} \frac{e^2}{|r_k - r_m|} \frac{\text{erf} \left( \sqrt{3} |r_k - r_m| / \sqrt{2(s_k^2 + s_m^2)} \right)}{\sqrt{2(s_k^2 + s_m^2)}}. \quad (10)$$

For simplicity we use the Hartree case, where kinetic energies are decoupled; in the antisymmetrized case the momenta should be renormalized with respect to the Fermi energy. Here the term “kinetic energy” denotes here the expectation value of the first two terms in the sum in (10). The quantity $E_{0k}$ is the energy of the equilibrium state for the width of each electron. For bound electrons this state corresponds to the electron localized at the ionic center, and for “free” or extended electrons it is determined either by Pauli repulsion (antisymmetrized case) or by the confinement walls. Assuming that in the thermally equilibrated plasma the mean contributions from the kinetic energy $(p_k^2/2m_e)$ and the “width potential” $(9h^2/(8m_e s_k^2) - E_0)$ equal to $(1/2)N_e kT$ we end up with the total excess energy of $N_e kT$ which should be subtracted from the total energy of the WPMD system for proper comparison with the classical MD and DPIMC results.

Summarizing our WPMD and WPMC model, in the present work we use a system of $N_e = 32$ electrons and $N_i = 32$ protons for simulations of the hydrogen plasma with the given electron density $n_e$. The wave packets are placed in the confinement potential with the flat floor of size $L$ and harmonic walls corresponding to the eigenstate with the width of $L/20$. The mean energy of the confinement potential (usually less than 5% of the total energy) is subtracted from the equilibrium result. Initially the particles are placed at random positions in the confinement with the widths of wave packets of 0.086 nm.
Figure 2. Total energy of hydrogen plasmas as a function of density for the temperature of $T = 30\,000\,\text{K}$. Black crosses represent the data obtained using the path integral Monte Carlo [20]. Blue triangles represent the classical MD results with the potentials (2) for e–e and (3) for e–i, green circles correspond to the potential (3) for both interaction types and aqua squares correspond to the Kelbg potential (5) for e–e, e–i, and i–i interaction. Brown diamonds represent WPMD simulation results. Black dashed line shows the formal degeneracy border $n_e\lambda_B^3 = 1$. Color dashed lines with symbols are related to potentially unphysical results. Black horizontal line is the ideal gas energy $E_{\text{id}} = 1.5k_BT$.

Monte Carlo sampling with variations in all coupled degrees of freedom, including ion positions, wave packet centers and momenta, width and width momenta is used to equilibrate the system at the given temperature $T$. Adaptive steps are used to keep the mean Monte Carlo acceptance rate at 0.5. For the AWPMC the phase space volume is corrected for the varying norm matrix $N$, corresponding to the additional weight of $\det N^{-1/2}$ per sample as described in [10]. The ionic kinetic energy is decoupled and assumed to be equal to $(3/2)N_ik_BT$. The correction of $N_e\lambda_B^3k_BT$ for extra degrees of freedom is subtracted from the obtained equilibrium energies.

3. Comparison of the results for thermodynamical properties
The internal energy and pressure of hydrogen plasma are calculated by different methods of atomistic simulation (figures 2 and 3). The results that we obtained in classical and wave packet MD are compared with the results of DPIMC. In general, the trends for the energy and pressure
dependencies on the density for MD and DPIMC are similar, however some systematic divergence is observed. The energy difference is independent from the plasma density and increases with the decreasing temperature.

Similar results are obtained for pressure (figure 4) which is calculated for the classical MD using the well known relation [8]

$$P = \frac{2}{3L^3} \left[ K_e + K_i - \frac{1}{2} \sum_{k,m>k} r_{km} \frac{\partial V(r_{km})}{\partial r_{km}} \right].$$

(11)

For evaluating the pressure in the AWPMC and WPMC calculations we use the Coulomb virial relation:

$$P = \frac{1}{3L^3} \left[ 2(K_e + K_i) + U_{ee} + U_{ii} + U_{ei} \right].$$

(12)

It holds exactly for our quantum model irrespectively of the number of basis wave functions per electron [38]. This virial expression is however very sensitive to the fluctuations and in case of
Figure 4. Pressure of hydrogen plasmas as a function of density for the temperatures of $T = 10\,000$ (a), $30\,000$ (b) and $50\,000$ K (c). Black crosses represent data obtained with DPIMC calculation [20], blue triangles are the MD results with the potential (2) for $e$–$e$ and (3) for $e$–$i$ interaction, green circles are the MD results with the potential (3) for all particle types, aqua squares are the MD results with the Kelbg potential (5), asterisks represent WPMC results. Black dashed line shows the formal degeneracy border $n_e \lambda_B^3 = 1$.

A confined system should be corrected for border effects. In this work we apply this expression directly and since we use very small number of particles, our results for pressure in the confined AWPMC and WPMC models may be regarded as preliminary.

Simulations that are performed with classical molecular dynamics show the effect of the interaction potentials choice on the internal energy. For the plasma density less than $10^{22}$ cm$^{-3}$ the form of electron–electron interaction at small separations has weak effect on the results of simulation (circles for $V_{ee}^{\text{erf}}$ and triangles for $V_{ee}^{\text{Coul}}$ in figure 3). Using the Kelbg potential (5) (squares in figure 3) for all interactions provides better matches with DPIMC simulation, but the energy divergence remains rather high. Using WPMD (diamonds in figure 3) provides results close to the classical MD with Kelbg potentials for $T = 30\,000$ K (figure 3(b)). As seen both from the energy and pressure dependencies on the density, at moderate densities (low degeneration) the results of the classical and the wave packet MD are very close to each other. The results of the WPMD simulation become closer to DPIMC for lower temperature $T = 10\,000$ K (figure 3(a)).
Figure 5. Binary correlation functions for different electron densities: $n_e = 10^{20}$ (a), $10^{21}$ (b), $10^{23}$ (c) and $3 \times 10^{23}$ cm$^{-3}$ (d). The red line corresponds to e–e correlations, the blue line to i–i correlations, and the black line to e–i correlations. The dotted blue line represents the unnormalized function $r^2 g_{ei}(r)$.

The obtained data demonstrate also the range of applicability for the classical MD with different pseudopotentials. Using the Coulomb potential (2) for electron–electron interaction restricts the simulation to the densities $n_e$ lower than $10^{22}$ cm$^{-3}$. With the increasing density, the rise of repulsive ion–ion and electron–electron interactions over the energy of the electron–ion interaction causes dramatical increase of the total energy (red triangles and dashed blue lines in figure 3). The potentials (3) and (5) allow to describe the system at much higher densities with the degeneracy parameter $\Theta > 1$. Unphysical effects in classical MD simulation were occurred
at density $n_e$ higher than $10^{23}$ cm$^{-3}$ for $V_{\text{erf}}$ and $10^{24}$ cm$^{-3}$ for the Kelbg potential. The mean distance between electrons becomes close to $r_0$ and the interaction force approaches zero. Due to this, electrons create unphysical structures seen at the binary correlation functions (figure 5(d)).

The wave packet MD without antisymmetrization has approximately the same range of applicability than the classical MD. Since the exchange and correlation energies are not accounted for, the AWPMC method fails at $\Theta > 1$ producing unphysical clusterization of the matter into large droplets. In contrast to that, the AWPMC method does not produce droplets and predicts the increase of pressure and energy at larger densities, similarly to DPIMC, however this increase is numerically largely overestimated by AWPMC. Note that being a Hartree–Fock type of method, AWPMC does not account for the electron correlation energy which appears to be crucial at high degenerations.

4. Conclusions
The results of different atomistic simulation methods are presented as applied to the dense hydrogen equation of state. It is shown that the results of the classical molecular dynamics with different electron–electron and electron–ion interaction potentials are close to each other within the statistical errors except for very high densities above the degeneracy limit. At such high densities electrons can form artificial structures due to a strong repulsion when the pure Coulomb electron–electron potential is used. In the case of using the Kelbg potential for both electron–electron and electron–ion interactions the reasonable results can be obtained for the densities up to an order of magnitude above the degeneracy limit.

For all temperatures we found significant deviations between MD and DPIMC results while the qualitative dependence of the internal energy on the density is the same. The deviations are greater for lower temperatures. A possible reason for that is the different account for electron–ion bound states.

As to the wave packet techniques, it is stated that they have an inherent problem of an extra degree of freedom related to the wave packet width and the corresponding problem of correct specification of temperature in the Monte Carlo algorithm. Nevertheless with the help of a simple correction the results for the WPMC and AWPMC simulations show a good agreement with the classical MD except for $T = 50000$ K and $n_e < 10^{21}$ cm$^{-3}$. Improvement of these results can be achieved by replacing the Monte Carlo equilibration by molecular dynamics with a proper thermostat. The WPMD and WPMC methods have a similar range of applicability for the ionized homogenous medium as the classical MD. Note that the wave packet methods are capable of describing atomic bound states and ionization phenomena and therefore have some advantage over the classical MD for simulation of partially ionized matter and transition processes. The predictive power of the AWPMC and AWMD methods at large degeneration requires more detailed study, especially with regard of taking the electron correlation energy into account.

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References
[1] Pierleoni C, Morales M A, Rillo G, Holzmann M and Ceperley D M 2016 Proc. Natl. Acad. Sci. U. S. A. 113 4953–7
[2] Holst B, Redmer R and Desjarlais M P 2008 Phys. Rev. B 77 184201
[3] Povarnitsyn M E, Fokin V B and Levashov P R 2015 Appl. Surf. Sci. 357 1150–6
[4] Hansen J P and McDonald I R 1981 Phys. Rev. A. A 23 2041–59
[5] Pschiwu T and Zwicknagel G 2003 J. Phys. A 36 6251–8
[6] Morozov I V and Norman G E 2005 J. Exp. Theor. Phys. 100 370–84
[7] Morozov I, Reinholz H, Röpke G, Wierling A and Zwicknagel G 2005 Phys. Rev. E 71 066408
[8] Bystryi R G, Lavrinenko Ya S, Lankin A V, Morozov I V, Norman G E and Saitov I M 2014 High Temp. 52 475–82
[9] Raitza T, Röpke G, Reinholz H and Morozov I 2011 Phys. Rev. E 84 036406
[10] Knaup M, Reinhard P G, Toepferr C and Zwicknagel G 2003 J. Phys. A 36 6165–71
[11] Su J T and Goddard III W A 2007 Phys. Rev. Lett. 99 185003
[12] Zwicknagel G and Pschiwu T 2006 J. Phys. A 39 4359–64
[13] Valuev I A and Morozov I V 2015 J. Phys.: Conf. Ser. 653 012153
[14] Jakob B, Reinhard P G, Toepferr C and Zwicknagel G 2009 J. Phys. A 42 214055
[15] Morozov I V and Valuev I A 2009 J. Phys. A 42 214044
[16] Graziani F R et al 2012 High Energy Density Phys. 8 105–31
[17] Lavrinenko Y S, Morozov I V and Valuev I A 2016 Contrib. Plasma Phys. 56 448–58
[18] Bertsch G F and Broglia R A 1994 Oscillations in Finite Quantum Systems (Cambridge University Press)
[19] Filinov V S, Bonitz M, Ebeling W and Fortov V E 2001 Plasma Phys. Controlled Fusion 43 743
[20] Filinov V S, Bonitz M, Fortov V E, Ebeling W, Levashov P R and Schlanges M 2004 Contrib. Plasma Phys. 44 388–94
[21] Militzer B and Ceperley D M 2001 Phys. Rev. E 63 066404
[22] Ceperley D M 1995 Rev. Mod. Phys. 67 279
[23] Militzer B and Ceperley D M 2000 Phys. Rev. Lett. 85 1890
[24] Militzer B and Pollock E L 2000 Phys. Rev. E 61 3470
[25] Pierleoni C, Ceperley D M and Holzmann M 2004 Phys. Rev. Lett. 93 146402
[26] Pierleoni C and Ceperley D M 2006 The Coupled Electron-Ion Monte Carlo Method vol 1 (Springer)
[27] Morales M A, Pierleoni C and Ceperley D M 2010 Phys. Rev. E 81 021202
[28] Stegailov V V, Orekhov N D and Smirnov G S 2015 HPC hardware efficiency for quantum and classical molecular dynamics Int. Conf. Parallel Computing Technologies PaCT 2015 (Springer) pp 469–73
[29] Zwicknagel G and Pschiwu Th 2003 Contrib. Plasma Phys. 43 393-7
[30] Filinov A V, Bonitz M and Ebeling W 2003 J. Phys. A 36 5957
[31] Lankin A V and Norman G E 2009 J. Phys. A 42 214032
[32] Lankin A V, Norman G E and Orekhov M A 2015 J. Phys.: Conf. Ser. 653 012155
[33] Morozov I V and Valuev I A 2012 Contrib. Plasma Phys. 52 140–4
[34] Gryaznov V K, Iosilevskiy I L and Fortov V E 2015 Plasma Phys. Controlled Fusion 58 014012
[35] Gryaznov V K and Iosilevskiy I L 2016 Contrib. Plasma Phys. 56 352–60
[36] Frost A A 1967 J. Chem. Phys. 47 3707–13
[37] Feldmeier H and Schnack J 2000 Rev. Mod. Phys. 72 655–88
[38] Jakob B, Reinhard P G, Toepferr C and Zwicknagel G 2007 Phys. Rev. E 76 036406