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Density-functional calculation of the Hugoniot of shocked liquid deuterium

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We have performed molecular dynamics simulations to obtain the internal energy and pressure of shock-compressed fluid deuterium at 24 separate (density temperature) points. Our calculations were performed using the generalized gradient approximation (GGA) in density-functional theory. We obtained a good fit to this simulation data with a thermodynamically consistent virial expansion. The single-shock Hugoniot derived from this equation of state is compared to previous theoretical and experimental results. We discuss several types of error inherent in the GGA, as they relate to the quality of our results.

Various experiments have probed the effect of a strong shock on liquid hydrogen or deuterium.[1–4] In recent experiments, single-shock pressures of up to 23 GPa have been reached for deuterium using a two stage gas gun,[3] corresponding to a density of around 0.58 g/cm^3, over three times greater than the liquid, and a temperature of around 4500 K. Previous gas-gun experiments had attained similar single-shock pressures.[1,2] Multiple shocks with much higher pressures and densities were also produced in all of the gas-gun experiments. These pressures have reached a range between 80 and 180 GPa at temperatures of between 2000 and 5000 K. The derived densities of nearly 1 g/cm^3 or $r_s \sim 1.4$ ($r_s = a_i / a_B$ with a_i the ion-sphere radius) correspond to almost a factor of 10 compression of the initial liquid. Other recent experiments[4] used a high-energy pulse from the Nova laser to create an initial shock wave, which then propagated into a liquid deuterium sample chamber. These experiments attained single-shock pressures of up to 350 GPa, with inferred densities of over 1.0 g/cm^3. They have cast doubt on the standard deuterium equation of state (EOS) since, for a given pressure, the Nova densities range up to 50% higher than conventional EOS predictions, such as SESAME.[5] These findings have profound ramifications for systems as diverse as the interiors of the giant gas planets[1] and inertial confinement fusion.[6]

A variety of direct simulation methods have been developed in recent years to treat hydrogen and other systems in this regime. The most sophisticated include the path-integral Monte Carlo[7] (PIMC) and density-functional theory (DFT) molecular dynamics (MD).[8,9] The DFT-MD approaches mainly employed the local-density approximation (LDA). For appropriate regimes, more approximate methods such as Thomas-Fermi,[10] wave packet,[11] and tight-binding (TB) molecular dynamics[9,12,13] have also been utilized.

By choosing the matrix elements to reproduce known properties, we originally fit a TB model[12,13] that accurately represented molecular vibrations, rotation, and dissociation, including interactions among separate molecules and dissociated atoms. The model also included ionization in an approximate way, correct to the extent that single atomic orbitals can be superposed to represent lower-lying excited states. We applied our original TB model to the understanding of electrical conductivity in shocked hydrogen,[12] as well as the EOS and Hugoniot of shocked liquid deuterium.[13] In recent work, we fit a second TB model and compared it to a physically based dissociation model.[14,15] Both our TB models are approximate, and generally not as accurate as DFT approaches. Furthermore, it is difficult to quantify the amount of error intrinsic in a tight-binding parametrization.

DFT provides a means of performing molecular-dynamics simulations in which the results do not depend on an arbi-

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trary choice of fitting parameters. Until recently, the great computational cost of DFT prevented it from being used to generate a complete deuterium single-shock Hugoniot. In this study, we present for the first time a deuterium single-shock Hugoniot produced using DFT. We have chosen to use the Perdew-Wang 91 parametrization of generalized gradient approximation (GGA),[16] which we have found to be highly accurate for the case of hydrogen. In DFT methods, the total energy is written as a functional of the electron density, which is obtained by summing the probability density over the occupied orbitals. In GGA formulations, electronic exchange and correlation energy are approximated using a functional which depends only on the density and its spatial derivatives. GGA methods provide a highly accurate means of studying the thermochemistry of chemical bonding by representing the inhomogeneities inherent in the electron charge density.

We performed our study using the VASP plane-wave pseudopotential code, which was developed at the Technical University of Vienna.[17] This code implements the Vanderbilt ultrasoft pseudopotential scheme[18] which is highly efficient. We used Vanderbilt-type pseudopotentials[18] as supplied by Kresse and Hafner.[19]

We performed fixed-volume molecular-dynamics simulations at 24 separate (density, temperature) conditions, chosen to span a range of densities from $r_s = 1.85$ to $r_s = 2.2$ and temperatures from $T = 2000$ K to $T = 31\,500$ K, with emphasis on the single-shock Hugoniot region. At each time step the energy and forces were calculated exactly. We used 128 hydrogen atoms in the unit cell and fixed the plane-wave cutoff at 400 eV. Additional MD simulations using a 500 eV cutoff produced nearly identical EOS values. Integration of the equations of motion proceeded with time steps of 0.25 or 0.50 fs with the smaller time step employed at higher temperatures. Simulations were performed for 1000 time steps; we let the system equilibrate for 700 time steps and then calculated properties using the final 300 time steps. This procedure proved sufficient to obtain accurate thermodynamic quantities, including pressure and internal energy.

The ionic temperature was fixed using a thermostat, and electronic eigenstates occupied using a Fermi-Dirac distribution. We retained enough excited states to treat the effect of ionization; 96 excited states were used at the lower temperatures, and 166 at the higher temperatures. We performed tests and found this to give very good convergence. Since our EOS exhibits thermodynamical consistency, we can conclude that sources of error in our MD simulations have been controlled. This observation does not rule out systematic error due to the GGA, which is approximate.

Given the results of the molecular dynamics simulations, we fit smooth functions for the fluid pressure P, and internal energy per atom, U:

$$P = \sum_{ij} c_{ij} n^i T^j, \tag{1}$$

$$U = \sum_{ij} d_{ij} n^i T^j, \tag{2}$$

where $n = N/V$ is the number of atoms per unit volume (a_B^{-3}) and T is the temperature (K), with P and U given in GPa and Ry/atom, respectively. We have chosen U so that the energy of the H_2 molecule is zero. With this choice U represents the change in internal energy relative to uncompressed liquid deuterium (ignoring its very small cohesive energy relative to isolated molecules). The 17 EOS coefficients c_{ij} and d_{ij} are given in Table I and Table II. The EOS fitting procedure was identical to that performed in our previous study.[13] For the present fit, the error for P was 2.2%, and for U, 2.0%. Given these errors, our equation of state should be reliable over the range of the fitting data.

As in our previous study, our EOS is smooth and essentially featureless, showing no evidence for a phase transition within its region of applicability. In particular $\partial P/\partial T$ is positive everywhere; we do not see the negative $\partial P/\partial T$ values cited as evidence for a phase transition within PIMC.[7] Our work also provides no evidence for the plasma phase transition that appears in the model of Saumon and Chabrier.[20]

We solved for the Hugoniot numerically using our equation of state, as was done in our previous work.[13] Our calculated Hugoniot (Fig. 1) resembles that derived from the SESAME model[5] and from our earlier work.[13] The main difference stems from the prediction of slightly more compression. The initial state was taken to be liquid deuterium at zero pressure with a volume $V_1 = 23.5\ \text{cm}^3/\text{mol}$, which corresponds to a density of $\rho_D = 0.171\ \text{g/cm}^3$. Our equation of state is fit for the energy $U_2 - U_1$, as the energy of the initial liquid has already been subtracted. In our previous TB study, we also adjusted the internal energy by an amount $\delta U = -0.02$ Ry/atom to improve agreement with gas-gun shock

TABLE I. EOS coefficients c_{ij}, expressing fluid pressure P as a function of density and temperature.

i	j	c_{ij}
2	0	1.733686×10^{4}
3	0	-2.005438×10^{6}
4	0	4.077582×10^{7}
1	1	1.257846×10^{-1}
2	-1	5.399585×10^{7}
3	-1	6.439983×10^{8}
2	-2	-6.684189×10^{10}

TABLE II. EOS coefficients d_{ij}, expressing internal energy U as a function of density and temperature. This energy is relative to unshocked liquid deuterium, as discussed in the text. The units of U are Ry per atom.

i	j	d_{ij}
0	0	6.235472×10^{-2}
1	0	1.178515×10^{0}
2	0	-6.816226×10^{1}
3	0	9.239453×10^{2}
0	-1	-4.534049×10^{2}
1	-1	7.340999×10^{3}
2	-1	4.377735×10^{4}
0	-2	6.265362×10^{5}
1	-2	-1.363122×10^{7}
0	1	1.239348×10^{-5}

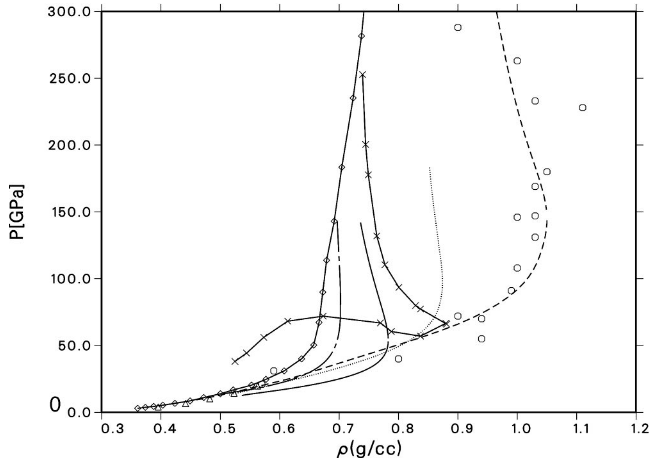

FIG. 1. Deuterium Hugoniots. Theoretical models: GGA-MD (solid line); SESAME (diamonds, Ref. 5); TB (chain, Refs. 12,15); Ross (dash; Ref. 25); DM (dot, Ref. 14); and PIMC (crosses, Ref. 7). Experiments: gas-gun (triangles, Ref. 2); and laser (circles, Refs. 4).

data.[2] In this study, keeping with the spirit of parameter-free *ab initio* methodology, we have made no such adjustment.

Table III displays the effect of the fitting parameter δU on the maximum compression ratio attained on the Hugoniot. If the TB equation of state is not adjusted to fit the gas-gun data ($\delta U=0$) the maximum compression ratio increases from 4.05 to 4.27. Conversely, if the GGA equation of state is adjusted to fit the gas-gun data ($\delta U=-0.03$ Ry/atom), its compression ratio drops from 4.61 to 4.23. Currently we feel the most meaningful comparison is for $\delta U=0$. In this case, the tight-binding model gives a compression ratio of 4.27, and the GGA result is 4.61. We regard this agreement as excellent given the difference between the methods.

The Nova[4] measurements reach much higher compressions than for our Hugoniot. As in our previous studies,[13] we are unable to explain the discrepancy with the Nova data. Some mechanism to absorb energy appears necessary to produce the higher Hugoniot densities. The cause of the disagreement, if real, remains uncertain: molecular dissociation of the fluid, excitation of rotational and vibrational molecular modes, and ionization all exhibit energy absorbtion mechanisms accurately treated in our GGA-MD calculations.

In order to examine further the validity of the GGA in representing the physical mechanisms that govern hydrogen in this regime, we have performed a set of ancillary calculations. We expect that the energetics of the GGA model is highly accurate, except possibly for ionization. The use of large plane-wave basis sets ($\sim 10^4$) and the extraction of the many roots needed for the Fermi-Dirac population at finite temperatures implies an effective representation of excited and continuum states of the extended system. GGA functionals share with LDA a tendency to underestimate the gap between occupied and unoccupied electronic eigenstates. On this basis, we would expect, if anything, that GGA overestimates the effect of ionization on the Hugoniot, resulting in too much absorption of energy. At the point of maximum compression on our Hugoniot, the fluid temperature is only about 11 400 K. We have tested the effect of ionization under these conditions by setting the Fermi-Dirac electronic temperature close to zero; we find that ionization has a very small effect on the pressure and internal energy at this relatively low temperature. Another indication of the effectiveness of this representation comes from the good agreement obtained with experiments[12,21] for the electrical conductivity, which depends critically on the quality of the excited states.

TABLE III. Sensitivity of the maximum compression ratio on the Hugoniot to adjustment of the internal energy by an amount δU, for TB and GGA equations of state.

δU	ρ_{max}/ρ_0 (TB)	ρ_{max}/ρ_0 (GGA)
0.00 Ry/atom	4.27	4.61
-0.01	4.16	4.48
-0.02	4.05	4.36
-0.03	3.97	4.23

We have tested the GGA, using the same pseudopotential and energy cutoffs used for molecular dynamics, on the H_2 molecule. We find that the shape of the H_2 binding curve is highly accurate near its equilibrium bond length and begins to depart from configuration-interaction (CI) calculations only for separations greater than about $4.0a_B$ in the weak-binding regime. We believe that under the conditions of the present study that this error is minimal. At these densities, when molecules dissociate into atoms, they only very rarely become separated from all their neighbors in the fluid by more than 4.0 Bohr.

In additional support of this observation, we again tested the GGA using the same pseudopotential and energy cutoffs used for molecular dynamics, on the H_4 potential energy surface. We considered about half of the 83 H_4 geometries studied by Schwenke[22] using a highly accurate CI method. We find that the GGA predicts the potential energy accurately (typically within a few percent or 0.1 eV) except when one of the atoms is separated from the other three by more than 4.0 Bohr. Interestingly, our TB models,[13] which have a much less accurate representation than GGA of H_4 but reproduce the H_2 binding curve nearly exactly, give roughly similar equations of state to GGA.

Finally to examine bulk properties, we have employed the GGA with very high energy cutoffs to calculate the pressure of the relaxed hcp molecular phase as a function of volume. Again, the agreement with experiment[23–25] remains good except at the lowest densities ($r_s>2.0$). These findings reinforce the basic validity of the GGA for this region while offering explanations for the disagreements with the single-shock gas-gun results. The latter occur at low temperatures and densities in which the system remains predominantly in a molecular state. Both zero-point nuclear motion, which is not treated in our model, and the long-range tail of the molecular interactions play vital roles in this regime and probably account for the differences. However, as demonstrated above, these two effects do not affect in any significant manner the higher density and temperature ranges probed by the laser experiments.

In summary, we have obtained an equation of state for deuterium using first-principles molecular dynamics with GGA density-functional theory. We found the Hugoniot for shocked liquid deuterium based on this equation of state. The maximum compression of the fluid is by a density factor of

4.61. This agrees reasonably well with some previous theoretical values, but is in sharp disagreement with some recent experiments.[4] Our Hugoniot also disagrees somewhat with some gas-gun shock data due to neglect of nuclear zero-point motion and inaccuracies in the weak long-range interactions. We chose not to fit our equation of state in order to improve agreement with the gas-gun data. We have identified several sources of error in our calculations. Although it would be difficult to estimate the total error in our equation of state, we believe it is physically based, and fairly reliable.

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