FERMIONIC PATH INTEGRAL SIMULATION OF DENSE HYDROGEN

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INTRODUCTION

Recent laser shock wave experiments by Da Silva et al. [1] have raised new interest in hydrogen and its isotopes at high pressure. Those are the first measurements in a region of pressure where hydrogen has been predicted to undergo a plasma-phase transition. The existence and the properties of this transition are topic of current discussions [2,3]. In this paper, we report path-integral Monte Carlo (PIMC) simulations [4] and compare with the experimental results for the equation of state. Further, we identify the number molecules, atoms and free particles in hydrogen using cluster analysis, which can be compared with chemical models [5,3]. At high densities, the analysis provides information about nature of the phase transition.

The PIMC simulations are a powerful tool to determine the static thermodynamic properties of a fully interacting quantum system. It is based on the density matrix, which can be expressed as a product of high temperature density matrices $\rho(\beta) = [\rho(\tau)]^M$ with $M = \beta/\tau$. This becomes a path-integral, which can be evaluate using a multi-stage Metropolis algorithm [4]. The well-known Fermion sign problem is treated by introducing a nodal restriction on the paths. In the simulation, we use the nodes of the free-particle density matrix [6].

COMPARISON WITH SHOCK WAVE EXPERIMENTS

The Nova laser shock wave experiments by Da Silva et al. [1] provided the first direct measurements of the equation of state of Deuterium in the pressure region of $0.25\,\mathrm{Mbar} \leq \mathrm{p} \leq 2.1\,\mathrm{Mbar}$ at temperatures above 1000 K. In these experiments, a shock wave propagates through a sample of precompressed liquid deuterium characterized by its initial state, (E_0, V_0, p_0). Assuming an ideal shock front, the variables of the shocked material (E, V, p) satisfy the Hugoniot relation [7]

$$H = E - E_0 + \frac{1}{2}(V - V_0)(p + p_0) = 0 \qquad (1)$$

The initial conditions in the experiment were $T = 19.6\,\mathrm{K}$ and $\rho = 0.171\,\mathrm{g/cm^3}$. We set $V_0 = 0.102\,\text{Å}^3$, $E_0 = -1.1676\,\mathrm{Ha}$ per molecule [8] and $p_0 \approx 0$.

Theoretical and experimental Hugoniots are shown in Figure 1. Experimentally, one sees a significantly increased compressibility in the range 0.7 Mbar to 2.1 Mbar. This differs substantially from the widely used Sesame data base. Comparing PIMC simulations and the experiment one finds reasonable agreement up to P=0.7 Mbar, In the region from 1.0 Mbar to 2.1 Mbar, however, they differ considerably. The PIMC becomes increasingly reliable as temperature increases. Hence, the discrepancy at pressures above 1.0 Mbar is a fundamental problem. According to PIMC, this region is associated with temperatures above 10 000 K as shown. By 15 000 K, almost all molecules are dissociated. At 50 000 K, approximately 60% of the atoms are ionized. These findings cast doubt upon the explanation of the experimental results given in [1], where they were interpreted as effects of dissociation of molecules. Since the ionized phase is not negligible one also has to question the explanation in terms of Ross's molecular dissociation model [9]. We also compare with the tight binding model in ref. [10]. If 1 eV per atom is added to that model, one finds good agreement with the PIMC above 0.5 Mbar. Finally, we compare with the *ideal* plasma model [5], in which one considers a gas of free molecules, atoms, ions, and electrons. We find that some of the measured data points lie at higher densities than predicted by this simple model.

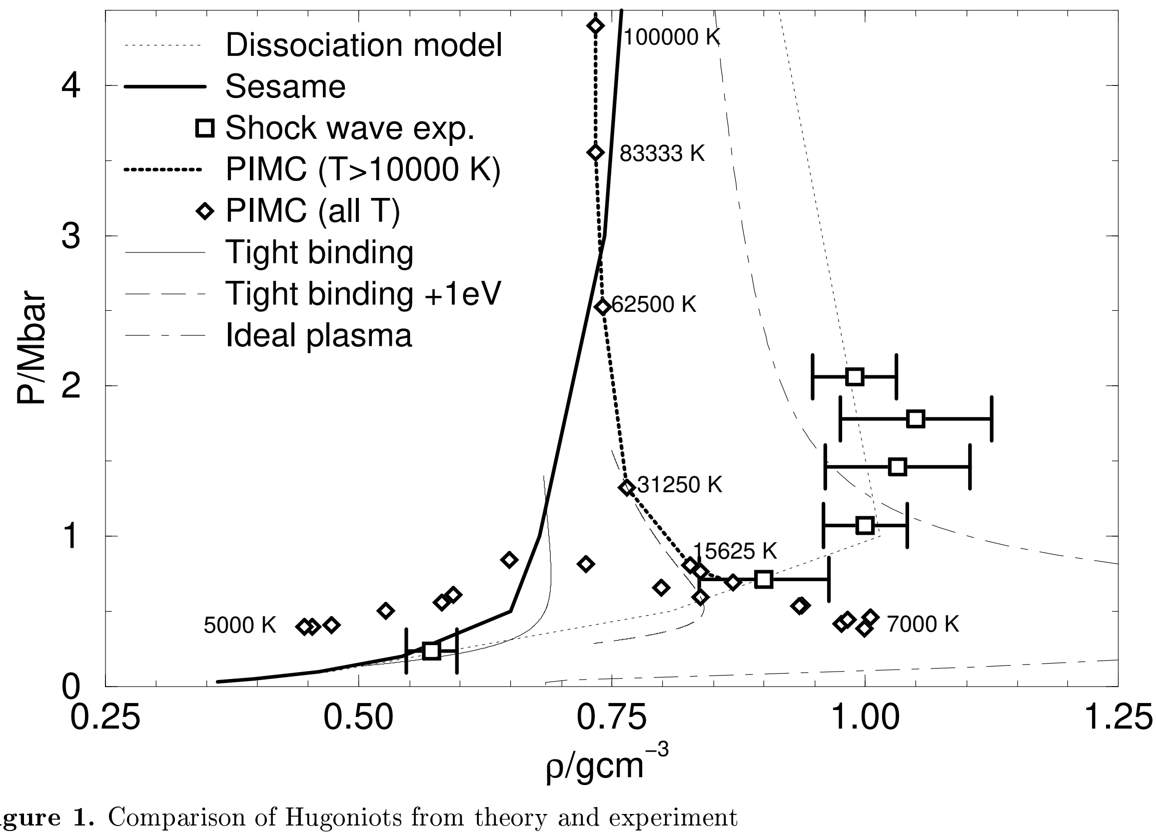

Figure 1. Comparison of Hugoniots from theory and experiment

CLUSTER ANALYSIS

Although our calculations describe hydrogen directly as electrons and protons, it is also useful to study the system in the chemical picture [5], in which hydrogen is composed of chemical species such as H atoms, H_2 molecules and the ions H^+, H_2^+, etc. In the following cluster analysis, we are going to identify the concentration of those compound particles from PIMC simulations.

Table 1. Percentages of clusters at $r_s = 3.0$

T/K	e	$H_{(1)}$	H^+	H	H^-	$H_{(2)}$	H_2^{++}	H_2^+	H_2
5000	**0**	**5**	2	3	0	**95**	1	25	69
6944	**0**	**13**	7	6	0	**87**	3	23	61
7812	**0**	**23**	8	14	1	**76**	1	15	60
10 000	**0**	**38**	15	23	0	**62**	2	20	41
15 625	**1**	**55**	17	37	1	**42**	1	12	29
31 250	**17**	**80**	26	51	3	**18**	1	8	9
62 500	**40**	**83**	38	43	2	**14**	1	8	5
125 000	**63**	**88**	58	28	2	**11**	3	6	2
166 667	**71**	**86**	63	21	1	**12**	5	5	1

Clusters Defined by Cutoff Radii

In this analysis, we identify clusters by studying the distances between the electrons and protons using the path centroids. We consider two protons as belonging to one cluster if they are less than 1Å apart. An electron belongs to one particular cluster if it is less than 0.75Å away from any proton in the cluster. The two cutoff radii were chosen from the molecular and atomic ground state distribution. This approach is adaptable to other systems and can give a cluster of any size. Studying hydrogen in the range of density from $r_s = 4$ and $r_s = 2$ and temperature from 5000 K to 167 000 K, we found a significant number of many different species including H, H^+, H^-, H_2^{++}, H_2^+, H_2. The numbers of these particles are shown in table 1 as a function of temperature at $r_s = 3$. $H_{(1)}$ denotes the total clusters with one proton H, H^+, H^-. $H_{(2)}$ stands for H_2^{++}, H_2^+ and H_2.

The proposed analysis shows qualitatively the expected temperature behavior of hydrogen. Around 10 000 K, many of the H_2 molecules are dissociated. The atoms ionize as the temperature is increased further, yielding an increase in the number of free electrons and protons. This analysis still shows some molecules and atoms at temperatures larger than 100 000 K where no stable compound particles can exist. This effect is caused by instantaneous particle collisions, which cannot be distinguished from bound states by a method based only on distances. Therefore, it leads to a significant overcounting of compound particles. This problems is partially overcome by an improved analysis described in the next section.

Cluster Analysis Based on Pair Correlation Functions

One can improve the analysis by replacing the criterion for a cluster. Instead of using two fixed cutoff radii, one can study the proton-proton and proton-electron pair correlation functions. We consider two limiting cases, the molecular gas at low temperature and ionized plasma at high temperature, and make a fit for any intermediate temperature,

$$g^{(T)}(r) = \alpha\, g^{(high\,T)}(r) + (1-\alpha)\, g^{(low\,T)}(r)\,. \tag{2}$$

We determined the degree of dissociation α_D by fitting g_{pp}. Similarly, we calculated the degree of ionization α_I by fitting g_{pe}. We found it advantageous to consider only the nearest neighbor distribution function, because it falls off rapidly within the simulation box and still contains the relevant information.

In our analysis, we use pair correlation functions from our simulations at 5000 K and at 166 667 K as low and high temperature limits. We assume that the first one is purely molecular and the latter is completely ionized and that the pair correlation functions for any species have little temperature dependence. We neglect compounds like H_2^+, H_2^{++} and H^-, which is questionable because of results of our previous analysis. We determine the number of protons, which are bound in molecules $n_{H2} = \alpha_D$, forming an atom $n_H = 1 - \alpha_D - \alpha_I$ and are free protons $n_H^+ = \alpha_I$. The results are shown in figure 2 for two different densities. At the lower density of $r_s = 4$, one finds a gradual dissociation occurring around $T = 10\,000\,\mathrm{K}$ and a smooth ionization process with α_I=0.5 at $T = 50\,000\,\mathrm{K}$. In the high density case at $r_s = 2$, one finds a rapid change in the number of molecules around $T = 8000\,\mathrm{K}$ and the resulting atoms can also exist in a small temperature interval before ionization takes place. We interpret these drastic changes as a first order plasma-phase transition described in [2,11].

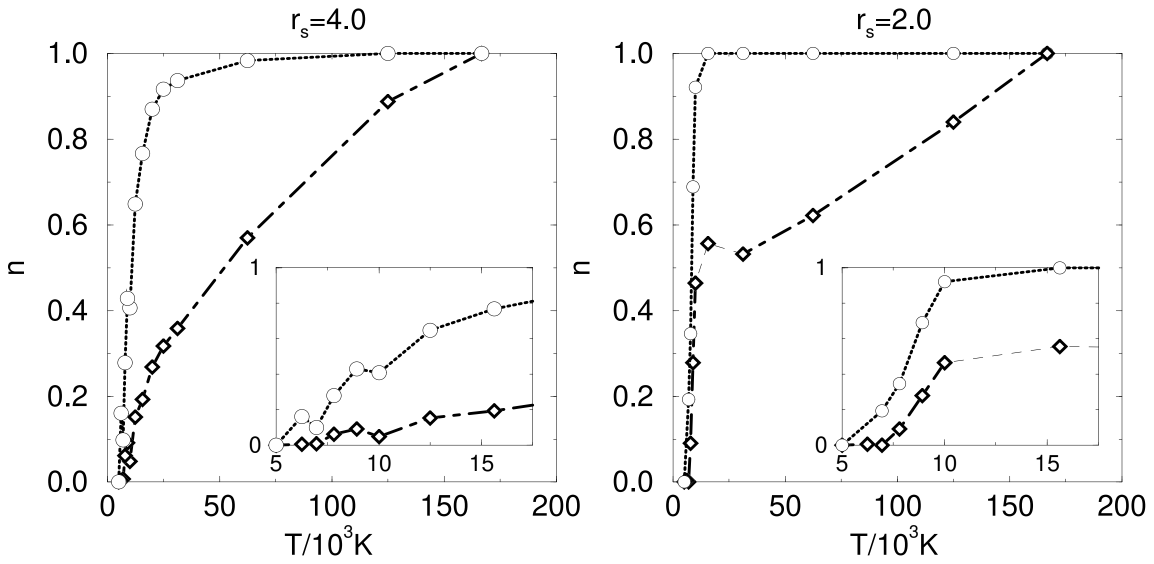

Figure 2. Cumulative plot of proportions of chemical species in the hydrogen plasma: The dash-dot line (⋄) indicates the number H^+, the dashed line (∘) the number of H^+ and H whereas area above gives the number of protons in H_2.

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REFERENCES

1. I. B. Da Silva, P. Celliers, G. W. Collins, K. S. Budil, N. C. Holmes, W.T. Jr. Barbee, B. A. Hammel, J. D. Kilkenny, R. J. Wallace, M. Ross, R. Cauble, A. Ng and G. Chiu, Phys. Rev. Lett. 78:483 (1997).
2. W. R. Magro, D. M. Ceperley , C. Pierleoni and B. Bernu, Phys. Rev. Letts. 76:1240 (1996).
3. D. Saumon and G. Chabrier, Phys. Rev. A 46:2054 (1992)
4. D. M. Ceperley, Rev. Mod. Phys. 67:279 (1995).
5. W. Ebeling, W. D. Kraeft and D. Kremp, Theory of bound states and ionisation equilibrium in plasma and solids, *in* “Ergebnisse der Plasmaphysik und der Gaselektronik”, Band 5, Akademie-Verlag, Berlin (1976).
6. D. M. Ceperley, Path integral Monte Carlo methods for fermions, *in* “Monte Carlo and Molecular Dynamics of Condensed Matter Systems”, Ed. K. Binder and G. Ciccotti, Bologna, Italy (1996).
7. Y. B. Zeldovich and Y. P. Raizer, “Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena”, Academic Press, New York (1966).
8. W. Kolos and L. Wolniewicz, J. Chem. Phys. 41:3674 (1964)
9. M. Ross, F. H. Ree and D. A. Young, J. Chem. Phys. 79:1487 (1983).
10. T. J. Lenosky, J. D. Kress and L. A. Collins, Phys. Rev. B 56:5164 (1997).
11. W. Magro, B. Militzer, and D. Ceperley, this volume.