Molecular Dissociation in Hot, Dense Hydrogen

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We present a path-integral Monte Carlo study of dissociation in dense hydrogen ($1.75 \leq r_s \leq 2.2$, with r_s the Wigner sphere radius). As the temperature is lowered from 10^5 to 5000 K, a molecular hydrogen gas forms spontaneously from a neutral system of protons and electrons. At high density, $r_s < 2.0$, thermally activated dissociation is accompanied by decreasing pressure, signaling the presence of a first order transition and critical point. The decrease in electron kinetic energy during dissociation is responsible for the pressure decrease and transition. At lower density the phase transition disappears.

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Despite its simple composition, hydrogen is a complex substance with a rich phase diagram. While recent attention has been directed primarily at its ground state properties, much of its behavior at high temperature and density, particularly important in astrophysics, remains uncertain. Molecular dissociation can occur, thermally or through compression, as the electrons are forced into high energy states by the increasing chemical potential. A fundamental question is whether hydrogen crosses a phase boundary as the dense molecular fluid transforms into a fully ionized plasma. The answer is not simple to deduce, since dissociation occurs in a region where both thermal and degeneracy effects, as well as many-body quantum effects, are important. Further, as in a liquid-gas transition, there is no change in symmetry. If such a "plasma phase transition," as it has come to be known, indeed exists, it remains unclear whether the dissociation and ionization processes occur simultaneously or if instead there exists an intermediate atomiclike state.

Direct observation of the dissociation process is hindered by the high pressures and temperatures required. Recent shock-wave compression measurements, the most promising experimental approach, see no evidence for a first order phase transition [1].

One theoretical approach to these questions has been to separately model the molecular and metallic phases, then equate the Gibbs free energies to locate a transition. More advanced models generally include more chemical species, such as H_2, H, protons, and electrons. A particularly sophisticated chemical treatment, the free energy model of Saumon and Chabrier [2], predicts a first order phase transition from the molecular fluid to a partially ionized atomic gas. The density discontinuity associated with this phase transition would sharply alter current estimates of the interior mass distribution of the giant planets. Chabrier *et al.* have shown that a plasma phase transition is in fact *required* to obtain agreement between the most sophisticated structural models of Saturn and the measured gravitational moments [3].

At such elevated temperatures and densities, it is unclear whether a chemical picture is adequate, since the very chemical species in the system are evolving and the relevance of the terms "atom" and "molecule" is uncertain. The restricted path-integral Monte Carlo (RPIMC) method is unique in its ability to simulate fully interacting many-fermion quantum systems in thermodynamic equilibrium with a minimum of approximations. In particular, hydrogen can be modeled within RPIMC as a collection of fully interacting electrons and protons. This relatively new method has been previously applied only to ^{3}He [4], isotopic helium mixtures [5], and the dense hydrogen plasma [6]. We apply it here to investigate the nature of molecular dissociation in dense hydrogen, thus circumventing the problems associated with chemical models.

We model hydrogen as a neutral mixture of 32 protons and 32 unpolarized electrons in a periodically repeated cubic cell and in equilibrium at a temperature, $T = 1/k_B\beta$. Density is specified in terms of the Wigner sphere radius r_s, defined by $4\pi/3(r_s a_0)^3 \equiv n^{-1}$, where a_0 is the Bohr radius and n is the average electron density. We use the fully interacting, nonrelativistic Hamiltonian for this system. The density matrix $\rho(\beta) \equiv e^{-\beta\mathcal{H}}$ contains complete thermodynamic information about the system with observables given as

$$\langle\mathcal{O}\rangle = \frac{\mathrm{Tr}[\mathcal{O}\rho(\beta)]}{\mathrm{Tr}[\rho(\beta)]} = \frac{\int dR\langle R|\mathcal{O}\rho(\beta)|R\rangle}{\int dR\langle R|\rho(\beta)|R\rangle}, \qquad (1)$$

where $R \equiv \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ specifies a configuration of the N particles. Due to its exponential form, the density matrix can be factored as $\rho(\beta) = [\rho(\tau)]^M$ if $M \equiv \beta/\tau$. Equation (1) then becomes a path integral which is well suited for Monte Carlo evaluation using a multistage Metropolis algorithm [7]. The problem is thus reduced to one of evaluating off-diagonal elements of the high-temperature density matrix, $\rho(\tau)$.

To develop an expression for $\rho(\tau)$, we first split the Coulomb potential into one short- and one long-ranged term. The high-temperature density matrix, $\rho_s(R, R'; \tau)$, in the absence of the long-range potential is written as a product of pairwise terms, which are computed with a matrix-squaring technique [7,8]. Next, we introduce the long-range interaction perturbatively and write

$$\rho(R, R'; \tau) = \rho_s(R, R'; \tau) e^{-(1/2)[U(R;\tau)+U(R';\tau)]} \qquad (2)$$

with the long-range action $U(R; \tau)$ determined using the random phase approximation [9] (details are given in Ref. [10]). Evaluation of the path integral requires a nonzero τ, which introduces a systematic "time-step error," which decreases with decreasing τ. In the present work, $\tau^{-1} = 10^6 k_B$ K, which gives a reasonable trade-off between computational effort and accuracy. At this value, the total energy is accurate to about 0.06 Ry or 5% per atom.

In the path-integral formulation, electrons and protons are put on equal footing from a quantum-mechanical point of view, since each particle is fully represented by a Feynman path. This causes no particular difficulty, in contrast to other methods, such as local density functional calculations. The Fermi temperatures of the protons and electrons at the highest density considered, $r_s = 1.75$, are 103 and 190 000 K, respectively. While the Fermi character of the protons is negligible under the conditions of this study, the effects of electron exchange are substantial. Without Pauli repulsion, a proton-electron mixture is thermodynamically unstable [11]. The density matrix must be antisymmetric under exchange of spinlike electrons, but a direct antisymmetrization procedure will be statistically very inefficient due to cancellation of negative and positive terms. This is the well-known *sign problem* of fermion Monte Carlo techniques. We circumvent this problem by using the fixed-node approximation, in which the paths are restricted to lie within a set of physically motivated trial nodes [4,12]. The procedure becomes exact when the trial nodes coincide with the exact fermion nodes. We use the nodes of the free-particle density matrix. While these nodes become exact only at high temperature, they capture more of the physics than one might expect. Their merits are discussed in more detail in Ref. [4]. In the absence of exact results, the errors due to incorrect trial nodes can be estimated only from analogous ground state calculations [13]. These show that for reasonable nodes the energy is largely insensitive to exact nodal positions. Typical fixed-node errors at $T = 0$ are about 0.004 Ry per atom, and the error at finite temperature should be smaller.

Dense hydrogen is therefore not only an interesting problem, but also an important test case for the method. Previously, we successfully applied the same method to a dense hydrogen plasma, obtaining good agreement with theoretical predictions [6]. We have also tested our program on the isolated hydrogen atom, hydrogen molecule, and helium atom.

In brief, our results for dense hydrogen near dissociation generally support the findings of Saumon and Chabrier from their chemical model [2], although the quantitative details differ. Most significantly, both approaches find behaviors consistent with and suggestive of a first order plasma phase transition. As in the chemical model, our molecular gas dissociates first into a partially ionized atomiclike fluid, then gradually transforms into an ionized plasma.

At the lowest temperatures and densities considered ($r_s = \{1.75, 1.86, 2.0, 2.2\}$, $T = 5000$ K), a molecular hydrogen gas forms, with the bond somewhat contracted from its free space length, 0.742 Å. At $r_s = 2.2$ the bond length is 0.67 Å and further decreases with increasing density, reaching 0.65 Å at $r_s = 1.75$. The bond contraction is nearly temperature independent and apparently results from a stiff effective intermolecular repulsion. This repulsion also leads to an excluded region surrounding each molecule. From $g_{pp}(r)$, the proton-proton pair distribution, at ($r_s = 2.2$, $T = 5000$ K) we estimate the radius of the repulsive core to be 0.6 Å, somewhat smaller than previous estimates [2].

As the temperature increases, dissociation occurs, as is evident from the correlation functions shown in Fig. 1. Dissociation also results from isothermal compression. As expected, $dn/dT < 0$ along the phase boundary, due to cooperative thermal and pressure effects on the electrons. While a first order dissociation transition would proceed isothermally at constant pressure, it occurs in a temperature interval at constant volume. At $r_s = 1.86$, dissociation occurs for $6000 < T < 8000$ K, compared with $13\,000 < T < 15\,000$ K in the chemical model [14]. For Coulomb systems, the pressure is $P = (n/3)[E + K]$, where E and K are, respectively, the total and kinetic energy per atom. Except at $r_s = 2.2$, the pressure *decreases* during isochoric dissociation, as shown in Fig. 2 for $r_s = 2$. In the corresponding isobaric system, this unusual behavior becomes a positive density discontinuity, consistent with the negatively sloping phase boundary. This is a strong indication of the presence of a first order phase transition which terminates in a critical point near ($r_s \approx 2.2$, $T \approx 11\,000$ K).

A possible explanation for the existence of a first order transition with these behaviors lies in the increasing kinetic energy associated with bond formation. As shown in Fig. 3, the electronic kinetic energy normally decreases with decreasing temperature. As molecules form, however, the kinetic energy increases. The total kinetic energy per atom for an isolated atom and H_2 molecule are also shown for comparison. Since $g_{pe}(r)$ is nearly invariant during molecular formation, the increase in kinetic energy results primarily from angular localization as electrons leave spherical atomiclike states in favor of

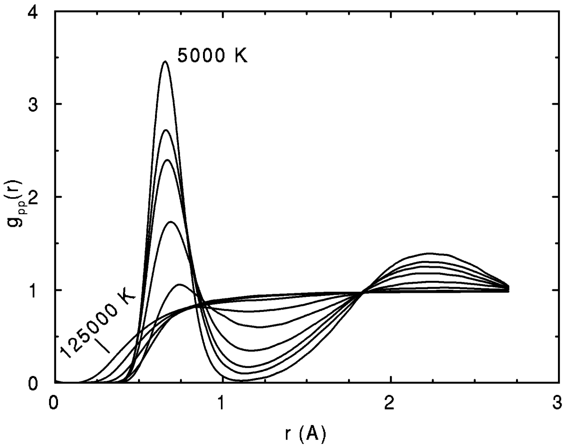

FIG. 1. Proton-proton pair correlation functions of hydrogen at $r_s = 2.0$. Temperatures shown are 5000, 6944, 7813, 8927, 10 000, 12 500, 15 625, 21 250, and 125 000 K. As temperature is lowered, a molecular hydrogen gas forms with bond length slightly contracted from the free space value.

molecular bonding states. Bond formation is clearly signaled by the pairing of spin-unlike electrons, as shown in Fig. 4. At low density, the increase in kinetic energy during bonding is small relative to the total energy gain, so the pressure decreases. As the density increases, however, the effects of the intermolecular repulsion begin to dominate, the molecules contract, and the additional confinement of the electrons leads to an increasingly high kinetic cost of binding. Eventually, $\Delta P \propto \Delta E + \Delta K$ changes sign, and the critical behavior appears.

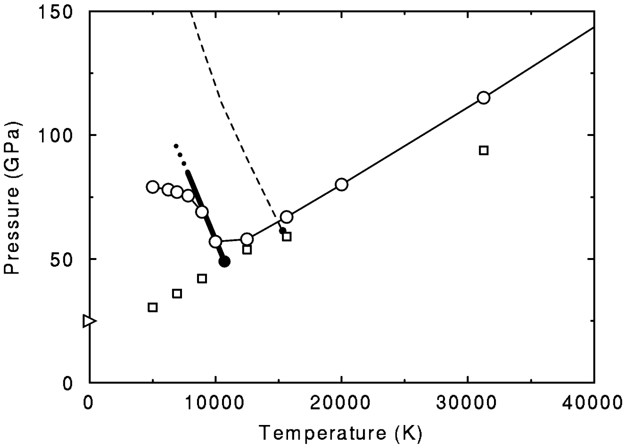

FIG. 2. Computed pressures (open circles) in the present work and from the chemical picture [14] (squares) for $r_s = 2.0$. Statistical errors are smaller than the symbol size. The dashed line is the phase coexistence line transition proposed by Saumon and Chabrier [2]. Our estimate of the same line is given by the thick solid line. The ellipses indicate the line continues to higher pressure. The triangle at $T = 0$ is the ground state pressure [16]. (Data from the chemical model do not have a region of negative dP/dT, since $r_s = 2.0$ lies entirely in the supercritical region. The $dP/dT < 0$ behavior does appear at higher densities.)

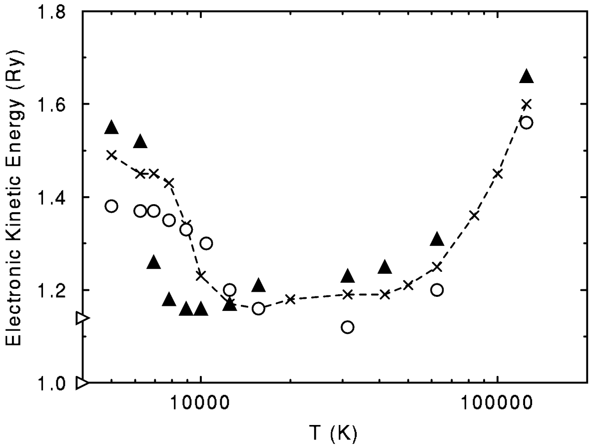

FIG. 3. Electron kinetic energy per atom under isochoric cooling from the plasma to molecular gas for three densities: $r_s = 1.86$ (filled triangles), $r_s = 2.0$ (crosses), and $r_s = 2.2$ (open circles). Statistical errors are smaller than the symbol size. The kinetic energy increases as electrons pair to form bonds. Different isochores cross, since compression suppresses molecular formation. The open triangles on the energy axis denote the kinetic energy per atom for an isolated hydrogen atom and molecule, respectively.

To conclusively demonstrate the presence of this phase transition, we must show that the above results persist in the limits $\tau \rightarrow 0$ and $N \rightarrow \infty$. At $\tau^{-1} = 10^6 k_B$ K, three-body and higher order terms in the density matrix are significant in dense hydrogen. Our pair-product density matrix slightly overestimates the probability for two electrons to simultaneously occupy the area between a pair of protons. This leads to a slightly shortened bond

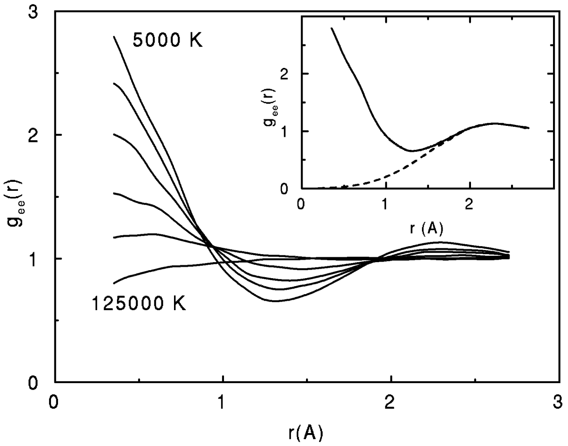

FIG. 4. Pair distribution functions, $g_{ee}(r)$, for spin-unlike electrons at $r_s = 2.0$. Temperatures shown are 5000, 7813, 8927, 10 000, 31 250, and 125 000 K. Spin-unlike electrons pair to form molecular H_2 bonds. Inset: spin-like (dashed) and spin-unlike (solid) distribution functions at $r_s = 2.0$, $T = 5000$ K.

length (by 0.01 Å) in H_2, overestimated kinetic, and correspondingly underestimated potential energy, due to the enhanced electron-proton correlation. Pressures, also affected, may be overestimated by as much as 15 GPa. Finite size effects, quite large in the 32 electron ground state, are substantially suppressed at finite temperature, due to smearing of the Fermi surface. Calculations of the free Fermi gas at $T = 5000$ and 50 000 K indicate that the finite size errors are smaller than the time-step errors.

It is interesting to consider the nature of the fluid into which the dissociating hydrogen transforms. This phase is not yet a plasma, as it retains very strong proton-electron correlations. It is perhaps best called a partially ionized atomic fluid, because the electron binds to the proton sufficiently long to prevent other electrons from approaching. This behavior, apparent from $r^2[g_{pe}(r) - 1]$, gradually disappears as the temperature or pressure is raised and the fluid becomes fully ionized. A more precise characterization of these electronic bound states and their eventual disappearance can be made with the aid of natural orbitals [15], but this requires a separate calculation of off-diagonal elements of $\rho(\beta)$. We hope to perform this analysis in the future.

In conclusion, we have simulated dense hydrogen fluids by assembling a fully interacting collection of protons and electrons. The dissociation transformation, relevant to interior models of the giant planets, occurs at somewhat lower temperatures than previous estimates. We have identified in this system behaviors characteristic of a first order phase transition. The phase boundary has negative slope, due to the cooperative effects of temperature and degeneracy in dissociation. Molecular hydrogen dissociates not directly into a plasma, but first into a partially ionized atomic fluid.

The spontaneous formation of molecules in this work, in which the only inputs are the Hamiltonian and the nodal surface of a free fermion gas, is an important and encouraging success for the restricted path-integral Monte Carlo method for many-body Fermi systems. All aspects of the method, including changing the trial nodes, can be improved, so more accurate calculations are underway. Although new calculations may alter these results, we expect the basic findings to remain true.

A detailed tabulation of the hydrogen equation of state at many experimentally inaccessible conditions, needed by planetary modelers, will be straightforward to obtain. Other possible applications include alkali metals, the electron-hole liquid, and helium-hydrogen mixtures. For the molecular fluid and solid at lower temperatures, the errors due to free-particle nodes and time-step error may become substantial, so more sophisticated nodes and high-temperature density matrices will be needed before these cases can be studied.

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