PHYSICAL REVIEW
LETTERS

VOLUME 73 | 17 OCTOBER 1994 | NUMBER 16

Equation of State of the Hydrogen Plasma by Path Integral Monte Carlo Simulation

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(Received 15 April 1994)

The equation of state of the hydrogen plasma is calculated by the restricted path integral Monte Carlo method. We have investigated the plasma from the classical weak coupling regime to the quantum strongly coupled regime. Good agreement is found with the existing theories for low electronic degeneracy. Inception of molecular formation is observed at low densities and temperatures.

PACS numbers: 05.30.−d, 02.70.Lq, 64.30.+t, 71.10.+x

The knowledge of the properties of dense ionized matter is important for a wide range of physical situations, from the hot and dense astrophysical plasmas to the cold electron plasma in solids. Despite this, exact (*ab initio*) calculations of the statistical properties of even the easiest Coulombic system, the hydrogen plasma, are nonexistent because of the difficulties of simulating fermion systems. Recently the method of restricted paths to treat Fermi statistics within path integral Monte Carlo (RPIMC) simulations has been introduced [1,2], and here it is applied to the hydrogen plasma at high density and high temperature, a regime which is physically important but still outside the present experimental capabilities.

For a system of N protons and N electrons in a volume Ω at temperature T, conventional dimensionless parameters are $\Gamma = e^2/ak_BT$ which measures the coupling in the classical limit, where $a = (3/4\pi n)^{1/3}$ is the ion-sphere radius, n is the electron density, k_B is the Boltzmann constant, and e is the charge unit. Classical weak coupling is for $\Gamma \ll 1$. At $T = 0$ the coupling is parametrized by $r_s = a/a_0$, where $a_0 = \hbar^2/m_e e^2$ is the electron Bohr radius and m_e the electron mass. The weak coupling limit is $r_s \ll 1$. At $T > 0$, $\theta = T/T_F$ measures the degree of degeneracy of the electrons, where $T_F = \hbar^2(3\pi^2 n_e)^{2/3}/2m_e k_B$ is the Fermi temperature of the fully degenerate, noninteracting electron gas. $\theta = 1$ roughly separates the quantum domain ($\theta < 1$) from the classical domain ($\theta > 1$). In Fig. 1 different lines of constant Γ (coupling) and θ (quantum effects) are shown. Fermi statistics of protons start to play a role at $\theta \sim m_e/m_p \sim 10^{-3}$ and will be ignored. Electron relativistic effects appear at temperatures and/or densities higher than those considered here [3]. Formation of atoms or molecules takes place in the left lower corner of Fig. 1. Partial ionization may occur around $k_BT_I = e^2/2a_0 = 13.6$ eV and for $n \leq n_I \sim 2 \times 10^{23}$ cm^{-3} defined by $T_F = T_I$ [3]. Molecules may form at lower temperatures, below $T_D \sim 50\,000$ K, the temperature of dissociation of an isolated H_2 molecule.

The domain in Fig. 1 can be split into three regions where different theoretical approaches are useful. In the first region $\theta \geq 10$, the system is nearly classical and weakly coupled ($\Gamma \leq 0.1$). The Debye-Hückel theory (DH) provides an exact limit for $\theta \gg 1$ (classic), $\Gamma \ll 1$ (weak coupling) giving $P^{\mathrm{DH}}/nk_BT = 1 - \sqrt{2/3}\Gamma^{3/2}$ [3]. The first corrections in density to this equation of state (EOS) have been obtained up to $n^{5/2}$ [4]. For stronger coupling ($\Gamma \sim 1$), thermodynamic and transport properties have been obtained by molecular dynamic simulations of semiclassical models [5–7]. Such models are limited to $\theta \geq 1$.

The second region is where the electrons can be considered in their ground state ($\theta \leq 0.1$). In the limit of high density ($r_s \ll 1$), the electrons behave as a uniform

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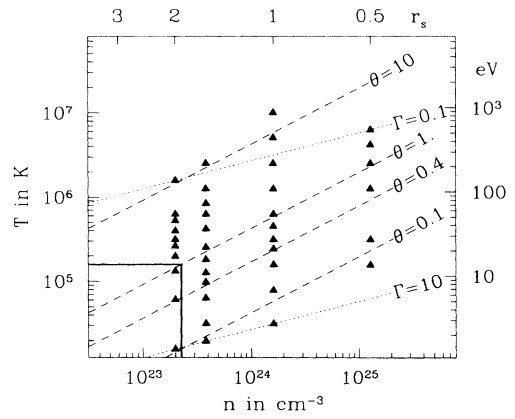

Fig. 1. Characteristic lines of the hydrogen plasma in the (n,T) plane. The solid thick lines are the pressure ionization threshold (vertical) $E_F = 13.6$ eV and the temperature ionization threshold (horizontal) $T = 13.6$ eV. The filled triangles indicate our calculations. The line $\theta = 0.4$ is the threshold for the permutations inside the system to occur.

background and one recovers the classical one component plasma model [3]. At smaller densities, the electron gas is polarized by the protons, and static and dynamic properties of the system have been computed by linear response theory based calculations [3] and by dynamical techniques [8,9].

In the intermediate domain ($0.1 \leq \theta \leq 1$), the electrons are partially degenerate correlated fermions, polarized by the protons. Electrons have been treated by density functional theories (DFT) at various degrees of approximation, and the correlations between protons have been calculated by classical integral equations [3,10–12]. Ichimaru and co-workers also provided an analytical expression for the EOS of the hydrogen plasma, obtained by fitting all the existing results in the above three domains.

Finally, a plasma phase transition has been predicted to occur at densities around $r_s \sim 2$ and for $T \leq 1$ eV outside of the domain investigated here [13].

All the methods mentioned so far are based on models or approximations which are specific to one domain and cannot easily be extended outside. Therefore an *ab initio* method which considers protons and electrons at the same microscopic level and is capable of treating all densities and temperatures is highly desirable. This is in principle provided by path integral Monte Carlo simulations. A simulation of two protons and two spin-unlike electrons has been already performed, but larger systems of distinguishable particles were unstable because Fermi statistics were neglected [14]. The recently developed RPIMC is capable of accurate simulations in all regions of the phase diagram. By RPIMC we have studied the hydrogen plasma for all the thermodynamic conditions reported in Fig. 1. Our main aim was to provide a test of the existing theories and to check the limits of applicability of the method. Investigation of the atomic-molecular regime is in progress and will be published separately [15]. We found a general good agreement between the theoretical predictions of DFT based approaches and our results for the thermodynamic properties and the pair correlation functions in the region of small electronic degeneracy $\theta \geq 0.4$, which is also where we observe a small number of exchanges in the system. At higher degeneracy, RPIMC results deviate significantly from theoretical predictions. Inception of molecular formation is observed only at $r_s = 2$ and for the lowest temperature investigated, namely $T = 0.05$ hartrees $= 1.36$ eV. Preliminary studies indicate that at this density, stable molecules are obtained only for temperature as low as $T \sim 5000$ K $\simeq$ 0.43 eV [15].

In the remainder of the paper we briefly describe the method, we discuss our result in more detail, and finally we draw some conclusions.

The path integral Monte Carlo simulation is a well-established computational technique to obtain statistical mechanics averages of quantum many-body systems [16]. The density matrix between configurations $\mathbf{R}$ and $\mathbf{R}'$ ($\mathbf{R} = \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$) at the inverse temperature β is written in terms of the density matrix at higher temperature as follows:

$$\rho_F(\mathbf{R},\mathbf{R}';\beta) \propto \sum_{\mathcal{P}} (-)^{\mathcal{P}} \int d\mathbf{R}_1 \cdots d\mathbf{R}_{M-1} \times \prod_{i=1}^{M} \rho_D(\mathbf{R}_{i-1},\mathbf{R}_i;\tau), \quad (1)$$

with the boundary conditions $\mathbf{R}_0 = \mathbf{R}, \mathbf{R}_M = \mathcal{P}\mathbf{R}'$. Here $\mathcal{H}$ is the Hamiltonian, M is an integer, $\tau = \beta/M$, and $\mathcal{P}$ is a permutation of electron coordinates. Subscripts D and F indicate distinguishable and Fermi particles, respectively. Simulation of fermions requires the following: (a) an approximation for the high temperature density matrix (HTDM) $\rho_D(\mathbf{R},\mathbf{R}';\tau)$; (b) an algorithm to sample efficiently the permutation space; (c) a method to treat the Fermi statistics.

(a) The choice of the HTDM must be accurate to minimize the number M of intermediate points (slices) in which the interval β has to be partitioned. We have used the pair-product approximation [16]. Essentially we put into the HTDM the exact hydrogen atom density matrix as well as the exact density matrix for a pair of electrons. We used the Ewald image method to calculate the potential energy and the "action." Our trial density matrix is

$$\rho_D(\mathbf{R}_{i-1},\mathbf{R}_i;\tau) = \rho^{(0)}(\mathbf{R}_{i-1},\mathbf{R}_i;\tau) \times \exp\left[-\sum_{i<j} u(\mathbf{r}_{ij},\mathbf{r}'_{ij};\tau) - U^{\mathrm{lr}}(\mathbf{R}_{i-1},\mathbf{R}_i;\tau)\right], \quad (2)$$

where $\rho^{(0)}(\mathbf{R}_{i-1}, \mathbf{R}_i; \tau)$ is the density matrix for free particles, $u(\mathbf{r}_{ij}, \mathbf{r}'_{ij}; \tau)$ is the short range action for a pair of particles, and $U^{\rm lr}(\mathbf{R}_{i-1}, \mathbf{R}_i; \tau)$ is the long range action. A complete derivation will be given elsewhere. The pair-product form for the HTDM has been previously found [17,18] to provide an essential improvement over the more commonly used "primitive" approximation [16]. In the present calculation, the optimal value of τ was found to scale as r_s^2 and we fixed τ according to the relation $\tau = (0.05 r_s^2)$ hartrees^{-1}. At the lowest temperatures this gives paths as long as 200 slices.

(b) Efficient sampling of the configuration and the permutation space can be achieved by the bisection method [16]. Typically 8–16 electronic time slices are moved at once. The proton paths are very localized, and to efficiently sample their configurations we also performed rigid Monte Carlo translations of the proton paths.

(c) Simple application of Eq. (1) would lead to extremely large error bars because of the minus sign associated with odd permutations. We applied the RPIMC method [2], adopting the nodal surfaces of the temperature dependent noninteracting density matrix (referred to NI in Ref. [2]). This is the finite temperature extension of the fixed-node approximation used to simulate fermions at $T = 0$. Only paths with positive trial density matrices are allowed which implies only even permutations and only positive contributions to any statistical average. As the trial density matrix approaches the exact density matrix this becomes exact. Occasional moves of only three-body permutations of like-spin electrons were found to suffice to the formation of "macroscopic" exchanges of the Fermi liquid state. We used two reference points as explained in [2]. Ground state studies on hydrogen suggest that the fixed-node error on the energy is less than 0.4%, and the error at finite temperature should be even smaller [19]. This is well within the error bars of our data (few percent).

We studied a system of 54 protons and 54 electrons. We checked that at $r_s = 1$ and for two values of temperature, namely $T = 4$ and $T = 0.25$ hartrees, we obtain the same results for systems of 54, 82, and 110 electrons.

Our main concern is to compare the EOS of the hydrogen with the existing theories, in particular the analytic form provided by Ichimaru and co-workers [11]. We found that irrespective to the density, RPIMC results for the potential energy V are described fairly well by the Ichimaru function, as given in Eq. (3.142) of Ref. [3] and Eq. (39) of Ref. [11], up to $\Gamma \sim 3$ above which it predicts a somewhat larger interaction energy. Figure 2 shows, for all densities investigated, the excess of total kinetic energy with respect to the ideal Fermi system as obtained by RPIMC and from the Ichimaru EOS. Deviations from the ideal gas behavior appear around $\theta \sim 2$ at all densities, and, at a given θ, they get more pronounced as the density decreases. For $\theta \geq 0.4$, the

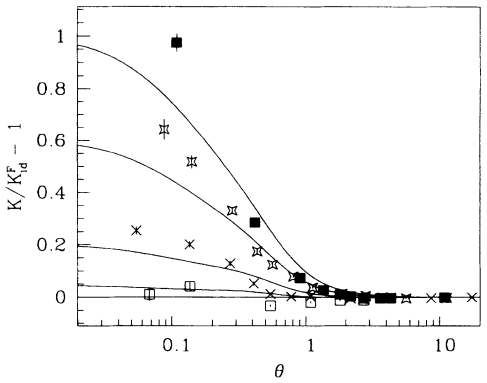

FIG. 2. Excess kinetic energy with respect the ideal quantum system versus the degeneracy parameter θ at $r_s = 0.5$ (open squares), $r_s = 1$ (crosses), $r_s = 1.61$ (open stars), and $r_s = 2$ (filled squares). The continuum curves are the Ichimaru's fit predictions [11].

Ichimaru prediction is rather good at $r_s = 2$ and $r_s = 1.61$, while at larger densities the agreement gets worse and, in particular, it fails in predicting the negative excess kinetic energy found at $r_s = 0.5$. On the other hand, for $\theta \leq 0.4$, the Ichimaru prediction works well at $r_s = 0.5$, while it underestimates the excess kinetic energy at lower densities, the disagreement gets larger for decreasing density. As already stated, $\theta = 0.4$ corresponds to the threshold for Fermi statistics. We note that a considerable number of permutations occur in the system for $\theta \leq 0.4$.

In Fig. 3 we show the excess pressure with respect to the ideal Fermi gas for two values of the densities investigated, namely $r_s = 1$ and $r_s = 2$, and we compare our results to the DH theory, to the virial expansion of

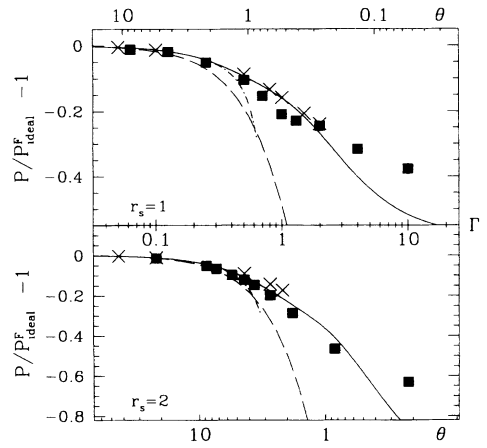

FIG. 3. Excess pressure with respect to the ideal quantum system at $r_s = 1$ (upper) and $r_s = 2$ (lower). Filled squares are RPIMC results, continuum line is the Ichimaru fit, dashed lines are the DH theory, and dot-dashed line is the virial expansion of Ref. [4]. The crosses indicate the results of semiclassical model calculations [6].

Ref. [4], to the Ichimaru function [3,11], and to results of semiclassical models [6]. As for the kinetic energy, the Ichimaru EOS fails below $\theta \leq 0.4$ and it predicts an absolute value of the excess pressure larger by about 30% at $\Gamma \sim 10$. The virial expansion at order $n^{5/2}$ gives a good prediction of RPIMC data for $\Gamma \leq 0.4$ at all densities. This indicates that the first correction to such theory is due to the Coulomb coupling. The DH prediction holds for $\theta \geq 3$, indicating as the first nonclassical term comes from the quantum kinetic energy in this range of densities. Finally, the semiclassical model denoted by I in Ref. [6] provides rather good predictions up to $\Gamma \sim 2$.

The general good agreement between RPIMC and the Ichimaru theory arises from the fact that the pair correlation functions have been accurately represented in the theory. In Fig. 4 we show at three values of the density, namely $r_s = 1, 1.61$, and 2, the proton-proton and the proton-electron correlation functions at $\Gamma = 10$ where the Ichimaru theory fails. We observe that as the density decreases the proton-proton correlation function changes its shape and develops at $r_s = 2$ a clear signature of molecular formation. This picture is further supported by the the spin-unlike electron-electron correlation function (not shown here) which at $r_s = 2$ presents a pronounced peak close to the origin as a signature of pairing to form bounding states of molecules. On the other hand, no firm proof of the formation of electron-proton bound states can be seen in the electron-proton correlation function.

In conclusion, we have investigated the phase diagram of the hydrogen plasma in the high-temperature–high-density region above and near the ionization thresholds. A good agreement has been found between the existing theories and our simulation results for values of the degeneracy parameter $\theta \geq 0.4$. Below this value we observe differences between theory and simulation, and we also note that the exchange of electrons occurs. Such results validate the theory and demonstrate that RPIMC is a powerful tool to investigate quantum plasmas. Although the method is not exact, the systematic error introduced by the fixed node constraint is about an order of magnitude smaller than the statistical errors in the hydrogen plasma and can be systematically improved. At sufficiently high coupling and low densities a clear signature of molecular formation is observed. A natural extension of the present calculation is the investigation of the plasma phase transition, a first order phase transition from the plasma to the molecular state [13]. This work is in progress. Another open issue is about the characterization of bound states and the definition of the degree of ionization of the plasma. To this aim a general criterion based on the analysis of the spectrum of the two-body off-diagonal density matrix has been proposed [20], and we plan to use it to analyze the RPIMC configurations to determine the population of the various chemical species.

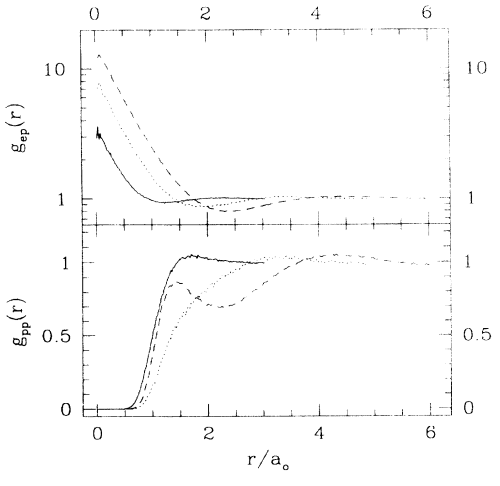

FIG. 4. $\Gamma = 10$. Electron-proton (upper) and proton-proton (lower) correlation functions versus r/a_0 at $r_s = 1$ (solid), $r_s = 1.61$ (dotted), and $r_s = 2$ (dashed).

This work has been supported by the Office of Naval Research Grant No. (ONR N00014-92-J-1320) and by the CNRS-NSF international travel Grant No. (NSF-INT91-15682). We thank A. Perez for providing us with his FORTRAN code. One of us (C. P.) is pleased to thank M. Boninsegni for very useful discussions. Part of the computer time has been kindly provided by CASPUR, University "La Sapienza" in Rome (Italy). We benefited from a grant of computer time at Centre de Calcul Vectoriel pour la Recherche (CCVR), Palaiseau, France. We acknowledge the Institute for Theoretical Physics at UCSB, Santa Barbara for its financial support in the final stage of this work.

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