Monte Carlo calculations of thermodynamic properties of deuterium under high pressures

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Abstract. Two different numerical approaches have been applied for calculations of shock Hugoniots and compression isentrope of deuterium: direct path integral Monte Carlo and reactive Monte Carlo. The results show good agreement between two methods at intermediate pressure which is an indication of correct accounting of dissociation effects in the direct path integral Monte Carlo method. Experimental data on both shock and quasi-isentropic compression of deuterium are well described by calculations. Thus dissociation of deuterium molecules in these experiments together with interparticle interaction play significant role.

1. Introduction
During last decades significant efforts have been made for the investigation of thermophysical properties of dense plasma. The importance of this activity is mainly connected with the creation of new experimental facilities. Powerful current generators and ultrashort lasers are used for production of very high pressures which can not be reached in traditional explosive devices and light-gas guns. Such experiments give information about different properties of strongly coupled plasma which can be exploited for the creation of wide-range equations of state and allows one to verify various theoretical approaches and numerical methods.

In this work we calculate shock Hugoniots of gaseous deuterium of different initial density corresponding to experiments [1, 2] as well as compression isentrope. We use two different methods: direct path integral Monte Carlo (DPIMC) [3] and reactive Monte Carlo (REMC) [4]. Brief description of these approaches together with calculation details are given below.

2. Method and simulation details
2.1. Path integral Monte Carlo method
The main idea of the path integral Monte Carlo method is in representaion of a density matrix of a quantum system of particles and, consequently, thermodynamic properties, as path integrals. This first-principle method which can be applied at any coupling parameters and significant degeneracy parameters, takes into account Fermi statistics and spin effects [3]. It has been used for calculation of thermodynamic properties of hydrogen and hydrogen-helium plasmas including hypothetical phase transition region. We have also applied this method to fully quantum electron-hole plasma in semiconductors.

Dissociation of deuterium molecules occurs under compression and essentially influences thermodynamic properties; therefore one must take into account this effect. As the path integral
Monte Carlo method operates with deuterons and electrons one should apply a criterion at which conditions a group of chosen deuterons and electrons can be considered as, for instance, an atom or molecule. A strict criterion of this kind is hardly possible to derive. However one can demonstrate the existence of bound states in calculations by analyzing the pair distribution functions. A comparison with chemical picture model [5] also gives good agreement which is an evidence of correctness of dissociation and ionization effects in DPIMC.

2.2. Reactive Monte Carlo method

Complete description of the REMC method can be found elsewhere [4, 6]. We consider only molecular hydrogen dissociation reaction and its inverse recombination reaction: \( \text{H}_2 \leftrightarrow 2\text{H} \). Ionization can be neglected at temperatures lower than the hydrogen ground state energy \( \propto 13.6 \text{ eV} \) and at moderate densities. Effective pair potentials between different sorts of particles have been considered by the Buckingham-EXP6 potential, corrected at small distances [7].

REMC simulations have been performed in the canonical ensemble for hydrogen and deuterium with a proper account of molecular dissociation. Accordingly, there are 3 types of Monte Carlo steps in a simulation box: particle movement, molecular dissociation into atoms and atoms recombination to a molecule. The expressions for probabilities of two last steps contain internal partition functions of atoms and molecules. All electrons in all particles are considered to be in the ground state. Further, the internal partition function of atom consists of the translational partition function only, for molecule besides it — of the rotational and vibrational partition functions. To calculate rotational and vibrational energy levels \( E_{nl} \) of a hydrogen molecule we solve the Schrödinger equation numerically in the central-symmetric field, described by Murrell-Sobie potential [8].

We calculate thermodynamic functions such as pressure \( P \) and configurational part of internal energy \( U_{\text{int}} \) by averaging over all Monte Carlo configurations [9].

To calculate an isentrope one should be able to determine entropy which is defined by the thermodynamic relation: \( S = -(\partial F(T,V,N)/\partial T)_V \), where \( F = \sum_{i=1}^{2} N_i \mu_i - PV \) — the free energy for a two-component system. We can obtain chemical potentials \( \mu_i \) of each component in the mixture with the help of the test particle method [10]: \( \mu = \mu^{id} + \mu^r \), where \( \mu^{id} \) is the ideal gas chemical potential: \( \mu^{id} = k_B T \log(\Lambda^3 N/V) \). Here \( \Lambda \) is the de Broglie wavelength of a particle.

The residual chemical potential \( \mu^r \) can be evaluated as [11]:

\[
\mu^r = -k_B T \log[L_a \exp(-\Delta U/k_B T)].
\]

Here \( \Delta U \) — the change in configurational energy produced by the insertion of one additional particle, \( L_a \) — the ratio of allowed (nonoverlapped) insertion intervals along trajectories which traverse (parallel to any of the axes) the simulation box from side to side, to the length of the box [11]. The test particle is then inserted randomly into some point in the allowed intervals and the change in configurational energy \( \Delta U \) is evaluated. The main advantage of this approach is the possibility of calculation of chemical potentials at high densities, where the usual test particle method tends to fail. Chemical potentials are calculated separately for atoms and molecules; the free energy is then determined as indicated above.

3. Results

Calculations were performed in a cubic simulation box with periodic boundary conditions, and with a cutoff radius equal to half of the box length. The initial configuration of particles was taken to be the fcc lattice for every input density \( \rho = N_H m_H/V + N_{H_2} m_{H_2}/V \) with \( N_H = N_{H_2} = 250 \). The system was equilibrated by \( 2 \cdot 10^7 \) steps and additional \( 10^7 \) steps
were used for the calculation of thermodynamic values. Averaging of 20 blocks was used to calculate statistical error, which did not exceeded 2% for pressure and energy.

In Fig. 1 shown are three shock Hugoniots of gaseous deuterium with experimental conditions corresponding to those in experimental data: \( \rho_0 = 0.1335 \text{ g/cm}^3 \), \( P_0 = 1.57 \text{ GPa} \) (I), \( \rho_0 = 0.153 \text{ g/cm}^3 \), \( P_0 = 2.03 \text{ GPa} \) (II) [1]; \( \rho_0 = 0.171 \text{ g/cm}^3 \), \( P_0 = 2.72 \text{ GPa} \) (III) [2]. The initial energy in calculations by both methods was \( E_0 = -15.875 \text{ eV/atom} \) and consisted of ionization energy of deuterium atom \( I = -13.6 \text{ eV/atom} \) and half of dissociation energy of deuterium molecule \( D_0/2 = -2.275 \text{ eV/atom} \). Simulation parameters (density and temperature) in both approaches were chosen in such a way that the calculated values of pressure \( P \) and energy \( E \) satisfied the Hugoniot equation 

\[
E = E_0 + 0.5(P + P_0)(1/\rho_0 - 1/\rho); \]

here index 0 denotes the values corresponding to the initial state.

It is worth to mention that at low pressures (up to 15 GPa) the calculated REMC shock adiabat is in very good agreement with light gas gun experiments [12]. All three shock Hugoniots agree with data [1,2] within experimental accuracy; adiabat III occupies intermediate position between points [13, 14] and [15]. As in the REMC method ionization was not taken into account calculations were performed up to temperatures 60 kK. On the other hand, computational difficulties prevented DPIMC from use at low temperatures. Thus, these two methods supplement each other; at intermediate pressures these two completely different approaches are in very good agreement (see Fig. 1).

![Figure 1](image1.png)

**Figure 1.** Shock Hugoniots of gaseous deuterium. Experiment: 1, 2 — [15] (NOVA); 3 — [12] (light-gas gun); 4 — [13] (Z-pinch); 5, 6 — [1] (hemisphere, gas); 7 — [14] (hemisphere, liquid). This work: 8 — REMC, 9 — DPIMC, from left to right \( \rho_0 = 0.1335 \text{ g/cm}^3 \), 0.153 g/cm\(^3\), 0.171 g/cm\(^3\).

In Fig. 2 we show the result of calculation of temperatures along 2 Hugoniot curves of deuterium in comparison with experimental data [1]. One can see that the REMC method shows a little overrated temperatures, whereas extrapolation of calculation by PIMC reveals good agreement with experiment [1] at low temperatures.

Dramatic rise of electrical conductivity of deuterium by 4–5 orders magnitude [16] at pressures \( \sim 1 \text{ Mbar} \) and densities about 1 g/cm\(^3\) indicates that one might also expect peculiarities in thermodynamic properties. Indeed, there are experimental results on quasi-isentropic
compression of deuterium in cylindrical explosive chamber which show 30% density jump at pressure about 1.4 Mbar [2]. Using free energy of deuterium from simulations by REMC and Widom’s test particle methods we calculated the compression isentrope of deuterium. The results are shown in Fig. 3 in comparison with the experimental data [2]. Excellent agreement proves that no special assumptions about phase transition are needed to explain such a remarkable behavior of experimental points and dissociation effects mostly contribute to this phenomenon. In the nearest future we plan to calculate the same isentrope by alternative computationally cheap Zel’dovich’s method.

Figure 3. Quasi-isentropic compression of deuterium. This work: 1 — REMC. Experiment: 2 — [17], 3 — [2].

Conclusions and Acknowledgments
We want to conclude that new experimental data on shock and quasi-isentropic compression of deuterium are in good agreement with calculations by two different Monte Carlo methods. The coincidence between two methods at intermediate pressure indicate that the direct path integral Monte Carlo method describes dissociation effects sufficiently well. Moreover, good agreement between REMC calculations of deuterium quasi-isentrope shows that 30% density jump is caused by dissociation of deuterium molecules.

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