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# Molecular dynamics simulations of hot, dense hydrogen

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Quantum mechanical molecular dynamics simulations have been performed in order to understand the structure and dynamics of hot, dense hydrogen. Both density functional and tight-binding methods were employed to represent the interatomic forces. Pair-correlation functions and self-diffusion coefficients are compared with other models over a range of temperatures (1–5 eV) and densities (0.1–3 g/cm$^3$). We find that quantum mechanical many-body interactions are crucial to modeling this regime. In addition, we examine transient phenomena and find evidence for short-lived complexes even at high temperatures.

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Interest in highly compressed hydrogen at various stages of thermal excitation spans a wide variety of fields including plasma, condensed matter, astro-, atomic, and molecular physics. For example, to reach ignition of the hydrogenic isotopes in inertial confinement fusion (ICF) devices [1] requires densities of hundreds of g/cm$^3$ and temperatures of millions of degrees K. In addition, surrounding hydrogens modify the spectral character of heavy impurity atoms, leading to profound consequences for diagnostics. In astrophysics, the modeling of both stellar [2] and planetary [3] interiors hinges on the properties of dense hydrogen. In particular, augmenting the traditional one-component plasma (OCP) [4] with quantal effects has important ramifications for the evolution and crystallization of white dwarfs [5]. Also, pulsed power devices [6], based on various pinch configurations, attain dense plasma conditions at elevated temperatures. Such plasma pinches are highly transient processes that require a dynamical component for full understanding. Finally, metals and even semiconductors [4] exhibit behaviors in certain regimes that resemble dense plasmas. Therefore an investigation of the properties and mechanisms of dense hydrogen provides insight into an extensive range of processes important to diverse areas of physics as well as chemistry and materials science.

For high compressions, considerable experimental and theoretical activity has focused on both very low and very high temperatures. At low temperatures, the basic phase diagram and equation of state have garnered the bulk of attention [7,8], in particular the transition between the molecular and atomic-metal states. Sophisticated techniques [9–14] have been devised from the union of classical treatments of the nuclear motion by Monte Carlo and molecular dynamics (MD) and of quantal treatments of the electrons based on Hartree-Fock (HF), density functional (DF), and semiempirical techniques. These methods have mainly been applied to investigating thermal and pressure dissociation of the molecular liquid as well as its structure. At the other extreme, a classical OCP with the bare ions in a homogeneous background sea of electrons appears adequate. By incorporating quantal effects into the particle interactions, Thomas-Fermi [14] and effective-potential [15] methods have been employed to push to lower temperatures and densities. However, the nature and extent of the transition region between the two extremes remain uncertain. To properly treat this realm requires precise experiments and sophisticated theoretical approaches with full accounting of electron exchange and correlation as well as temperature effects. The former still lies in the future while the latter has only been accomplished for the tightly bound helium (He) system [10].

In order to further explore this transition region, we have performed molecular dynamics simulations of dense hydrogen (0.1–3 g/cm$^3$) at high temperatures ($1 \times 10^4$–$6 \times 10^4$ K) using both density functional and tight-binding (TB) methods. The former, while very accurate, requires considerable computational resources and provides a benchmark over small numbers of atoms ($N \leq 54$). The latter, although less accurate, allows a quantal treatment of large samples sizes ($N \leq 686$) that provide statistically meaningful thermodynamic properties and prevent trapping in anomalous structures.

For both methods, we have performed constant volume, constant temperature molecular dynamics simulations with $N$ hydrogen atoms in a cubic box with periodic boundary conditions. We started from a high-symmetry configuration of atoms, such as body-centered-cubic, with velocities determined randomly from a Boltzmann distribution at the desired temperature $T$. We advance the system in time by a two-step procedure that treats the electrons quantum mechanically (QM) and the nuclei classically. First, for a fixed configuration of atoms, the forces are calculated from the diagonalization of the electronic Hamiltonian in an appropriate basis. Second, the nuclei are then moved according to the applied QM force by integrating the classical equations of motion using the standard velocity Verlet prescription [16]. We maintain a fixed temperature by a simple velocity-scaling procedure [16]. Trajectories as long as 700 fs with step sizes as short as 0.07 fs were employed to give accurate bulk and thermodynamical properties. To introduce the effects of excited and continuum states, we invoke local thermodynamical equilibrium (LTE). Therefore we equate the electron and ionic kinetic temperatures and populate the electronic state eigenfunctions according to a Fermi-Dirac distribution [10,12,17]. From these weighted eigenfunctions, we determine the force. Transitions to such states become important to properly represent hot, ionized systems.

In the density functional approach, we employ the local density approximation (LDA), expand in terms of a plane-wave basis, and use a periodically replicated cell of 54 atoms. This basic formulation follows closely that reviewed by Remler and Madden [18]. The standard Kohn-Sham equations are iterated at each time step to self consistency by a Lanzcos-style diagonalization prescription [19], which in turn provides eigenstates only for the populated levels of the Fermi-Dirac (FD) distribution. The Perdew-Zunger form [20] is used for the exchange-correlation term. In addition, we invoke the local pseudopotential prescription of Troullier and Martins [19]. The use of a pseudopotential for H allows the number of plane waves to be greatly reduced. Tests indicate that the MD results remain insensitive to a pseudopotential cutoff ($r_c$) on the order of the ion-sphere radius. We typically choose $r_c$ between 1.0 and 1.4 bohr and include plane waves with energies up to 30 Ry.

In tight-binding molecular dynamics [21], the interatomic potential is provided by two terms: (1) a sum of the eigenvalues of occupied states from the tight-binding Hamiltonian; (2) a pairwise potential representing ion-ion repulsion and correction for double counting the electron-electron interaction. We use a basis of ground ($s$) and excited ($s'$) orbitals for each hydrogen atom. The $s'$ orbital is included since at high density ($\rho \geq 1$ g/cm$^3$) and high temperature ($T \geq 1$ eV), the probability of electrons to occupy excited states is not negligible. The basic form of the hopping matrix elements and on-site energies in the $ss'$ TB Hamiltonian were derived from fits to the appropriate ground and excited states of $H_2$. Further adjustments were made to give a reasonable total energy phase diagram of bcc, fcc, and diamond structure solid phases of H. The details of the $ss'$ potential modeling, which is the extension of an $s$ only parametrization [22], are planned to be published in a separate paper [23].

As an initial step, we performed a series of calculations at low temperature (0.1 eV, 1160 K) to test our LDA program against other similar *ab initio* treatments and to ascertain the accuracy of the TB model. Our LDA results [12] for the pair correlation function $g(r)$, which gives the probability of finding an atom at a distance $r$ from a reference origin atom [16], showed very good quantitative agreement with other DF [13] and HF [10] studies. We reproduce the basic density behavior of the medium, finding a molecular liquid at low densities and pressure dissociation between 0.75 and 1.0 g/cm$^3$ ($r_s$=1.5–1.4 or 150–300 GPa). In addition, the $ss'$ TB MD simulations compared reasonably well with the more sophisticated models with the dissociation coming at a slightly higher density ($\sim$ 1 g/cm$^2$). To obtain an accurate equation of state at this $T$, we would need to include the zero-point motion ($\sim$ 0.1 eV) in the dynamics. However, since our interest lies in the transition region with temperatures on the order of electron volts, we can safely neglect this small contribution as do the other techniques [10,13] to which we compare. Having established the efficacy of our LDA and TB methods in this low-temperature regime, we extend them to hotter and denser media.

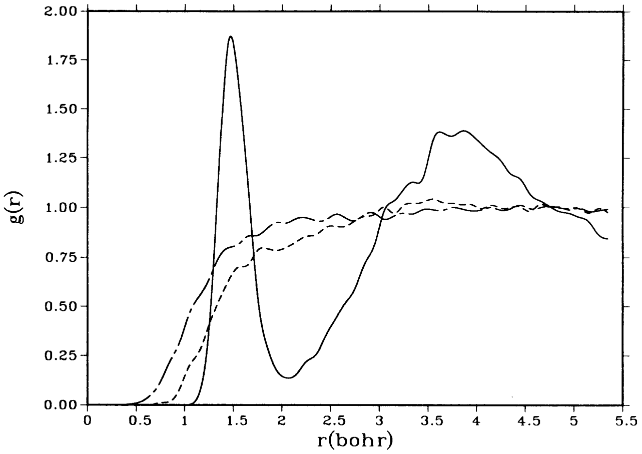

FIG. 1. Pair-correlation function $g(r)$ as a function of radial distance at $\rho$ = 0.5 g/cm$^3$ for three temperatures: 0.1 eV (solid line), 1 eV (dash), and 3 eV (chain) with the LDA.

We first examine the behavior of the system as the temperature increases. In Fig. 1, we display $g(r)$ as a function of $T$ for the LDA case for a fixed density, $\rho$=0.5 g/cm$^2$. At the low $T$ of 0.1 eV, we observe the distinct peak of molecular hydrogen at $r$=1.4 bohr. As the temperature increases, the molecules begin to dissociate due to collisions imparting sufficient energy to break the internal bonds. By 1 eV, $g(r)$ has the characteristics of a completely disordered atomic system. Further increasing the temperature leads to a distribution of similar shape. The more rapid rise of $g(r)$ at 3 eV results from atoms that on average have a greater energy to penetrate more deeply. For a fixed $T$, we observe a similar trend in the pair-correlation function as the density increases. In addition, we found analogous behavior for the $ss'$ TB case and no strong dependence on the sample size, which ranged from 128 to 686 atoms. Therefore, in this transition region, we find a highly disordered atomic fluid.

The coefficient of self diffusion $D$, obtained from either the velocity autocorrelation or mean-square displacement function [16], provides an important measure of structure and dynamics in a hot, dense plasma. In Fig. 2, we present $\rho D$ as a function of $\rho$ at two elevated temperatures. For the whole range of density at $T$=1 eV, the OCP [24] stays significantly lower than the LDA and TB. This represents the strongly coupled plasma regime [$\Gamma \equiv e^2/r_s k_B T$= 9–28] in which the potential energy of atomic interactions prevails over the thermal motion. However, quantum many-body effects still dominate over the bare Coulombic interactions. As we increase the temperature to 5 eV ($\Gamma$ = 2–6), we observe better agreement between the OCP and TB, as displayed in Fig. 2(b). The thermal effects clearly compete with the particle interactions. The high

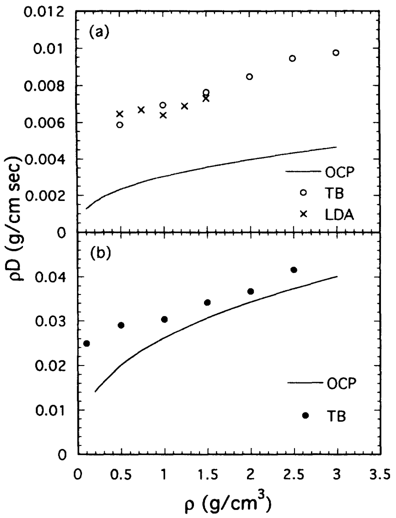

FIG. 2. Self-diffusion coefficient multiplied by density as a function of density; (a) at $T$=1 eV, with the LDA-MD (cross), the TB MD (open circle), and the OCP (solid line); (b) at $T$=5 eV, with the TB MD (solid circle) and the OCP (solid line).

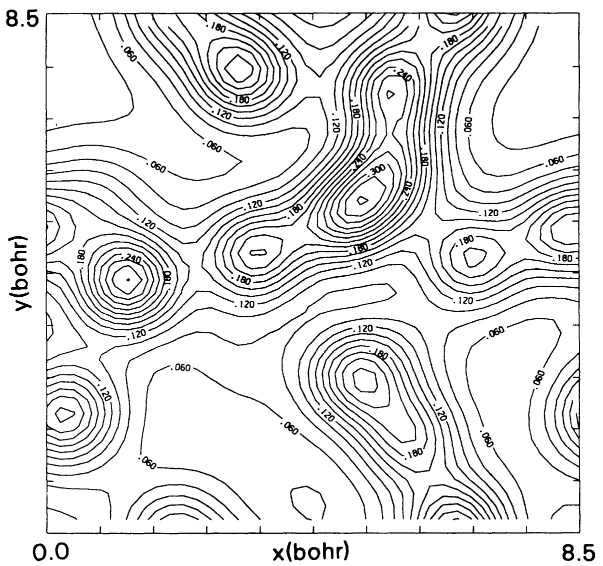

FIG. 3. Representative electronic charge density per unit volume for a DF-LDA simulation at a specific time step for $T$=3 eV and $\rho$ = 1 g/cm$^3$ in the $x$-$y$ plane.

kinetic energy of the electrons yields a smoother distribution that more resembles the OCP assumptions. Similar behavior was found by Younger [10] for He in which the HF and OCP self-diffusion coefficients become comparable at about $\rho = 8$ g/cm$^3$ at $T$=5 eV. For H, given its more diffuse electron cloud, the two agree at lower densities. We also compare with the Thomas-Fermi results of Zérah *et al.* [14] at $\rho = 2.5$ g/cm$^3$. At a low temperature ($T$=0.5 eV, $\Gamma \simeq 50$, $r_s \simeq 1$), we obtain with the TB model a diffusion coefficient twice the TF and thrice the OCP value. Again, as we move to higher temperatures, the methods come into better accord; at $T$=2.5 eV ($\Gamma \simeq 10$), the TB MD result ($D = 8.7 \times 10^{-3}$ cm$^2$/s) is within 11% and 47% of the TF and OCP, respectively. Once more, the thermal excitation appears to provide a charge distribution characteristic of the simpler models.

The pair-correlation function, while providing a description of the time-averaged structure of the system, may mask important transient effects. Considerable interest has focused on the possible formation of short-lived complexes of several atoms [10,11,25]. Speculation centers on such quasimolecular structures as important contributors to transport and radiative properties, especially linewidths. To this end, we have investigated the temporal behavior of the quantum mechanical electronic charge distribution and found significant distortions due to close, lingering atomic approaches. Such distortions as depicted in Fig. 3 represent a significant sharing of the electrons among atomic centers and a considerable departure from simple perturbed-atom schemes. In fact, for the four-atom complex in the upper half of Fig. 3, the charge density between atomic centers is enhanced substantially from the simple addition of individual atomic components, representing a true molecular complex as opposed to the superposition of noninteracting atoms. These encounters can occur many times over the lifetime of an excited state, yielding a detectable effect on its lifetime. While our calculations center on pure hydrogen, the experiments [25] have involved impurities within a H medium. To this end, static calculations at the HF level for an argon impurity embedded in a H lattice indicate the strong influence of surrounding H atoms on the $n$ = 2 and $n$ = 3 manifolds. More thorough dynamical calculations, now in progress, will be needed to yield precise experimental comparisons.

In conclusion, we find that sophisticated representations of the quantum mechanical many-body interactions are crucial to modeling hot, dense plasmas over a significant range of temperatures and densities. In addition, we find evidence for strongly interacting complex structures even at elevated temperatures.

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