

## Proton-proton pair distribution in dense fluid hydrogen

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Recent experiments on hydrogen at very high pressures have stimulated new quantum statistical studies of this simplest Coulomb system since a transition from nonconducting to metallic behavior occurs at Mbar pressures which is forced by drastic changes of the electronic and structural properties in the molecular system with increasing density. The variation of the thermodynamic and structural properties as a function of the density and temperature can be studied within molecular dynamics and Monte Carlo simulations as well as within analytical approaches such as integral equation techniques. In the region where hydrogen molecules still dominate the physical behavior, the proton-proton pair distribution function is determined both from a modified hypernetted chain approximation which starts with effective intermolecular and interatomic potentials in the neutral system, and a wave-packet molecular dynamics simulation with the Coulomb interaction between protons and electrons as the basic interaction. Comparison of both complementary approaches gives hints for the validity region of the chemical picture as well as for the accuracy of computer simulations. [S1063-651X(98)13505-5]

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### I. INTRODUCTION

The study of matter at high densities is of fundamental interest for a better understanding of the equation of state (EOS) and related phenomena such as phase transitions. Drastic changes of the electronic properties such as metallization may occur together with a strong variation of the structure with the density. For instance, metallization of fluid hydrogen has been verified experimentally at 140 GPa around a relatively low temperature of 3000 K using multiple shocks [1]. Dissociation of hydrogen molecules has been found to be important already at these conditions [2,3].

Laser driven shock wave experiments have been performed using both direct and indirect illumination of solid targets [4]. Single shock experiments have compressed liquid deuterium up to pressures of 250 GPa and temperatures of about  $30 \times 10^3$  K [5]. The corresponding equation of state follows estimates of Ross [2] within a dissociation model, but disagrees with rather approximate results such as the SESAME tables above 25 GPa [31].

For a better understanding of matter at high pressures, it is necessary to elaborate a quantum statistical approach up to densities where, e.g., the above-mentioned metallization transition occurs in hydrogen. This can be done for strongly coupled plasmas using, e.g., the Green function method [6]. There, perturbation theory is used to evaluate the equation of state. For practical applications, interpolation formulas can be given which are valid for a large domain of the density-temperature plane [7]. However, only approximate results are available for the region of strong coupling where the interparticle potential energy is larger than the typical kinetic energy, i.e.,

$$\Gamma = \frac{e^2}{4\pi\epsilon_0 a k_B T} \geq 1. \quad (1)$$

The Wigner-Seitz radius  $a$  is related to the density  $n$  of the system by

$$a = (3/4\pi n)^{1/3}, \quad (2)$$

so that distances can be scaled in terms of the Bohr radius  $a_B = 0.529 \times 10^{-10}$  m via  $r_s = a/a_B$ . Furthermore, the degeneracy parameter

$$\Theta = k_B T / E_F \quad (3)$$

can be introduced where  $E_F = \hbar^2(3\pi^2 n)^{2/3}/2m$  is the Fermi energy and  $m$  the electron mass. Strongly degenerate systems  $\Theta \leq 1$  at weak coupling  $\Gamma \leq 1$  can be handled by the Vlasov equation for fermions [8]. In the strong coupling regime  $\Gamma \geq 1$ , classical molecular dynamics (MD) computer simulations can account for all sorts of correlations [9]. However, the wave nature of the electrons has to be taken into account in addition.

In this paper we want to discuss a quantum regime with  $\Theta = 0.014 - 0.034$  at moderately strong coupling  $\Gamma = 32 - 79$ . The protons and electrons become strongly correlated through the Coulomb interactions and bound atomic and molecular states are formed. We will focus our attention on the proton-proton pair distribution function  $g_{pp}(r)$  which gives the probability to find two protons at a distance  $r$ . Quite generally, the pressure  $p$  of a system at given temperature and density, i.e., the EOS, can be calculated from the interparticle potentials and the pair distribution functions [10]. If, however, the latter are extracted from numerical data obtained in simulations, the unavoidable statistical fluctuations yield rather unprecise results for the pressure. Fortunately, there exists a fundamental method for obtaining the inner energy which is independent from any assumptions on the chemical composition (H, H<sub>2</sub>, ...) or the physical structure (neutral or ionized, metallic or dielectric, etc.) of the system.

For many-particle systems with Coulomb interaction, the virial theorem is strictly valid and yields the EOS directly via  $p = (n/3)(K + E)$  [11]. Here  $K$  and  $E$  are the kinetic and total energy, respectively, and  $n$  is the number density.

In the regime considered here, most electrons are bound in molecular states. This calls for a quantum mechanical description of coupled electron-ion systems, e.g., the path-integral Monte Carlo method (PIMC) [12] or ionic MD on electronic Born-Oppenheimer surfaces [13,14]. These powerful techniques allow detailed calculations, which are *ab initio* in the sense that the true Coulomb interaction is employed. On the other hand they involve compromises resulting mainly from exchange, e.g., the nodes of the density matrix have been taken from a noninteracting system in Ref. [12]. This is certainly doubtful in the molecular phase. Moreover they are numerically very expensive so that typically only samples with 32 electrons can be treated at present.

Here, we employ an efficient quantum mechanical simulation scheme, the wave-packet molecular dynamics (WPMD) [15]. The technical simplifications of this method permit much larger samples, e.g., 2048 electrons in this work. This allows a more detailed study of structures on a larger scale. The WPMD was developed for simulations of dense two-component plasmas where quantum effects play a crucial role to guarantee the stability of the system [16,17]. It is intended as an extension of classical MD with just the necessary effort to include the essential quantum effects. The simplifications consist in describing each electronic wave function by a Gaussian wave packet, whose position, momentum, and complex width are the free dynamical parameters. The time-dependent variational principle leads to a pseudo-Hamiltonian propagation. As a further approximation, antisymmetrization is expanded into a hierarchy of exchanges, which is cut at the level of pairwise exchange. This approximation is justified for temperatures down to one-tenth of the Fermi temperature if the electrons are delocalized. It holds for even lower temperatures if the electrons are localized in molecular orbits. However, the numerical accuracy of this method has to be checked in the low-density limit. Our aim is to compare both analytical and numerical approaches considering regions where these models are applicable.

## II. WAVE-PACKET MOLECULAR DYNAMICS SIMULATIONS

The WPMD was originally used by Heller for a description of the scattering of composite particles like simple atoms and molecules [15]; later it was also applied to heavy ion reactions [18]. In the present application to a Coulomb system of electrons and protons, we characterize the state of the system by the set  $\{\mathbf{R}_I(t), \mathbf{P}_I(t), \Psi(\mathbf{x}_i, t)\}$  of classical coordinates  $\mathbf{R}_I(t)$  and momenta  $\mathbf{P}_I(t)$  for the protons and quantum mechanical wave function  $\Psi(\mathbf{x}_i, t)$  for the electrons. The dynamics of the system is governed by the classical equations of motion

$$\dot{\mathbf{R}}_I(t) = \partial_{\mathbf{P}_I} \langle \Psi | \hat{H} | \Psi \rangle, \quad \dot{\mathbf{P}}_I(t) = -\partial_{\mathbf{R}_I} \langle \Psi | \hat{H} | \Psi \rangle \quad (4)$$

for the protons and the principle of stationary action

$$\delta \int_{t_1}^{t_2} dt \langle \Psi | i \partial_t | \Psi \rangle = \delta \int_{t_1}^{t_2} dt \langle \Psi | \hat{H} | \Psi \rangle \quad (5)$$

for the electrons. The Hamiltonian  $\hat{H}$  contains a classical part, consisting of a Hamilton function for the kinetic energy of the ions and their mutual Coulomb interactions, and a quantum mechanical operator for the kinetic energy of the electrons, their mutual interactions, and their interactions with the ions. In order to make the system of equations (4) and (5) tractable, the electron wave function  $\Psi$  is parametrized as a set of Gaussian wave packets, i.e.,

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t) = \hat{A} \left( \prod_{i=1}^N \varphi_i(\mathbf{x}_i, t) \right), \quad (6)$$

with

$$\varphi_{\mathbf{q}}(\mathbf{x}) = \left( \frac{3}{2\pi\beta} \right)^{3/4} \exp \left[ -\left( \frac{3}{4\beta} + i p_{\beta} \right) (\mathbf{x} - \mathbf{r})^2 - i \mathbf{p} \cdot (\mathbf{x} - \mathbf{r}) \right]. \quad (7)$$

Here,  $\mathbf{q} = \{q_{\nu}\} = (p_{\beta}, \beta, \mathbf{p}, \mathbf{r})$  is a set of variational parameters. While  $\mathbf{p}$  and  $\mathbf{r}$  are the classically conjugate parameters for the position of the wave packet,  $p_{\beta}$  and  $\beta$  describe the evolution of its width. The antisymmetrization operator is denoted by  $\hat{A}$ .

With the ansatz (6) and (7), the dynamics of the electron wave function is reduced to a pseudoclassical Hamiltonian dynamics for the parameters  $\mathbf{q}$ . Application of the variational principle (5) to the parametrized wave functions (6) yields

$$\sum_{\mu} N_{\nu\mu} \dot{\mathbf{q}}_{\mu} = \partial_{\mathbf{q}_{\nu}} \langle \Psi | \hat{H} | \Psi \rangle, \quad (8)$$

which differs from the conventional Hamiltonian equations by the occurrence of the norm overlap

$$N_{\nu\mu} = i \langle \Psi | \overleftarrow{\partial}_{\mathbf{q}_{\nu}} \overrightarrow{\partial}_{\mathbf{q}_{\mu}} - \overleftarrow{\partial}_{\mathbf{q}_{\mu}} \overrightarrow{\partial}_{\mathbf{q}_{\nu}} | \Psi \rangle. \quad (9)$$

It is one of the advantages of the Gaussian ansatz (7) that the norm overlap takes the classical symplectic form

$$N_{\nu\mu} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad (10)$$

if the antisymmetrization in Eq. (6) is neglected, i.e., in the Hartree limit. The solution of Eq. (8) requires the inversion of the norm overlap at every time step. In order to limit the numerical expense, the antisymmetrization is restricted to two-particle exchanges which give a correction  $\delta N$  to the norm. The correction to the inverse is also calculated up to the second order in the exchanges. This approximation is justified for the treatment of delocalized electron states at temperatures down to about one-tenth of the Fermi temperature  $T_F$ . It holds at even lower temperatures for localized states as they are realized, e.g., in molecular hydrogen.

Of course computer simulations, while being *ab initio* in spirit involve certain simplifying prejudices in practice. In the WPMD, antisymmetrization is limited to pairwise exchange while assumptions about the nodes of the density matrix must be made in the PIMC method. In the chemical

picture, on the other hand, it is a difficult task to account for the change of the properties of the constituents due to the surrounding medium. In fact the usual strategy of kinetic theory, namely, expansion of the equations of motion into subdynamics involving 2,3,..., $N$ -particle correlations, may not be very successful in plasma applications because of the infinite range of the Coulomb force.

### III. DISSOCIATION MODEL

An alternative approach to study the behavior of hydrogen at low to medium pressures is given by the chemical picture. Hydrogen is considered as a mixture consisting of  $H_2$  molecules, H atoms, and possibly of protons and electrons. These components interact via effective potentials. Furthermore, chemical reactions such as dissociation and ionization are possible so that the composition of the system is given by the chemical equilibrium. As is well known, this simple chemical picture breaks down at high densities. Modifications of the constituents and their interactions can be treated in a systematic way using the technique of Green functions [6]. We will restrict our considerations to the region where these medium modifications are small. Furthermore, we consider low temperatures so that thermal ionization can be neglected. In general, we have then to allow only for the pressure dissociation of hydrogen molecules into atoms via the chemical equilibrium  $H_2 \rightleftharpoons H + H$ .

Within such a dissociation model, we take dense fluid hydrogen to be a mixture of molecules and atoms with corresponding partial densities  $n_{H_2}$  and  $n_H$ , respectively, and a dissociation degree  $\beta = n_H / (n_H + 2n_{H_2})$ . The molecules and atoms interact via effective two-body potentials which approximate the effects of the real many-body interactions. These interactions are given by empirical expressions which, in principle, can be derived from atomic quantum calculations. Ross, Ree, and Young [19] use data from single shock experiments up to pressures of 10 GPa to model such an effective two-body potential between hydrogen molecules. They propose both a highly accurate 15-parameter potential and a more approximate three-parameter (exponential-six) potential of the form

$$V_{H_2H_2}(r) = \frac{\varepsilon}{\alpha - 6} \left\{ 6 \exp \left[ \alpha \left( 1 - \frac{r}{r^*} \right) \right] - \alpha \left( \frac{r^*}{r} \right)^6 \right\}, \quad (11)$$

where  $\varepsilon/k_B = 36.4$  K,  $\alpha = 11.1$ , and  $r^* = 6.482a_B$ . In order to avoid unphysical behavior in the limit of short distances  $r \rightarrow 0$ , we replace the potential by an exponential function for  $r < 2.95a_B$ , the inflection point, with parameters set to ensure continuity of the potential (11).

Unfortunately, no similar experimental results exist to fit the other interaction potentials  $V_{HH}(r)$  and  $V_{HH_2}(r)$ . Ree [20] has suggested a potential of the form (11) also for the interaction between hydrogen atoms,  $V_{HH}(r)$ , with the parameters  $\varepsilon/k_B = 20.0$  K,  $\alpha = 13.0$ , and  $r^* = 2.646a_B$ . This potential yields a minimum energy for close-packed monoatomic hydrogen solid near  $2.4 \text{ cm}^3/\text{mol } H_2$ , in very good agreement with results from the local density approximation [21]. The parameters for the atom-molecule potential

$V_{HH_2}(r)$  are derived from the Berthelot mixing rule which gives  $\varepsilon/k_B = 27.0$  K,  $\alpha = 12.0$ , and  $r^* = 4.565a_B$ .

The fraction  $\beta$  of dissociated molecules is determined by the correlation contributions to the chemical potential according to

$$n_{H_2} = \frac{n_H^2 \Lambda_H^3}{\sqrt{2}} \sigma^{\text{int}} \exp[(-D_0 + \mu_{H_2}^{\text{cor}} - 2\mu_H^{\text{cor}})/k_B T],$$

$$\sigma^{\text{int}} = \frac{k_B T}{hcB} \left[ 1 - \exp \left( -\frac{hc\omega}{k_B T} \right) \right]^{-1}. \quad (12)$$

$D_0 = -4.735$  eV is the dissociation energy of isolated  $H_2$  molecules and  $\Lambda_H^2 = 2\pi\hbar^2/(m_H k_B T)$  the thermal wavelength of H atoms.  $\sigma^{\text{int}}$  denotes the internal partition function of vibrational and rotational states with  $B = 60.853 \text{ cm}^{-1}$  and  $\omega = 4401 \text{ cm}^{-1}$  as the characteristic rotational and vibrational constants of the  $H_2$  molecule [22];  $c$  is the speed of light. These parameters are, in principle, also density dependent.

We have calculated the correlation parts of the chemical potentials via  $\mu^{\text{cor}} = (\partial F^{\text{cor}}/\partial N)_T$ . The correlation parts of the free energy are derived using fluid variational theory (FVT) of Ross, Ree, and Young [19] for the pure molecular and atomic system using the pair potentials (11); for details, see [3]. There we have shown that FVT gives results for the equation of state of hydrogen which agree with those obtained within the modified hypernetted chain (MHNC) approximation and classical Monte Carlo (MC) simulations up to the metallization pressure of 140 GPa. The correlation contributions in Eq. (12) are not negligible for the chemical equilibrium at high pressures.

In the present chemical picture we can define three pair distribution functions  $g_{H_2H_2}$ ,  $g_{H_2H}$ , and  $g_{HH}$ . They can be derived using computer simulation techniques or analytical methods. In the MHNC scheme [23], the Ornstein-Zernike equation for a two-component system with species  $\{\alpha, \beta\} = \{H, H_2\}$

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\nu} n_{\nu} \int c_{\alpha\nu}(|\mathbf{r} - \mathbf{r}'|) h_{\nu\beta}(r') d^3 r', \quad (13)$$

has to be solved together with the closure relation for the pair distribution functions,

$$g_{\alpha\beta}^{\text{MHNC}}(r) = \exp \left[ h_{\alpha\beta}(r) - c_{\alpha\beta}(r) - \frac{V_{\alpha\beta}(r)}{k_B T} + B_{\alpha\beta}^{\text{HS}}(r) \right]. \quad (14)$$

$h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$  is the total correlation function,  $c_{\alpha\beta}(r)$  the direct correlation function, and  $B^{\text{HS}}$  the bridge function of the hard-sphere reference system.

Classical MC simulations have been performed for the mixture of hydrogen molecules and atoms with dissociation degree  $\beta$  [3], and three different pair distribution functions  $g_{HH}$ ,  $g_{HH_2}$ , and  $g_{H_2H_2}$  are derived using the respective pair potentials (11). For low temperatures and densities, the dissociation degree is small. For instance, at temperature of  $T = 2000$  K and a mass density of  $\rho = 0.33 \text{ g/cm}^3$ , we have

found a dissociation degree of 0.07%. Therefore the molecular pair distribution function is clearly dominant.

In order to extract the proton-proton pair distribution function  $g_{pp}$  from the molecule-molecule, molecule-atom, and atom-atom distribution functions, we need to determine the proton distribution in the  $H_2$  molecule. For isolated molecules in the singlet state, this distribution is very well known from the Kolos-Wolniewicz solution of the Schrödinger equation [24]. For a first qualitative evaluation, we neglect in-medium corrections to the molecular structure in Eq. (12) such as the vibron shift [25,26] or a variation of the binding length of  $1.401a_B$ . The vibrational and rotational spectrum of the  $H_2$  molecule is then derived by standard techniques. The probability of finding a proton at a distance  $r$  from another proton in the  $H_2$  molecule at a temperature  $T$  is given by the eigenfunctions  $\phi_i$  and eigenvalues  $E_i$  for the singlet potential via

$$w_{pp}^{H_2}(\mathbf{r}) = \frac{\sum_i |\phi_i(\mathbf{r})|^2 \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)}. \quad (15)$$

The ground and first excited state have been taken into account for the evaluation of Eq. (15) which is sufficient for the low temperatures considered here.

Recalling that the total number of protons is given by  $n_p = n_H + 2n_{H_2}$ , the explicit proton-proton distribution function is given by four terms representing the possible cases of finding a neighboring proton:

$$\begin{aligned} g_{pp}(\mathbf{r}) = & \frac{2n_{H_2}}{n_p^2} w_{pp}^{H_2}(\mathbf{r}) + \frac{n_H^2}{n_p^2} g_{HH}(\mathbf{r}) \\ & + \frac{4n_H n_{H_2}}{n_p^2} \int d^3s w_{pp}^{H_2}(\mathbf{s}) g_{HH_2}(\mathbf{r}-\mathbf{s}/2) \\ & + \frac{4n_{H_2}^2}{n_p^2} \int d^3s_1 \int d^3s_2 w_{pp}^{H_2}(\mathbf{s}_1) w_{pp}^{H_2}(\mathbf{s}_2) \\ & \times g_{H_2H_2}(\mathbf{r}-\mathbf{s}_1/2-\mathbf{s}_2/2). \end{aligned} \quad (16)$$

The first term describes the internal proton-proton distribution in the  $H_2$  molecule and the second one the proton-proton distribution for the H-H interaction. The third term represents the H- $H_2$  distribution, and the fourth one the  $H_2$ - $H_2$  contribution. The convolution integrals in Eq. (16) are evaluated in Fourier space.

#### IV. RESULTS FOR THE PROTON-PROTON PAIR DISTRIBUTION FUNCTION

We have evaluated the proton-proton pair distribution function using the methods described in Secs. II and III for different values of temperature and density. First, we discuss the low-density low-temperature region where the dissociation model is well founded.

In Fig. 1, results are shown for  $T=2000$  K and a mass density of  $\varrho=0.33$  g cm $^{-3}$  which corresponds to a proton number density of  $n_p=2 \times 10^{23}$  cm $^{-3}$ . For these conditions,

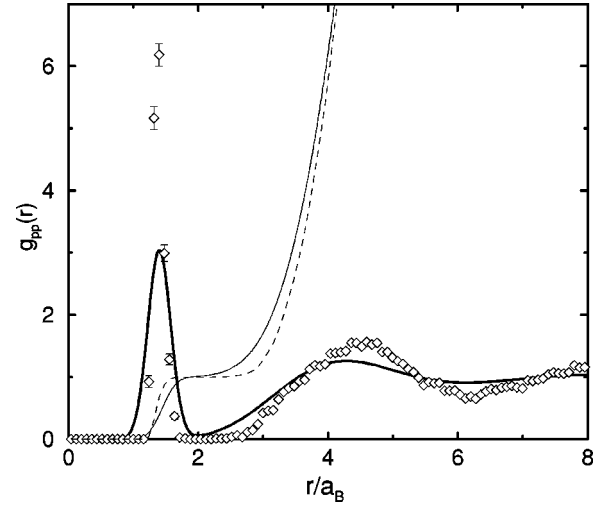


FIG. 1. Proton-proton pair distribution function at  $T=2000$  K and  $\varrho=0.33$  g/cm $^3$ . The WPMD result (data points) is compared with the dissociation model (full line). The dashed (WPMD) and thin line (dissociation model) indicate the respective coordination numbers calculated as  $N=4\pi n \int g(r)r^2 dr$ .

the degree of dissociation calculated within the dissociation model is 0.07%. The proton-proton pair distribution function shows a strong first peak at the bond length of the  $H_2$  molecule at  $1.4a_B$ . The second, broader peak around  $4.3a_B$  is due to the next-neighbor molecules. The contributions of the other partial pair distribution functions  $g_{HH}$  and  $g_{HH_2}$  to  $g_{pp}$  according to Eq. (16) are small in correspondence to the low degree of dissociation. The sharp minimum around  $2a_B$  can be considered as an indication for the molecular structure of hydrogen under these conditions. The integrated proton-proton pair distribution function shows that the first peak contains one proton which is just the bond partner in the  $H_2$  molecule.

The data points in Fig. 1 are the results of WPMD simulations. The correlation function was calculated for each particle in the simulation box. The error bars were obtained from averaging over all particles, their length representing the mean error of the mean value. The WPMD yields both a more pronounced intramolecular correlation, as well as a sharper intermolecular structure than the dissociation model.

Results at the same mass density  $\varrho=0.33$  g cm $^{-3}$  but at a higher temperature of  $T=5000$  K are shown in Fig. 2. There, the dissociation degree amounts already to 5.9%. The dissociated H atoms contribute to the flattening of the minimum near  $2a_B$  in comparison to Fig. 1. The same behavior is also obtained from the WPMD simulation. Furthermore, we compare in Fig. 2 with results of PIMC [27,28] and tight-binding molecular dynamics (TBMD) simulations [29,30] for the same conditions. Compared with the WPMD simulation, the proton-proton pair distribution function derived from PIMC simulations is sharper peaked. The maximum of the first peak occurs at a smaller value than the proton-proton distance in the isolated  $H_2$  molecule. On the other hand, the proton-proton pair distribution function derived from the TBMD simulation is less structured than the WPMD result. At larger distances, a good agreement with the distribution function resulting from the dissociation model can be stated.

Comparing the dissociation model and the WPMD simu-

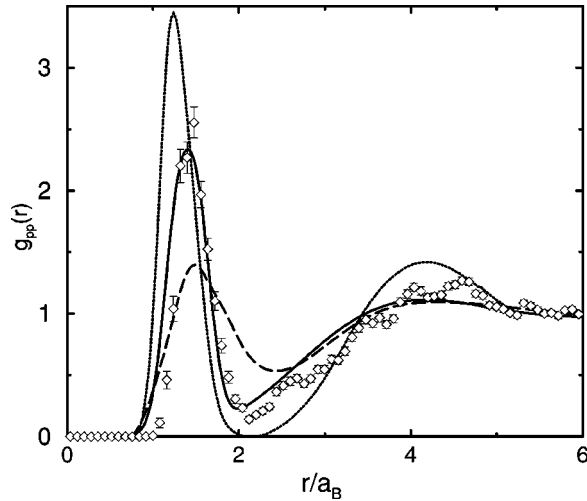


FIG. 2. Proton-proton pair distribution function at  $T=5000$  K and  $\rho=0.33$  g/cm<sup>3</sup>. We compare the present WPMD result (data points) and the dissociation model (full line) with the PIMC simulations of Magro *et al.* [28] (dotted line) and the TBMD results of Lenosky *et al.* [30] (dashed line).

lations, we conclude that the agreement between both treatments is satisfactory in the low-density low-temperature region. At lower temperatures, the WPMD simulation yields somewhat stronger structures in the correlation function and a larger next-neighbor distance than the dissociation model. This may be attributed to the increasing contribution of excited states in the dissociation model according to Eq. (15) which are modified due to density effects.

PIMC simulation data are at present available only for temperatures  $T \geq 5000$  K [27,28]. At that lowest temperature, they yield a more pronounced structure in the pair distribution function and a shift towards smaller bond lengths. It should be noted in this context that this PIMC simulation involves a high-temperature approximation insofar as the nodes of the density matrix are taken from free particles. One

may expect that this assumption becomes progressively questionable if the temperature is lowered into a region where bound molecules dominate as considered here. Therefore an extension of that method to lower temperatures would be highly desirable.

We also note that the PIMC simulations are presently carried out with 32 electrons whereas the WPMD simulation are performed with 2048 electrons corresponding to a cube with fourfold edge length. A larger set of particles is essential at low temperatures where long-range and long-time correlations are built up. At  $T=300$  K and  $r_s=1.78$ , for example, the correlation functions obtained from the WPMD [16] agree quite well with those from a Car-Parrinello calculation [13] in a smaller simulation cube of the latter, but shows, however, beyond that size another peak around  $7.5a_B$  in the proton-proton pair distribution function which is due to the correlations of next-nearest neighbors. It is expected that a better coincidence of both simulation methods is achieved systematically with increasing temperatures.

## V. CONCLUSIONS

The proton-proton pair distribution function is an important quantity to describe properties of dense hydrogen fluids and plasma. Comparing with the WPMD simulations, we conclude that the dissociation model yields relevant results up to mass densities of about  $1$  g cm<sup>-3</sup>, depending also on temperature. At higher densities, the dissociation model has to be improved by including further medium effects as well as ionization.

On the other hand, the dissociation model yields a benchmark for the simulations such as WPMD, PIMC, or TBMD in the low-density low-temperature limit. The different results obtained up to now from the various simulation methods for the proton-proton pair distribution function in this regime are a challenge to improve the numerical accuracy and to increase the number of particles to get a better estimate of the quantum effects inherent in the system.

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