PATH INTEGRAL MONTE CARLO SIMULATION
OF HYDROGEN PLASMA

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ABSTRACT

The path integral Monte Carlo method is exploited to compute the equation of state of hydrogen plasma and to investigate the occurrence of the plasma phase transition. We have spanned the thermodynamic plane from the classical weak coupling regime to the quantum strongly coupled regime. Good agreement is found with existing theories in the fully ionized regime for low electronic degeneracy. Molecules spontaneously form at low densities and temperatures. Thermal molecular dissociation at fixed density is accompanied by a pressure decrease, for $r_s \approx 2$ and below, which suggests the presence of a first order phase transition and a critical point in qualitative agreement with theoretical predictions.

1. Introduction

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 under compression, in particular the occurrence of an insulating-metal transition, much of its behaviour at high temperature and high density remains both important and uncertain. In various forms, hydrogen constitutes over 70% of the mass of the universe, and, in particular, the major overwhelming of the mass of some solar system planets (80% - 90%)². The knowledge of its equation of state (EOS) at finite temperature is an essential ingredient of all reliable planetary models.
In the fully ionized state various theoretical treatment have been addressed in order to predict the EOS and the transport properties of the system. Such state is reached at high densities and high temperatures typical of the interior of Jovian planets but still beyond the present experimental capabilities. As temperature and density are decreased, formation of electronic bound states and molecular hydrogen is expected. Here the fundamental question is whether hydrogen crosses a phase boundary as the fully ionized system transforms into a dense molecular fluid. The answer is not simple to deduce since dissociation occurs in a region where both thermal and degeneracy effects, as well as many-body effects, are important. Further, as in the liquid-gas phase transition, there is no change in symmetry. If a plasma phase transition (PPT), as it has been come to known, indeed exists, do the dissociation and ionization processes occur simultaneously, or is there perhaps an intermediate state? A theoretical route to address this problem is through the so called chemical picture of the system. Early approaches have been to separately model the molecular and the metallic state and then to equate the Gibbs free energies of the two phases in order to locate the transition. More advanced models generally include more chemical species, such as $H_2$, $H$, protons and electrons. One of the most sophisticated chemical model up to date predicts, at sufficiently high pressure, a first order phase transition from a molecular, low-density phase to a partially ionized atomic, high-density phase. The coexistence curve terminates with a critical point located at $T_c = 15300K$, $P_c = 0.614Mbar$ and $\rho_c = 0.35g/cm^3$. The density discontinuity associated with the phase transition would sharply alter the interior mass distribution of the giant planets. Chabrier et al. have shown that a PPT is required to obtain agreement between the most sophisticated structural models of Saturn and the measured gravitational moments. Despite this, very recent shock-compression data lead to the opposite conclusion: “One consequence of our conductivity results is that the first-order plasma phase transition predicted to occur at 100Gpa and 10,000K between weakly ionized and substantially ionized fluid phases of hydrogen probably does not occur. A continuous transition to metallic fluid occurs within the molecular phase at lower temperature.”

Recently the method of the restricted paths to treat Fermi statistics within Path Integral Monte Carlo (RPIMC) has been introduced. It is unique in its ability to simulate ab-initio fully interacting many-body quantum systems in thermodynamic equilibrium. It involves only one approximation, namely the nodal location of the Fermi density matrix, which can be improved in a systematic way. During the last few years we extended such technique to systems with coulomb interactions and we applied it to hydrogen. We study the fully ionized regime with the aim to provide a test of the existing theories and to check the limits of applicability of the RPIMC within the present implementation. Further, we investigate the occurrence of the PPT, a study which is still in progress.

Our results can be summarized as follow. In the fully ionized regime we found a
general good agreement between theories and RPIMC results 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.

Molecular formation, as indicated by the proton-proton correlation function \( g_{pp}(r) \), is observed at low enough density and temperature. Although still in a qualitative stage, our results generally support the findings of Saumon e Chabrier from their chemical model\(^6\). Both approaches find behaviors consistent with and suggestive of a first order phase transition. As in the chemical model, our molecular gas dissociates first into a partially ionized atomic-like fluid, then continuously reaches the fully ionized state.

The organization of the paper is as follows. In section 2 we present the model and we describe the various theoretical approaches to the EOS in the fully ionized state. In the following section 3 we sketch the main lines of the RPIMC and in section 4 we report our results and make comparison with the existing theories. Finally we draw some conclusion and perspectives.

2. The Model

We consider a neutral mixture of \( N \) protons and \( N \) unpolarized electrons \((N_+ = N_\downarrow = N/2)\) in a periodically repeated cubic cell of fixed volume \( \Omega \), and in thermo-dynamic equilibrium at a temperature \( T \). Conventional dimensionless parameters for this system 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 \( e \) the charge unit. Classical weak coupling is for \( \Gamma \ll 1 \), while at \( \Gamma \sim 1 \) the potential energy is about the same as the classical kinetic energy. At \( T = 0 \) the coupling is parameterized 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\(^7\). The weak coupling limit is \( r_s \ll 1 \), where the electrons form a weakly interacting, fully degenerate Fermi system. At finite temperature, \( \theta = T/T_F \) 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, non-interacting electron gas. \( \theta = 1 \) roughly separates the quantum domain (\( \theta < 1 \)) from the classical domain (\( \theta > 1 \)).

The Hamiltonian of the non relativistic system is

\[
\mathcal{H} = -\sum_i \lambda_c \nabla_i^2 + \sum_{i<j} \frac{q_i q_j}{r_{ij}},
\]

where \( q_i \) is the charge and \( \alpha_i \in \{e, p\} \) is the species of the \( i \)-th particle. By expressing \(~r_s \) is related to the mass density \( \rho \) in g/cm\(^3\) by \( \rho = 2.006/r_s^3 \).
the distances in reduced coordinates $x_i = r_i/a$ we can rewrite

$$\beta H = \left( \frac{4}{3\pi} \right)^{\frac{2}{3}} \theta^{-1} \nu \sum \frac{1}{i<j} x_{ij},$$

where

$$\nu = \sum_{\alpha \neq \alpha} \frac{m_i}{m_\alpha} \sum_i \nabla^2 x_i$$

is, within a constant factor, the kinetic energy in reduced coordinates. Eq. (2) shows the relevance of the parameters $\theta$ and $\nu$ to describe the thermodynamic status of the system. In particular the partition function depends upon these two parameters only and it is easy to show$^3$ that the excess free energy with respect to the ideal quantum system can be obtained by a thermodynamic integration over $\nu$ of the coulomb interaction energy computed at constant $\theta$. From the knowledge of the excess free energy all the thermodynamics follows in the standard way.$^3$

![Graph](image)

Fig. 1. Characteristic lines of the hydrogen plasma in the $n, T$ plane. The solid thick lines are the pressure ionization threshold (vertical) $T_P = 13.6\text{eV}$ and the temperature ionization threshold (horizontal) $T = 13.6\text{eV}$. The black triangles indicate our calculations. The line $\theta = 0.4$ is the threshold for the permutations inside the system to occur.
In fig. 1 different lines of constant $\Gamma$ (coupling) and $\theta$ (quantum effects) are shown. Fermi statistics for protons starts 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. Formation of atoms or molecules is expected to occur in the left lower corner of fig. 1. Partial ionization may occur around $k_B T_1 = e^2/2a_0 = 13.6 \text{ eV}$, and for $n_i \sim 2 \times 10^{23} \text{ cm}^{-3}$ defined by $T_F = T_1/3$. Molecules may form at lower temperatures, below $T_D \sim 50000 \text{ K}$ 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 $P_{\text{DH}} = nK_B T = 1 - \sqrt{2/3}\Gamma^{3/2}$. Recently, the first corrections in density to this equation of state (EOS) have been obtained analytically up to $\Gamma^{5/2}$. For stronger coupling ($\Gamma \sim 1$), thermodynamic and transport properties have been obtained by Molecular Dynamic simulations of semi-classical models, where all particles are classical and they interact through pseudo-potentials which account for diffraction and symmetry effects.

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 ($n_i \ll 1$), the electrons behave as a uniform background and one recovers the classical one component plasma model. 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 and by dynamical techniques.

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 calculated by classical integral equations. Dharma-Wardana and Perrot applied finite temperature DFT within Local Density Approximation (LDA) to hydrogen plasma in the region $1 < n_i < 2$ and $0.5 < \Gamma < 10^{-3}$. Ichimaru and coworkers applied the dielectric function formalism beyond the random phase approximation (local field corrections) at various degrees of approximation. Ichimaru and coworkers also provided an analytical expression for the EOS of the hydrogen plasma, obtained by fitting all the existing results in the above three domains.

Besides the Car-Parrinello simulation studies where the appearance of bound states and molecules arises naturally (within LDA), the theory become considerably more difficult when the effects of neutral species and bound states, which form as temperature and density are lowered, must be considered. An alternative and conceptually simpler, route to problem is to adopt the so called "chemical picture" where the existence of several species is assumed from the beginning, as we briefly discussed in the introduction.
All the methods mentioned so far are based on models or approximations which are specific to one domain and cannot easily be extended outside. 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. 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\textsuperscript{29}. 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.

3. The Restricted Path Integral Monte Carlo Method

Path integral Monte Carlo is a well established computational technique to obtain statistical mechanics averages of quantum many body systems\textsuperscript{30}. The density matrix between configurations $\mathbf{R}$ and $\mathbf{R}'$ ($\mathbf{R} = \{\mathbf{r}_1, ..., \mathbf{r}_N\}$) at the inverse temperature $\beta$ is written in terms of the density matrix at higher temperature as follows

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

with the boundary conditions $\mathbf{R}_0 = \mathbf{R}, \mathbf{R}_M = \mathbf{PR}'$.

Here $\rho_D(\mathbf{R}, \mathbf{R}'; \tau) = \langle \mathbf{R}|exp(-\tau\hat{H})|\mathbf{R}' \rangle$ is the density matrix for distinguishable particles at temperature $T = 1/\tau$; $\hat{H}$ is the hamiltonian, $M$ is an integer; $\tau = \beta/M$ and $P$ is a permutation of electron coordinates. Subscripts $D$ and $F$ indicate distinguishable and Fermi particles respectively. Any diagonal observable is then obtained as:

$$\langle \mathcal{O} \rangle = \frac{Tr [\mathcal{O} \rho_F(\beta)]}{Tr [\rho_F(\beta)]} = \frac{\int d\mathbf{R} \mathcal{O}(\mathbf{R}) \rho_F(\mathbf{R}, \mathbf{R}'; \beta)}{\int d\mathbf{R} \rho_F(\mathbf{R}, \mathbf{R}; \beta)}$$

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 $\beta$ has to be partitioned. We have used the pair-product approximation\textsuperscript{30,31}. 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 HTDM has the form:

$$\rho_D(\mathbf{R}_{i-1}, \mathbf{R}_i; \tau) = \rho^{(0)}(\mathbf{R}_{i-1}, \mathbf{R}_i; \tau) \exp[- \sum_{i<j} u_{sr}(\mathbf{r}_{ij}, \mathbf{r}'_{ij}; \tau) - U^{tr}(\mathbf{R}_{i-1}, \mathbf{R}_i; \tau)]$$

where $\rho^{(0)}(\mathbf{R}_{i-1}, \mathbf{R}_i; \tau)$ is the density matrix for free particles, $u_{sr}(\mathbf{r}_{ij}, \mathbf{r}'_{ij}; \tau)$ is the action for a pair of particles interacting through to the short range component of
the coulomb potential in the Ewald decomposition, and $U^{tr}(R_{i-1}, R_i; \tau)$ is the long range action. An approximate form for $U^{tr}$ can be obtained if one i) neglects the short range-long range coupling in the Bloch equation, ii) takes the primitive form $U^{tr}(R, R'; \tau) \approx \left[ U^{tr}(R, R; \tau) + U^{tr}(R', R'; \tau) \right]$, and iii) solve the long range Bloch equation within the random phase approximation (full detail of the derivation can be found in\textsuperscript{32}).

The pair-product form for the HTDM has been previously found\textsuperscript{33-34} to provide an essential improvement over the more commonly used “primitive” approximation\textsuperscript{31}.

In the present calculation, the optimal value of $\tau$ was found to scale as $r_g^2$ and we fixed $\tau$ according to the relation $\tau = (0.05 \ r_g^2) \ a.u.^{-1}$ for the simulations in the fully ionized region. All calculations in the dissociation-recombination region were performed with $\tau = 0.3155 a.u.$, about 50% larger than the optimal value. This was a reasonable tradeoff between computational effort and accuracy in this region where a phase transition is expected. At the lowest temperatures ($5000 K$) this gives paths as long as 200 slices. With such choice for $\tau$ the total energy per atom is accurate to about 0.03$a.u.$ or 5%.

b) Efficient sampling of the configuration and the permutation space can be achieved by the bisection method as described in details in ref.\textsuperscript{30,31}. Typically 8-16 time slices are moved at once both for electrons and protons. The proton paths are however very localized and to efficiently sample their configurations we also performed rigid Monte Carlo translations of the proton paths.

c) Simple application of Eq. (5) with Eq. (4) would lead to extremely large error bars because of the minus sign associated with odd permutations. We circumvented the sign problem by using the RPIMC method\textsuperscript{12,13}. This is the finite temperature extension of the fixed-node approximation used to simulate ground state fermions. According to the nodal location of some given trial density matrix, only paths with positive trial density matrix are allowed which, for diagonal observables, implies only even permutations and only positive contributions to the statistical averages\textsuperscript{13}. As the nodes of the trial density matrix approach the nodes of the exact density matrix the method becomes exact. We adopted the nodal surfaces of the temperature dependent non-interacting density matrix (referred to NI in ref.\textsuperscript{12}). Although the temperature dependence of the nodes is a first essential ingredient to recover the high temperature Boltzmann statistics, this form for the nodes remains still very primitive as it disregards all the effects of the interactions between electrons and with the protons. Several improvements are possible but they have not yet been implemented\textsuperscript{13}. Occasional moves of only three-body permutations of like-spin electrons were found to suffice to the formation of “macroscopic” exchanges characteristic of the normal Fermi liquid state. We used two reference points as explained in ref. \textsuperscript{13} to minimize the nodal error. Ground state studies on hydrogen\textsuperscript{35} suggests that the fixed-node error on the energy is less than 0.4% and the error at finite temperature should be even smaller. This is well within both the statistical and the systematic errors of our
data (few percent).

4. Results

4.1. Fully ionized regime

We studied a system of 54 protons and 54 unpolarized electrons. To address the finite size effects problem, we checked that at $r_s = 1$ and for two values of temperature, namely $T = 4\text{a.u.}$ and $T = 0.25\text{a.u.}$, we obtain the same results for systems of 54, 82 and 110 electrons. This gives us confidence in the results although the finite size problem deserves more investigation. With present computational resources this remains a formidable task.

In this section we compare the RPIMC data for the EOS of hydrogen to the existing theoretical predictions, in particular the analytic form provided by Ichimaru and coworkers\textsuperscript{24}.

![Graph showing negative interaction energy times $r_s$ vs $\Gamma$. RPIMC results at various densities compared to the Ichimaru predictions (lines). The thick straight line is the Debye-Hückel theory prediction: $-\sqrt{3/\Gamma^{2/3}}$.]

As shown in fig. 2 we found that irrespectively of the density, RPIMC results for the potential energy $V$ are described fairly well by the Ichimaru function, as given in equation (3.142) of reference \textsuperscript{3} and equation (39) of reference \textsuperscript{24}, up to $\Gamma \sim 3$
above which it predicts a somewhat larger interaction energy. For the kinetic energy agreement between RPIMC and Ichimaru predictions is less good as shown in fig. 3. Deviations from the ideal gas behaviour appear around $\theta \sim 2$ at all densities, and, at a given $\theta$, they get more pronounced as the density decreases. For $\theta \geq 0.4$, 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 $\theta \leq 0.4$, 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. $\theta = 0.4$ corresponds approximatively to the threshold for Fermi statistics as we observed that a considerable number of permutations occur in the system for $\theta \leq 0.4$.

![Fig. 3. Excess kinetic energy with respect the ideal quantum system vs $\theta$ 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.](image)

In fig. 4 we show the excess pressure with respect to the ideal Fermi gas at $r_s = 1$ and $r_s = 2$, and we compare RPIMC data to the DH theory, to the virial expansion of ref.16, to the Ichimaru function and to results of semiclassical models. 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 of 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 non classical term comes from the quantum kinetic energy in this range of densities. Finally, the semiclassical model denoted by I in reference $^{18}$ provides rather good predictions up to $\Gamma \sim 2$.

![Graph](image)

**Fig. 4.** Excess pressure at $r_s = 1$ (upper) and $r_s = 2$ (lower). Squares are RPIMC results, continuum line is the Ichimaru EOS, dashed line is the DH theory and dot-dashed line the virial expansion of ref.$^{16}$. The crosses indicate the results of semiclassical model calculations$^{18}$.

### 4.2. Molecular formation and Plasma Phase Transition

In this subsection we focus on the molecular formation-dissociation region that is the left lower corner in fig. 1 ($5000K \leq T \leq 30000K, 2.2 \leq r_s \leq 1.75$). The results presented here refers to a system of 32 protons and 32 unpolarized electrons. As we already mentioned, we have chosen a value for the time slice $\tau = 0.3155 a.u. = 10^6 K$ which gives a reasonable compromise between accuracy and feasibility. When molecules start appearing, the description of the system in terms of $\Gamma$ and $\theta$ looses
its physical significance (although it remains perfectly valid from the aim of thermodynamic integration) and we will rather discuss the results in terms of \( r_s \) and \( T \) (in \( K \)).

\[ \begin{align*}
&\text{rs = 2.2} & &\text{rs = 2.0} & &\text{rs = 1.86} & &\text{rs = 1.75} \\
&0.0 & 1.0 & 2.0 & 0.0 & 1.0 & 2.0 & 0.0 & 1.0 & 2.0 & 0.0 & 1.0 & 2.0 & 0.0 & 1.0 & 2.0 & 0.0 & 1.0 & 2.0 & 0.0 & 1.0 & 2.0 & 0.0 & 1.0 & 2.0 \\
&1.0 & 2.0 & 3.0 & 1.0 & 2.0 & 3.0 & 1.0 & 2.0 & 3.0 & 1.0 & 2.0 & 3.0 & 1.0 & 2.0 & 3.0 & 1.0 & 2.0 & 3.0 & 1.0 & 2.0 & 3.0 & 1.0 & 2.0 & 3.0 \\
&4.0 & 5.0 & 6.0 & 4.0 & 5.0 & 6.0 & 4.0 & 5.0 & 6.0 & 4.0 & 5.0 & 6.0 & 4.0 & 5.0 & 6.0 & 4.0 & 5.0 & 6.0 & 4.0 & 5.0 & 6.0 & 4.0 & 5.0 & 6.0 \\

\end{align*} \]

Fig. 5. Proton-proton pair correlation function in the molecular formation region.

In fig. 5 we show the proton pair correlation function obtained by RPIMC at four densities for the lowest five temperatures investigated. We observe that at low enough density, molecules form spontaneously as temperature is decreased. Characteristic of the presence of molecules is the pronounced peek in the correlation function followed by a very deep (nearly zero) minimum. This is quite different from an atomic liquid-like structure. We observe that the bond length depends slightly on density (from 0.67\( \text{Å} \) at \( r_s = 2.2 \) to 0.65\( \text{Å} \) at \( r_s = 1.75 \)) but is nearly temperature independent. Moreover as molecules form the pair distribution between spin-unlike electrons develops a large correlation peak near the origin as a signature of pairing to form bonding states inside the molecules. An example is given in fig. 6 where we report the spin-unlike and the spin-like electron-electron pair correlation at \( r_s = 2.2 \) and \( T = 7813 \text{K} \), just in the middle of the molecular region.

A related phenomenon, shown in fig. 7, is the increase of electron kinetic energy observed during molecular formation. This is indeed due to the electron’s loss of angular degrees of freedom when going from spherical atomic like orbitals to molecular bonding states. At a given temperature, such effect increases with density.
Fig. 6. Spin-like (lower curve) and spin-unlike (upper curve) electron-electron pair correlation function at $r_s = 2.2$ and $T = 7813K$.

Fig. 7. Electron kinetic energy under isochoric cooling. The density parameter $r_s$ is indicated in parentheses. The kinetic energy increases as an electron localizes in a bond. The protons are essentially classical, except at the lowest temperatures.
For high enough densities, the pressure is expected to *increase* during isochoric molecular formation. In the corresponding isobaric system, this unusual behavior corresponds to a negative density discontinuity as the signature of a first order phase transition with a negative sloping coexistence line.

![Graph showing pressure (P) versus temperature (T) for different isochors.](image)

Fig. 8. Pressure along four isochors from Chabrier's model. The densities correspond to $r_s = 1.75$ (squares), $r_s = 1.86$ (diamonds), $r_s = 2.0$ (triangles) and $r_s = 2.2$ (stars). Also shown is the proposed coexistence line for the same model.

In fig. 8 we report the results obtained from Chabrier's chemical model along the same isochors we studied. We also show the proposed coexistence line which terminates with a critical point at $r_s = 1.97$ and $T = 15,300K$. We can see that a step in pressure appears when crossing the coexistence line ($r_s < 2$) while for lower densities the pressure changes monotonously with temperature.

We obtain a qualitative similar behavior from RPTMC data. Except at $r_s = 2.2$, the pressure increases during molecular formation as shown in fig. 9 at $r_s = 2$. Similar behaviors are observed at $r_s = 1.86$ and 1.75. Our data suggest that the coexistence line is shifted to temperatures lower than proposed earlier. The critical point should be around $T = 10,000K$ (rather than $T = 15,000$) and for $r_s$ between 2,0 and 2.2.

To conclusive demonstrate the presence of a first order phase transition and to locate the critical point we should study the convergence of our data in the limits $\tau \rightarrow 0$ and $N \rightarrow \infty$. This work is still in progress. We believe that the qualitative features of the observed behavior will be confirmed while quantitative conclusions could change somewhat. A first estimate suggests that systematic effects on pressure due to the finite value of $\tau$ are smaller than 0.15Mbar. Finite size effects, quite large in the 32 electrons ground state, are substantially suppressed at finite temperature. Calculations for the free Fermi gas at $T = 5000K$ and $T = 50000K$ indicate that
finite size effects are smaller than imaginary time step errors.

5. Conclusions

We have simulated dense hydrogen plasma modelled as an assembly of protons and electrons interacting by pure coulomb potential. We have spanned the phase diagram of the system in the high temperature/high density region above 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 occur. 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.

Furthermore, we have investigated the molecular formation region around the expected Plasma Phase transition line. Our results are in a qualitative agreement with the theoretical picture\footnote{8}: they suggest the existence of a first order phase transition from a molecular, low density phase to a atomic partially ionized, high density phase. They also support the existence of a critical point which should however be located to somewhat lower temperature and density than suggested before. A more quantitative...
study of the location of the phase boundary and the critical point is in progress.

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