Monte Carlo results for the hydrogen Hugoniot

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We propose a theoretical Hugoniot relation obtained by combining results for the equation of state from the direct path integral Monte Carlo technique (DPIMC) and those from reaction ensemble Monte Carlo (REMC) simulations. The main idea of this proposal is based on the fact that the DPMIC technique provides first-principle results for a wide range of densities and temperatures including the region of partially ionized plasmas. On the other hand, for lower temperatures where the formation of molecules becomes dominant, DPIMC simulations become cumbersome and inefficient. For this region it is possible to use accurate REMC simulations where bound states (molecules) are treated on the Born-Oppenheimer level. The remaining interaction is then reduced to the scattering between neutral particles which is reliably treated classically by applying effective potentials. The resulting Hugoniot is located between the experimental values of Knudson *et al.* [Phys. Rev. Lett. **87**, 225501 (2001)] and Collins *et al.* [Science **281**, 1178 (1998)].

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The H plasma is a very important and interesting many particle system. Hydrogen is the simplest and at the same time the most abundant element in the universe. Due to its high relevance for modern astrophysics, inertial confinement fusion, and fundamental understanding of condensed matter, hydrogen continues to be actively studied both experimentally [1–6] and theoretically [7–14]. At high temperatures and pressures, the hydrogen behavior is defined by the interaction between free electrons and protons (plasma state). With decreasing temperature, the contribution of bound states such as atoms and molecules to the equation of state (EOS) of hydrogen becomes of increasing importance, which at low temperatures completely defines the hydrogen properties. Furthermore, as pointed out in many papers (Norman and Starostin [15], Ebeling *et al.* [16], Haronska *et al.* [17], Schlanges *et al.* [18], Saumon and Chabrier [19], Filinov *et al.* [20]) there are strong theoretical arguments for a phase transition between two plasma phases. This issue which is of importance, for example, for models of Jovian planets is still actively debated. Among other important questions we mention the high-pressure compressibility and details of the pressure ionization and dissociation.

For this reason, in recent decades considerable experimental and theoretical investigations were carried out to accurately determine the EOS of hydrogen at high pressures. Experimentally, the EOS for this region can be obtained using shock-wave techniques. The results of these experiments are usually discussed in the form of a Hugoniot relation,

$$E = E_0 + \frac{1}{2}(p + p_0)\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right), \tag{1}$$

where the specific internal energy E at a state with the density ρ and the pressure p is connected to the initial conditions with the density ρ_0, the pressure p_0, and the internal energy E_0.

One of the well established experimental techniques for the creation of shock waves uses gas gun devices. With gas gun experiments, Nellis *et al.* [3] reached maximum pressures of 20 GPa and temperatures of 7000 K. More advanced techniques, the laser-driven experiments used by Collins *et al.* [2] and Da Silva *et al.* [4], allow one to reach pressures up to 300 GPa. At such pressures, as expected, hydrogen transforms from a molecular to a metallic state [5]. The results of laser-driven experiments have shown an unusual high compression $\rho/\rho_0 = 6$ of deuterium, which deviates significantly from the maximum compression of $\rho/\rho_0 = 4.4$ obtained within the SESAME EOS [21]. However, the experiments of Knudson *et al.* [1] which used magnetically driven flyer techniques (Z pinch) do not support such high compressibilities and are close to those of SESAME [21] and restricted path integral Monte Carlo (RPIMC) [7] results. The reason for this discrepancy of the two experiments is not yet completely understood and requires more detailed study [22], including independent theoretical investigations which is the aim of this paper. It is also necessary to mention other important experimental techniques such as the *convergent geometry* technique [6]. The experimental point obtained by Belov *et al.* [6] within this technique is located between the results of *laser-driven* and *magnetically driven flyer* experiments.

A Hugoniot relation can also be determined theoretically from the equation of state. This enables us to compare different theoretical approaches and computer simulations with experimental results, which cover a large region in the phase diagram of hydrogen. They start at temperatures of about 20 K and at a density of $\rho_0 = 0.171\ \mathrm{g/cm^3}$, which corresponds to the liquid state, and go up to temperatures and densities where only free electrons and nuclei exist. To our knowledge, there is no theory or computer simulation which rigorously and consistently describes the complete region of the EOS achievable by experiments. For example, the linear mixing model of Ross [23] predicts rather well the behavior of the laser-driven experiments; however it is a semiempirical theory which interpolates between molecular and metallic states of hydrogen.

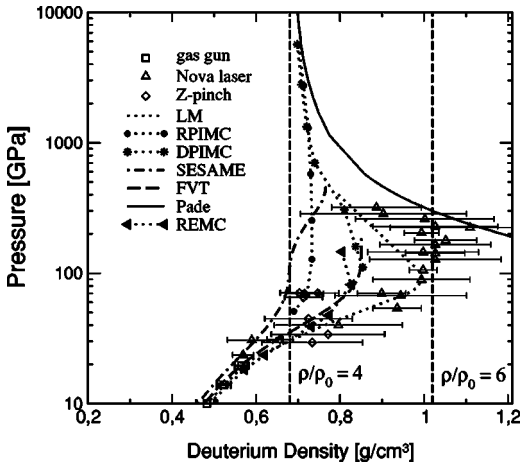

FIG. 1. Experimental and theoretical results for the deuterium Hugoniot curve.

Further, the region of completely and partially ionized hydrogen can be described analytically using the methods of quantum statistics [16,24,25]. In such methods, an EOS is obtained from a fugacity expansion (ACTEX) [25] and modified fugacity expansions which are upgraded by means of quantum-field-theoretical methods (leading to dynamical screening, self-energy, and lowering of the ionization energy [16,24]). In the latter case it is useful to condense the results in the form of Padé approximations [26] (from Debye to Gellman-Brueckner). Of course, the EOS following from these theories cannot reproduce the Hugoniot relation over the full range of density and pressure. It gives only the asymptotic behavior at higher temperatures. The typical behavior of the analytical theory [26] is shown in Fig. 1. It coincides only asymptotically with the *ab initio* RPIMC calculations and, with decreasing temperature, deviates considerably from those results. The Hugoniot relation calculated within the ACTEX theory which is not shown here exhibits a similar behavior [25].

The main reason for the failure of the analytical theories is obvious. As we mentioned already, for lower temperatures, the neutral particles, i.e., H atoms and H_2 molecules, become increasingly important, giving rise to a strongly coupled dense gas or liquid. Under such conditions it is necessary to invoke the methods of the theory of liquids. The simplest theory for this region is the fugacity expansion of the EOS up to the second virial coefficient [27]. This theory is applicable only for low densities and cannot correctly describe the molecular dissociation which is an important process occurring during shock wave experiments. For moderate densities, the fluid variational theory (FVT), proposed by Ross *et al.* [28], can be applied. This theory was further developed by Juranek and Redmer [12] to many-component systems, where molecular dissociation occurs. The effective interaction potentials [28,29] between components used within the FVT achieve good agreement with the experimental gas gun data of Nellis *et al.* [3], Fig. 1.

A powerful tool for the investigation of the hydrogen EOS is *ab initio* computer simulation. Quantum molecular dynamics simulations, based on a density functional theory, are usually applied to investigate the atomic and molecular region [8,13] but have difficulties in describing the partially ionized plasma. The wave packet molecular dynamics also covers the region of the fully ionized plasma [9] but yields unexpectedly high compressibilities. In this work we will not discuss these methods in detail and refer to the work cited.

The *path integral Monte Carlo* method is another first principle method which is well suited for the investigation of the EOS of hydrogen over a wide parameter range. Except for the problem of the Fermi statistics, it is an exact solution of the many-body quantum problem for a finite system in thermodynamic equilibrium. The reason for the difficulty with the Fermi statistics is the antisymmetry of the many-electron density matrix ρ (or, equivalently, the wave function) which is a superposition of $N!$ density matrices differing among each other by permutations of particles. Of these, $N!/2$ terms are positive (even permutations) and $N!/2$ negative (odd permutations). With increasing degeneracy the contributions of both terms to thermodynamic quantities grow in magnitude and largely compensate each other essentially reducing the efficiency of the simulations. This "sign problem" is handled differently in various simulations. The restricted PIMC method used by Ceperley and Militzer replaces the density matrix ρ by an approximate one the nodes of which are known; for details see [7] and references therein. On the other hand, the direct path integral Monte Carlo (DPIMC) method used by Filinov *et al.* [10,11] and others attempts to evaluate the exact density matrix without additional approximations. This method will be used below and, therefore, is briefly discussed in the following.

The idea of the DPIMC method is well known: any thermodynamic property of a two-component plasma with N_e electrons and N_p protons at a temperature T and volume V is defined by the partition function $Z(N_e,N_p,V,T)$ which is the trace of the density matrix:

$$Z(N_e,N_p,V,T) = \frac{1}{N_e!\,N_p!}\sum_{\sigma}\int_V dq\,dr\,\rho(q,r,\sigma;T), \quad (2)$$

where q and r comprise the coordinates of the protons and electrons, respectively, σ the spins of the electrons, and ρ denotes the antisymmetrized density matrix of the whole system which includes $N_e!N_p!$ permuations, as explained above. Taking into account the electron spin and the Fermi statistics (antisymmetrization), the density matrix is expressed by a path integral, e.g., [30], where all electrons are represented by fermionic loops with a number of intermediate coordinates (beads); for details see Ref. [11]. In our simulations, we used an effective quantum pair potential, which is finite at zero distance [31] and was obtained by Kelbg as a result of a first-order perturbation theory [35]. Improvements beyond the perturbative level are also possible [36,37].

The simulations have been performed at temperatures of 10^4 K and higher in a wide range of particle densities for which proton exchange effects are negligible. In the present calculations, we used an improved treatment of the electron exchange where we took into account the exchange interaction of electrons from neighbor Monte Carlo cells, namely, first from the 3^3-1 nearest neighbor cells, then from the 5^3

TABLE I. Thermodynamic properties of deuterium plasma calculated by DPIMC simulations.

	$r_s=1.7$		$r_s=1.86$		$r_s=2$			
T (K)	P (GPa)	E (eV)	P (GPa)	E (eV)	P (GPa)	E (eV)	ρ_H (g/cm^3)	ρ_H (GPa)
15 625	227.01	−18.995 3	101.41	−9.6854			0.8539	111.32
31 250	186.25	−9.948 54			134.30	−6.0186	0.8370	160.53
62 500			314.11	−1.2281	261.05	−0.1776	0.8104	306.69
1.25×10^5			7.9579	1727.41	6.2214	0.7395	0.7395	700.75
2.5×10^5			1596.84	48.2211	1237.67	46.8531	0.7204	1330.47
5×10^5			3261.65	112.7294	2645.01	114.5706	0.7082	2797.26
10^6			6765.75	245.9921	5439.83	246.4489	0.6979	5672.16

−1 next neighbors and so on. The calculated thermodynamic properties of hydrogen allowed us to compute the shock Hugoniot curve of deuterium using Eq. (3),

$$H = E - E_0 - \frac{1}{2}(p + p_0)(V - V_0) = 0. \tag{3}$$

Following the work [7] we chose $p_0=0$, $\rho_0=0.171$ g/cm^3, $E_0=-15.886$ eV per atom and computed the pressure p_i and the energy E_i at a given constant temperature T (from 10^4 to 10^6 K) and three values of the volume $V_i=1/\rho_i$ corresponding to $r_s=1.7$, 1.86, and 2, where $r_s=\overline{r}/a_B$, $\overline{r}=(3/4\pi n_p)^{1/3}$, n_p is the particle density, and a_B the Bohr radius. The results of the calculations are presented in Table I. Substituting the obtained values p_i, E_i, and V_i into the Hugoniot curve we determine the volume range V_1, V_2 where the function $H(p,V,E)$ changes its sign. The value of the density at the Hugoniot curve is calculated by linear interpolation of the function H between V_1 and V_2. The values of the pressure and of the total energy are shown in the Table I only for those density values between which the value of the density lies on the Hugoniot curve at a given temperature. The values of density and pressure on the Hugoniot curve are placed in the last two columns of Table I and are plotted together with selected theoretical and experimental data in Fig. 1. The lowest temperature included in this figure for the DPIMC calculation is 15 625 K.

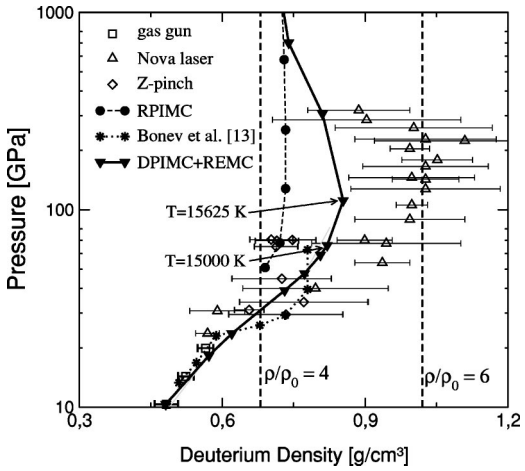

FIG. 2. Results for the combined Hugoniot relation.

In order to correctly describe the quantum mechanics of the formation of molecules at temperatures lower than 10 000 K, it is necessary to take many beads. In this region, DPIMC calculations become very time consuming and the convergence is poor. The natural proposal which appears for this region is to use the asymptotic property of the path integral which, for heavy particles, goes over into the classical partition function. For such systems, the classical Monte Carlo scheme can be applied. An advanced version of the classical Monte Carlo scheme is the reaction ensemble Monte Carlo (REMC) technique [32]. This method incorporates the quantum mechanical description of bound states, while the scattering states are treated classically. As was shown by Bezkrovniy *et al.* [14], the REMC technique describes the low temperature region very well, and yields good agreement with the gas gun experiments by Nellis *et al.* [3] (cf. Fig. 1). In these simulations the energy levels for the molecular partition functions of hydrogen and deuterium are obtained by solving the Schrödinger equation with the potential calculated by Kolos and Wolniewicz [33]. Further, the interaction between the neutral particles is modeled by an exponential-six (EXP6 modified Buckingham) potential proposed by Ross *et al.* [28] the parameters of which have been optimized to agree with molecular beam data of Bauer *et al.* [34]. On the basis of the REMC calculation, results are obtained much more easily as compared to those from molecular dynamics based on density functional theory; see Bonev *et al.* [13] and Fig. 2. Our REMC data are presented in Table II.

In order to get a unified picture combining DPIMC and REMC results, we use the fact that the REMC result turns out to be the limiting case of the DPIMC calculation at low temperatures, where hydrogen consists only of atoms and molecules. Therefore, it is obvious to use the asymptotic results of both methods to construct a Hugoniot relation which

TABLE II. Hugoniot data calculated by REMC simulations.

T (K)	2000	4000	5000	8000	10 000	13 000	15 000
ρ (g/cm^3)	0.470	0.570	0.618	0.729	0.771	0.804	0.815
P (GPa)	9.183	18.690	23.96	39.35	47.823	58.71	65.43

can be applied in the entire range of compression. For the construction of the combined Hugoniot curve we carefully analyzed the region where the Hugoniot data produced by the two methods can be connected to each other. As we can see from Fig. 1 the Hugoniot curve calculated within the DPIMC method ends at the point 15 625 K. At this temperature, the largest contribution to the EOS are given by molecular states. As a natural continuation of the DPIMC Hugoniot relation, we take the point of 15 000 K produced by the REMC simulation. We want to stress here that these two methods are completely independent and no interpolation procedure is used. Just two points at 15 625 K of DPIMC and 15 000 K of REMC simulations are connected to each other. The final Hugoniot curve is plotted in Fig. 2 and shows a maximum compressibility of approximately 4.75 as compared to the initial deuterium density.

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