Hugoniot of shocked liquid deuterium up to 300 GPa: Quantum molecular dynamic simulations

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Quantum molecular dynamic (QMD) simulations are introduced to study the thermophysical properties of liquid deuterium under shock compression. The principal Hugoniot is determined from the equation of states, where contributions from molecular dissociation and atomic ionization are also added onto the QMD data. At pressures below 100 GPa, our results show that the local maximum compression ratio of 4.5 can be achieved at 40 GPa, which is in good agreement with magnetically driven flyer and convergent-explosive experiments. At the pressure between 100 and 300 GPa, the compression ratio reaches a maximum of 4.95, which agrees well with recent high power laser-driven experiments. In addition, the nonmetal-metal transition and optical properties are also discussed.

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Recent studies of materials under extreme conditions, which require improved understandings of the thermophysical properties in the new and complex regions, have gained much scientific interest \(^1\). The combination of high temperature and high density defines “warm dense matter” (WDM) - a strongly correlated state, which is characterized by partially dissociated, ionized and degenerated states, and the modelling of the dynamical, electronic, and optical properties for such system is rather challenging. Due to their simplicity, hydrogen and its isotopes (deuterium and tritium) have been studied intensively \(^2\), where the relative pressure and temperature have reached megabar range and several eV. Specially, as one of the target materials in the inertial confinement fusion experiments \(^3\), deuterium has been extensively investigated through experimental measurements and theoretical models. Gas gun \(^4\), converging explosive \(^5\), magnetically driven flyer \(^6\), and high power laser-driven \(^7\)\(^–\)\(^9\) experiments have been applied to probe the physical properties of deuterium during single or multiple dynamic compression. Theoretically, approximations have been introduced to simulate warm dense hydrogen (deuterium), such as, linear mixing model \(^10\), chemical model FVT \(^11\), path integral Monte Carlo (PIMC) \(^12\)\(^–\)\(^14\), and quantum molecular dynamics \(^15\)\(^–\)\(^16\).

To date, although a number of explanatory and predictive results in some cases have already been provided by experimental and theoretical studies, however, many fundamental questions of deuterium under extreme conditions are still yet to be clarified. The equation of states (EOS), especially the Hugoniot curve, are essential in this context. Since five to six-fold the initial densities have been detected by laser-driven experiments at megabar pressure regime \(^7\)\(^–\)\(^9\) and supported by PIMC simulations \(^12\)\(^–\)\(^14\), considerable controversies in the deuterium EOS have been raised. Meanwhile, converging explosives \(^5\) and magnetically driven flyer \(^6\) experiments indicate that the compression ratio \((\eta)\) shows a maximum close to 4.3, which is in good agreement with QMD results \(^15\)\(^–\)\(^16\). Furthermore, in adiabatic and isentropic compressions, the nonmetal-metal transition of deuterium (hydrogen), which is accompanied by the change of optical spectroscopies \(^17\), has been a major issue recently. The links between nonmetal-metal transition and dissociation (ionization) under dynamic compression are of particular significance \(^2\).

The chemical pictures of deuterium under extreme conditions could be briefly described as two processes: (i) partial dissociation of molecules, \(D_2 \rightleftharpoons 2D\), and (ii) a subsequent ionization of atoms, \(D \rightleftharpoons e^+ + D^+\). QMD simulations, where electrons are modelled by quantum theory, are convinced to be a powerful tool to describe the chemical reactions, such as dissociation and recombination of molecules. Meanwhile, the dynamical, electrical and optical properties of warm dense matter have already been proved to be successfully investigated by QMD simulations \(^18\)\(^–\)\(^19\). However, the ionization of atoms is not well defined in the framework of density functional theory (DFT). Considering these facts, thus, in this paper we applied the corrected QMD simulations to shock compressed deuterium, and the calculated compression ratio is substantially increased according to the ionization of atoms in the warm dense fluid.

We have performed simulations for deuterium by employing the Vienna Ab-initio Simulation Package (VASP) \(^20\)\(^–\)\(^21\). A fixed volume supercell of \(N\) atoms, which is repeated periodically throughout the space, forms the elements of the calculation. By involving Born-Oppenheimer approximation, electrons are fully quantum mechanically treated through plane-wave, finite-temperature DFT \(^15\), and the electronic states are populated according to the Fermi-Dirac distribution at temperature \(T_e\). The exchange correlation functional is determined by generalized gradient approximation (GGA) with the parametrization of Perdew-Wang 91 \(^22\). The ion-electron interactions are represented by a projector augmented wave (PAW) pseudopotential \(^23\). The system is calculated with the isokinetic ensemble (NVT), where the ionic temperature \(T_i\) is kept constant every time step by velocity scaling, and the system is kept in local thermodynamical equilibrium by...
setting the electron \( T_e \) and ion \( T_i \) temperatures to be equal.

The plane-wave cutoff energy is selected to be 600.0 eV, so that the pressure is converged within 5% accuracy. \( \Gamma \) point is employed to sample the Brillouin zone in molecular dynamic simulations, because EOS (conductivity) can only be modified within 5% (15%) for the selection of higher number of \( k \) points. A total number of 128 atoms (64 deuterium molecules) is included in a cubic cell, and over 300 (densities and temperatures) points are calculated. The densities adopted in our simulations range from 0.167 to 0.9 g/cm\(^3\) and temperatures between 20 and 50000 K, which highlight the regime of principal Hugoniot. All the dynamic simulations are lasted for 4 \( \sim \) 6 ps, and the time steps for the integrations of atomic motion are 0.5 \( \sim \) 2 fs according to different densities (temperatures). Then, the subsequent 1 ps simulations are used to calculate EOS as running averages.

TABLE I: Coefficients \( a_{ik} \) in expansion for the internal energy \( E \).

| \( i \) | \( a_{i0} \) | \( a_{i1} \) | \( a_{i2} \) | \( a_{i3} \) | \( a_{i4} \) |
|------|--------|--------|--------|--------|--------|
| 0    | 4.1065 | -0.1111| 13.4393| -6.7345| 0.2532 |
| 1    | 2.7497 | -0.5432| 2.6361 | -9.6771| -8.2198|
| 2    | 12.8700| 1.6686 | 15.9184| 8.8453 | -3.3917|
| 3    | -37.4966| -18.1714| 30.6954| 2.8396 | 3.1274 |
| 4    | 2.4465 | 3.1352 | 3.6421 | -9.6771| 1.5115 |

In QMD simulations, zero point vibration energy \( (\frac{1}{2}h\nu_{vib}) \) and ionization energy \( (13.6 \text{ eV/atom}) \) are excluded, thus, the internal energy and pressure should be corrected as follows:

\[
E = E_{QMD} + \frac{1}{2} N (1 - \alpha) E_{vib} + N \beta E_{ion},
\]

\[
P = P_{QMD} + (1 + \beta) \frac{\rho k_B T}{m_D},
\]

where \( N \) is the total number of atoms for the present system, and \( m_D \) presents the mass of deuterium atom. The density and temperature are denoted by \( \rho \) and \( T \) respectively, and \( k_B \) stands for Boltzmann constant. \( \alpha \) and \( \beta \) are the dissociation degree and ionization degree, while \( E_{vib} \) and \( E_{ion} \) correspond to the zero point vibration energy and ionization energy, respectively. \( E_{QMD} \) and \( P_{QMD} \) are calculated from VASP. Various corrections to QMD simulations have already been applied to model warm dense matter \cite{15, 16}, but contributions from atomic ionization, which are particularly important at high pressure, are still in absence. Ionization degree of aluminium under extreme conditions has been successfully quantified through Drude model \cite{24}, however, the simple metallic model is not suitable for the present system. Here, a new and effective method in accounting for contributions to the EOS from molecular dissociation and atomic ionization has been demonstrated.

TABLE II: Coefficients \( b_{jk} \) in expansion for the total pressure \( P \).

| \( j \) | \( b_{j0} \) | \( b_{j1} \) | \( b_{j2} \) | \( b_{j3} \) | \( b_{j4} \) |
|------|--------|--------|--------|--------|--------|
| 0    | 41.9168| -1.2676| -8.5830| -55.5348| 5.4594 |
| 1    | 101.2582| 6.0739 | 15.4631| -29.1378| -8.2198|
| 2    | 60.8838 | -0.6898| 4.6233 | -124.8318| 24.2147|
| 3    | 277.4649| -10.0840| 46.9646| -233.0212| -5.4740|
| 4    | 8.0324  | -3.8221| 1.0263 | 30.4031 | 0.3011 |

The dissociation degree is important in determining the internal energy, from which EOS can be derived, especially at low temperatures and the initial state on the Hugoniot curve. The dissociation degree could be evaluated through the coordination number:

\[
K(r) = \frac{N - 1}{\Omega} \int_0^r 4\pi r'^2 g(r') dr',
\]

where \( \Omega \) is the volume of the supercell. The coordination number is a weighted integral over the pair correlation function (PCF) \( g(r) \) of the ions. The doubled value of \( K \) at the maximum of \( g(r) \) \( (r = 0.75 \text{ Å}) \), is equal to the fraction of atoms forming molecules in the supercell. The sampled PCF and \( K(r) \) are labelled in Fig. 1. Fast dissociation of molecules emerges at the temperature between 4000 and 7000 K, and a region featured with \( \frac{\partial P}{\partial T} < 0 \), which is not presented here, is observed. Our results show that molecular deuterium can be neglected above 15000 K due to thermal dissociation.

The ionization degree of the system can be evaluated through Saha equation:

\[
\frac{\beta^2}{1 - \beta} = \frac{2 \Omega}{\lambda^3} \exp(-\frac{E_{ion}}{k_B T}),
\]

\[
\lambda = \sqrt{\frac{\hbar^2}{2 \pi m_e k_B T}},
\]

FIG. 1: (Color online) Calculated pair correlation function (black line) and coordination number (red line) at temperatures of 3000 K (solid line), 5000 K (dashed line), and 10000 K (dotted line). Inset is the contour plot of the ionization degree as a function of density and temperature.

TABLE I: Coefficients \( a_{ik} \) in expansion for the internal energy \( E \).
where only one level of ionization process is considered. In the present formula, $m_e$ stands for the electron mass. As shown in the inset in Fig. 1, the ionization of deuterium could be neglected below 10000 K. At the temperature between 10000 and 50000 K, where the modeling of the principal Hugoniot of deuterium is rather difficult, partially ionized warm dense fluid is formed, and the ionization of atoms is of predominance in determining the EOS.

Following Lenosky et al. [25], Beule et al. [26], and Holst et al. [16], we fit the internal energy and pressure by expansions in terms of density (g/cm$^3$) and temperature (10$^5$ K). The corrected QMD data for internal energy (eV/atom) can be expanded as follows:

$$E = \sum_{i=0}^{4} A_i(T) \rho^i,$$

$$A_i(T) = a_{i0} \exp[-(\frac{T - a_{i1}}{a_{i2}})^2] + a_{i3} + a_{i4} T.$$

The total pressure given in GPa can be similarly expanded as $E$ with the expansion coefficients $b_{jk}$. The expansion coefficients $a_{ik}$ and $b_{jk}$ for $E$ and $P$ (accuracy better than 5%) are summarized in Tab. II and Tab. III, respectively.

Based on the EOS, the principal Hugoniot curve can be derived from the following equation:

$$(E_0 - E_i) = \frac{1}{2} (\frac{1}{\rho_0} - \frac{1}{\rho_1})(P_0 + P_i),$$

where the subscripts 0 and 1 refer to the initial and shocked states. In our present simulations, the initial density $\rho_0$ is 0.167 g/cm$^3$ with the respective internal energy $E_0 = -3.28$ eV/atom at $T_0 = 20$ K. The pressure $P_0$ of the starting point on the Hugoniot can be neglected compared to high pressures of shocked states.

The principal Hugoniot is shown in Fig. 2 where previous theoretical and experimental results are also provided for comparison. At pressures below 100 GPa, our results indicate that the principal Hugoniot experiences a local maximum compression ratio of 4.5 around 40 GPa, which can be attributed to the dissociation of molecules. The present Hugoniot agrees well with previous experiments, such as gas gun [4], magnetically launched flyer plates [6], and converging explosives [5]. At the pressure between 40 and 100 GPa, the Hugoniot curve shows a stiff behavior, and the compression ratio lies between 4.25 and 4.5. Meanwhile, the ionization of atoms increases remarkably at $P > 50$ GPa (see the inset in Fig. 3) and consequently interates the fluid. Thus, the combined effect of the molecular dissociation and atomic ionization results in a local minimum of $\eta$ (4.25) along the Hugoniot.

Recent high power laser-driven experiments [8, 9] suggest that deuterium is stiff ($\eta_{max} \approx 4.2$) below 100 GPa and become softer ($\eta \approx 4.5 \sim 5.5$) above 110 GPa, which can be described by the present simulations. Our results indicate that molecular deuterium can be neglected at this stage, and the atomic ionization dominates the characteristic of the Hugoniot with $\eta$ lies between 4.5 and 4.95 (maximum is reached at 200 GPa), which is accordant with recent experiment [27]. The wide-range behavior of the Hugoniot is characterized by two stage transitions—dissociation under low pressure and ionization at higher pressure, and the present results show excellent agreement with experimental ones. The Hugoniots from mere QMD simulations hardly exceed 100 GPa [15] except for that of Holst et al. [16], but $\eta$ does not exceed 4.5 (at $P > 100$ GPa). Although some PIMC simulations [12, 14] show five to six-fold compressions, the simulated data are not yet comparable with experiments. Due to the intrinsic approximations, no consistency has been detected between our results and those of linear mixing model [10] and chemical model FVT [11].

Let us turn now to see the nonmetal-metal transition by studying the optical and conductive behaviors of the warm dense deuterium. The real part of dynamic conductivity $\sigma_1(\omega)$ can be evaluated through the following Kubo-Greenwood formula:

$$\sigma_1(\omega) = \frac{2\pi}{3}\sum_k w(k)\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\alpha=1}^{3} [f(\epsilon_i, k) - f(\epsilon_j, k)] \times |\langle \Psi_{j,k} | \nabla_{\alpha} | \Psi_{i,k} \rangle|^2 \delta(\epsilon_{j,k} - \epsilon_{i,k} - \hbar\omega),$$

where $i$ and $j$ summations range over $N$ discrete bands included in the calculation. The $\alpha$ sum is over the three spatial directions. $f(\epsilon_i, k)$ describes the occupation of the
FIG. 3: (Color online) Calculated dc conductivity along the Hugoniot curve (solid squares). Previous data [16] are also shown for comparison. Inset is the ionization degree along the Hugoniot.

FIG. 4: (Color online) Calculated optical reflectivity of wavelength 808 nm along the Hugoniot. Previous data [16, 17, 28] are also plotted for comparison.

ith band, with the corresponding energy $\epsilon_{i,k}$ and the wavefunction $\Psi_{i,k}$ at $k$, $w(k)$ is the $k$-point weighting factor.

From the calculated dynamic conductivity along the Hugoniot curve, the dc conductivity $\sigma_{dc}$, which follows the static limit $\omega \to 0$ of $\sigma_1(\omega)$, is then extracted and plotted in Fig. 3 as a function of the Hugoniot pressure. As shown in Fig. 3, $\sigma_{dc}$ increases rapidly with pressure up to 40 GPa towards the formation of metallic state of deuterium, which agrees well with the experimental measurements [4]. Similar tendency has also been found in the QMD simulations of warm dense hydrogen [16]. When further increasing the Hugoniot pressure, one finds from Fig. 3 that $\sigma_{dc}$ keeps almost invariant and the warm dense deuterium maintains its metallic behavior. Here we address that the nonmetal-metal transition is induced by gradual dissociation of molecules and thermal activation of electronic states, instead of atomic ionization, which is not observed until 50 GPa according to the charge density distribution in the QMD simulations. Quantitative analysis can be clarified through plotting the ionization along the Hugoniot as shown in the inset in Fig. 3. Meanwhile, optical reflectivity, with the respective wavelength of 808 nm, is shown along the principal Hugoniot in Fig. 4 where good agreement has been achieved between our present work and previous experiments [17]. The increase of reflectance (from 0.05 to 0.6) is observed, and this can be interpreted as a gradual transition from a molecular insulating fluid to a partially dissociated and metallic fluid at above 40 GPa.

In summary, we have performed QMD simulations to study the thermophysical properties of deuterium under extreme conditions. The Hugoniot EOS has been evaluated through QMD calculations and corrected by taking into account the molecular dissociation described by the coordination number $K(r)$ and the atomic ionization described by Saha equation. The corrected Hugoniot has shown good agreement with the experimental data in a wide range of shock conditions, which thus indicates the importance of physical picture of a two-stage transition, i.e., dissociation and ionization. The principal Hugoniot reveals a local maximum compression ratio of 4.5 at 40 GPa. With the increase of pressure, $\eta$ reaches a maximum of 4.95 at about 200 GPa, and the contribution from atomic ionization demonstrates softened character of the Hugoniot. Smooth transition from a molecular insulating fluid to an partially dissociated and metallic fluid are observed at 40 GPa. Our calculated optical constants along the Hugoniot have shown excellent agreement with experiments. In addition, smooth fit functions constructed in the present paper for the internal energy and total pressure are expected to be useful for the future studies of warm dense deuterium.

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