RESTRICTED PATH INTEGRAL MONTE CARLO CALCULATIONS OF HOT, DENSE HYDROGEN

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INTRODUCTION

Hydrogen is the most abundant element in nature and has the simplest composition. Despite considerable research, many aspects of its phases and structure remain unclear. In particular, when dense hydrogen is compressed or heated, it is not obvious whether molecular dissociation proceeds via a first order transition or a continuous transformation. Second, at high density, it is uncertain whether the molecular fluid transforms directly to an ionized plasma or into an intermediate atomic phase [1]. Recent advances have allowed experimentalists to probe the relevant region [2,3], but these issues remain unresolved. In this paper, we use a fully interacting quantum many body method, restricted path integral Monte Carlo (PIMC) [4], to model dense hydrogen at finite temperature and address these issues.

METHOD

We modeled hydrogen and deuterium as a neutral, spin zero system of electrons and nuclei at temperature $T \equiv \beta^{-1}$, interacting with Coulomb potentials in a periodically repeated cube. The quantum statistical mechanics of the system was incorporated via Feynman's path integral formulation [5], which expresses the low temperature physics of the system in terms of its high temperature physics, given by the density matrix, ρ_τ:

$$\rho_\beta = e^{-\beta \hat{H}} = \left(e^{-\tau \hat{H}} \right)^M.$$

(1)

Once the density matrix is known, operators are computed as

$$\left\langle \hat{O} \right\rangle \equiv \frac{\mathrm{Tr}\left[\hat{O} \rho_\beta \right]}{\mathrm{Tr}\left[\rho_\beta \right]}$$

(2)

$$= \frac{\sum_P (-1)^P \int dR dR_1 \cdots dR_{M-1} \left\langle R | \hat{O} \rho_\tau | R_1 \right\rangle \left\langle R_1 | \rho_\tau | R_2 \right\rangle \cdots \left\langle R_{M-1} | \rho_\tau | PR \right\rangle}{\sum_P (-1)^P \int dR dR_1 \cdots dR_{M-1} \left\langle R | \rho_\tau | R_1 \right\rangle \left\langle R_1 | \rho_\tau | R_2 \right\rangle \cdots \left\langle R_{M-1} | \rho_\tau | PR \right\rangle}.$$

(3)

The sum is taken over all permutations of spin like electrons,* with odd permutations yielding a negative contribution. The negative sign is problematic for Monte Carlo methods and is eliminated using the fixed node approximation [6]. In this approximate formulation, the domain of integration is limited to the positive domain of a trial density matrix, and permutations are restricted to even exchange cycles. The observable expression then becomes

$$\left\langle \hat{O} \right\rangle = \frac{\sum_{P_+} \int_{\Omega_+} dRdR_1 \cdots dR_{M-1} \left\langle R|\hat{O}\rho_\tau|R_1 \right\rangle \left\langle R_1|\rho_\tau|R_2 \right\rangle \cdots \left\langle R_{M-1}|\rho_\tau|PR \right\rangle}{\sum_{P_+} \int_{\Omega_+} dRdR_1 \cdots dR_{M-1} \left\langle R|\rho_\tau|R_1 \right\rangle \left\langle R_1|\rho_\tau|R_2 \right\rangle \cdots \left\langle R_{M-1}|\rho_\tau|PR \right\rangle}, \quad (4)$$

with P_+ and Ω_+ denoting all even permutations and the positive domain, respectively.

The Coulomb potential is first broken into long- and short- range pieces using an optimized Ewald breakup. The many-body high-temperature density matrix, ρ_τ, is then constructed from a product of two-body short-range density matrices and a long range many-body correction. The density matrix is constructed to become exact as the time step, τ, vanishes; τ is chosen sufficiently small to provide a reasonable tradeoff between computational effort and accuracy. Simulation temperatures ranged from $5000\,\mathrm{K}$ to $125\,000\,\mathrm{K}$ with $\tau^{-1} = 10^6\,\mathrm{K}$, yielding the number of 'time slices,' $M \equiv \beta/\tau$, in the range of eight to two hundred.

The resulting high-dimensional path integral is evaluated using a generalized Metropolis Monte Carlo method [6,7]. Many details of the computational techniques employed may be found in Refs. [6,8,9].
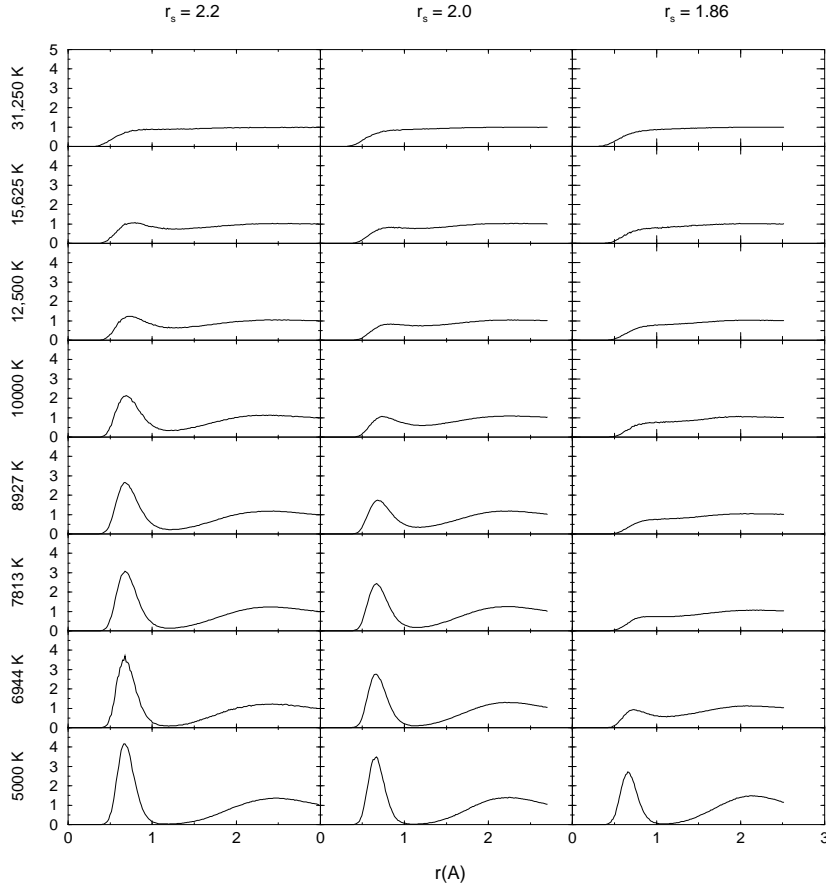

Figure 1. Proton-proton pair correlations, $g_{pp}(r)$.

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*Proton exchange is negligible at the conditions we considered and, so, was not considered.

MOLECULAR FORMATION AND DISSOCIATION

Figure 1 provides an overview of the simulations at several temperatures and densities. At the lowest density, $r_s = 2.2$, molecules begin to appear near $15\,625$ K. Molecular formation is essentially complete at 5000 K [10]. It is apparent from the figure that $dP/dT < 0$ for the region separating the plasma from the molecular fluid. This behavior is expected, since dissociation can be separately achieved from any molecular state point by heating or compression. In fact, as reported in Ref. [11], we find a region of $dP/dT < 0$ at constant density for $r_s < 2.2$, which we interpret as coexistence of two phases. This region is the manifestation, at constant volume, of a density discontinuity at constant pressure. Similar results are obtained for deuterium.
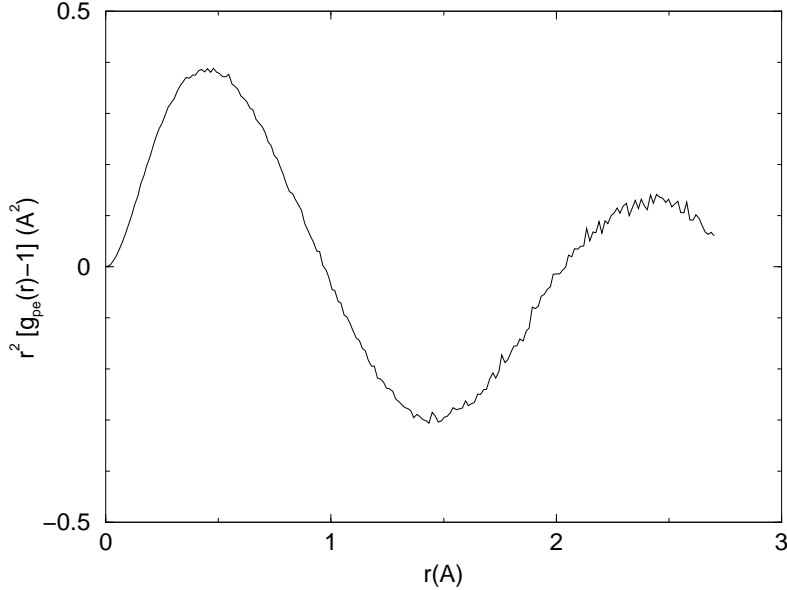

Figure 2. The proton-electron radial correlation function, $r^2 \left[g_{pe}(r) - 1 \right]$ at $(r_s = 2.0, T = 12\,500\,\text{K})$.

While the cooler phase is clearly a molecular fluid, the hotter phase is not a plasma, but rather a partially ionized atomic fluid. This can be seen from Figure 2, which exhibits the $(r_s = 2.0, T = 12\,500$ K) electron-proton pair correlation, $r^2 \left[g_{pe}(r) - 1 \right]$. This function shows the radial redistribution, relative to free particles, of electrons in the presence of protons. The maximum density is achieved near one Bohr radius, as expected for an atomic-like phase. Further, a broad minimum exists near 3 Bohr, indicating the electrons localize near protons long enough to exclude other electrons, even when very few molecules are present. This feature disappears around $30\,000$ K, as hydrogen begins to ionize into a plasma [10].

Figure 3 shows the electron exchange probability versus density and temperature. In the plasma phase above $100\,000$ K, there is very little probability for an electron to be involved in a quantum exchange. As temperature is lowered, however, the exchange probability grows and peaks at the phase line, near $10\,000$ K. At constant temperature, exchange increases with density. It is suppressed somewhat as molecules form but remains substantial well into the molecular phase. Spin-like electrons form long, directed exchange cycles that span the simulation cell. Since electrons of opposite spin occupy each molecular bond, these electron exchanges are *inter*-molecular. In liquid helium, exchange cycles of this type are directly related to superfluidity [9], so it seems likely
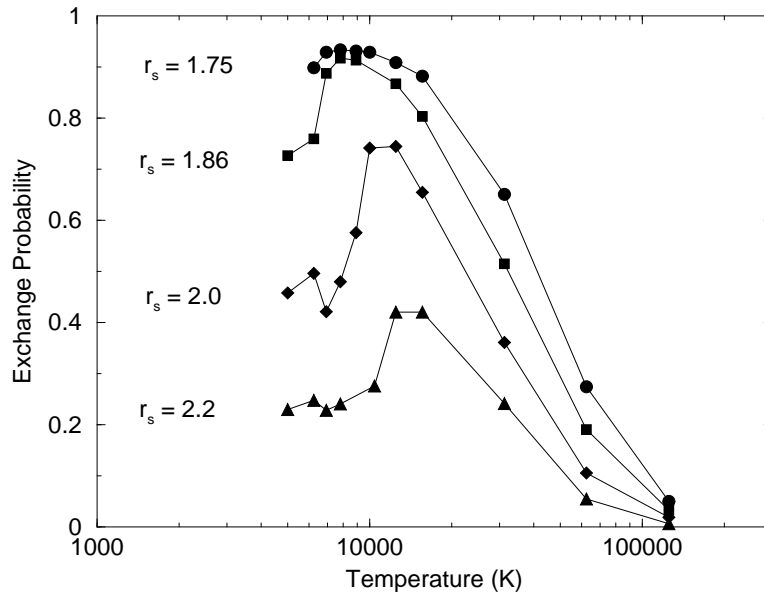
Figure 3. Probability of an electron participating in an exchange.

that electronic exchange is related to electrical conductivity. The electrons, then, would be in an unusual state in which they simultaneously provide molecular bonding and contribute to the conductivity. This may explain the recent experimental finding [2] that shock-compressed hydrogen metallizes before the molecular state is substantially dissociated.

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