Shock compression of liquid deuterium up to 109 GPa

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Hugoniot points of liquid D_2 were measured at shock pressures of 107, 54, and 28 GPa using converging explosively driven systems (CSs). The two data sets measured with a laser (L) and pulsed currents (PCs) differ substantially. Our results are in excellent agreement with the PC data and the error bars of the CS-PC data are less than half those of the L data. The limiting compression obtained from the best fit to the CS-PC data is 4.30 ± 0.10 at 100 GPa. The CS-PC data are in good agreement with path integral Monte Carlo and density functional theory calculations, which is expected to be the case at even higher shock temperatures and pressures, as well.

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The single-shock compression curve (Hugoniot) of deuterium up to 100 GPa (1 Mbar) pressures has been controversial because limiting shock compression close to sixfold of initial liquid density has been reported using a high-intensity laser (L) (Ref. 1) and limiting compression close to fourfold has been reported using large pulsed currents (PCs).[2–4] That is, as pressure achieved with a single shock increases, so too does temperature, which limits compression at sufficiently high pressures. Examination of the systematics of single-shock compression of diatomic liquids suggests that the PC data are correct.[5] Deuterium in all the shock experiments is in thermal equilibrium because there are more than 10^4 collisions between atoms and/or molecules within the respective time resolutions. Deuterons in these experiments are classical.[6] Thus, there is no *a priori* reason why fluid deuterium would be expected to behave differently than other low-Z diatomics, as reported in Ref. 1. In order to determine the correct Hugoniot of D_2, we began experiments on solid[7,8] and liquid samples in 1999. In this paper we report Hugoniot points at 109, 54, and 28 GPa for liquid D_2 samples.

Strong shock waves were generated with hemispherical convergence driven by explosives (CS), the same method we used previously to measure points at 121 and 61 GPa for solid samples.[7,8] Our points at 109 and 121 GPa achieve limiting compression. Our points at 109 and 121 GPa and at 54 and 61 GPa used liquid and solid D_2 samples, respectively, to demonstrate self-consistency and reproducibility. Our point at 28 GPa demonstrates agreement with data measured at lower pressures with a two-stage gas gun (GG).[9]

To minimize uncertainties, our CS method[10,11] requires that a given experiment be repeated several times and the results averaged. We have performed thirteen cryogenic, explosively driven experiments to obtain the three data points for liquid samples reported here. Our method produces data at 100 GPa pressures in the simple materials Al and Cu which are in excellent agreement with data obtained with a two-stage gun and planar explosives.[12,13] Thus, while our method produces relatively few data points, our results are in excellent agreement with data obtained by other techniques of demonstrated accuracy at shock pressures which can be obtained with all three methods.

High shock pressures were generated by impact of a converging hemispherical steel shell accelerated to velocities as large as 14 km/s (Ref. 14) onto an Al sample holder containing liquid D_2 near 20 K. The data were analyzed with the shock-impedance match method.[11] Shock velocities were determined from shock transit times over measured distances. Measured shock transit times in both the Al sample holder and liquid D_2 were corrected for spherical convergence. Shock transit times in liquid D_2 were corrected for transit times through thin Al covers on detectors. We used an Al Hugoniot in excellent agreement with recent measurements to 500 GPa.[15] Our calculated Al release isentropes used to match shock impedances agree with measured Al release isentropes at conditions in liquid D_2.[2,16] Initial Al density was corrected for its 20 K initial temperature. The points reported here (CS) and achieved in the previous L, PC, and GG experiments were performed in u_s-u_p space, where u_s is shock velocity and u_p is mass velocity. The Hugoniot equations[17] were used to calculate P and ρ from u_s and u_p, where P is shock pressure and ρ is shock-compressed density. The shock states achieved in deuterium are listed in Table I.

The error analysis is described in Ref. 18. Mass velocity u_p of deuterium is determined in P-u_p space by matching shock impedance of an Al shock release isentrope with the shock impedance of deuterium on its Hugoniot $(\rho_0 u_s) = P/u_p$, where ρ_0 is initial density of liquid D_2 at 20 K. We used Al release isentropes which are in good agreement with measured Al states releasing into aerogel with essentially the same density and shock impedance as liquid D_2.[2,16] In the case of these deuterium experiments, uncertainties in measured u_s are the dominant source of error in determining u_p. Systematic errors in u_p are negligible because our Al release isentropes agree with experiment. This is in contrast to previous experiments[9] in which systematic uncertainties in u_p were taken into account because at that time Al release isen-

TABLE I. Shock-compressed states of deuterium, where ρ_0 is initial density, u_p is particle velocity, u_s is shock velocity, P is pressure, and ρ is density. The lower initial densities are for liquid samples; the higher initial densities are for solid samples (Refs. 7 and 8). To obtain these five data points, twenty three cryogenic explosively driven experiments were performed and the results averaged.

ρ_0 (g/cm^3)	u_p (km/s)	u_s (km/s)	P (GPa)[a]	ρ (g/cm^3)	Ref.
0.171	10.95±0.20	15.23±0.3	28.5±0.8	0.608±0.05	
0.171	15.38±0.4	20.38±0.3	53.6±0.6	0.697±0.06	
0.199	15.06±0.15	20.51±0.2	61.4±0.8	0.749±0.04	7
0.171	22.05±0.3	28.87±0.4	108.8±3	0.724±0.07	
0.199	21.59±0.4	28.64±0.4	123.0±2	0.808±0.08	8

[a]100 GPa=1 Mbar.

tropes could only be calculated.[18] The error analysis described above gives error bars of the u_s-u_p points, which were then used to calculate the corresponding error bars for the pressures and densities in Table I.

Since our goal is to minimize uncertainties, we now make use of the fact that there are 19 CS and PC u_s-u_p points in excellent agreement at pressures near 100 GPa and these points have a linear u_s-u_p relation. In this situation, the uncertainty in calculating a value of u_s from the linear fit is substantially lower than the uncertainty in any one experimental point. Thus, we now determine least-squares fits to the u_s-u_p data and use these fits and the uncertainties in them, caused by uncertainties in the experimental data, to calculate P, compression ρ/ρ_0, and the uncertainty in ρ/ρ_0.

It is straightforward to least-squares fit the data because u_s-u_p relations of low-Z diatomic molecules are linear or nearly so with small ($\sim$3%) deviations caused by molecular dissociation.[5] Since two points were measured with solid samples,[7,8] shock velocities of these two points were corrected downward by 1.5% to account for their higher initial density relative to that of the liquid samples. Weighting factors equal to the reciprocal of the uncertainty in each measured u_s were used in the fitting procedures. The CS, PC, L, and GG u_s-u_p data are plotted in Fig. 1 along with the fits.

The CS, PC, and GG data were analyzed in regions 1–3, the dark curves in Fig. 1. In the first region, $3<u_p<9$ km/s, the fit to the GG data is linear ($u_{s1}=C_1+S_1u_p$) with slope $S_1=1.21\pm0.04$.[9] In the third region, $15<u_p<22$ km/s, the fit to the combined CS-PC data is linear ($u_{s3}=C_3+S_3u_p$) with $C_3=1.704\pm1.5$ km/s and $S_3=1.22\pm0.08$. The standard deviations in C and S are $\sigma_C=[\Sigma_j(\delta C_j)^2]^{1/2}$ and $\sigma_S=[\Sigma_j(\delta S_j)^2]^{1/2}$, where $\delta C_j=C_j-C$, $\delta S_j=S_j-S$, C and S are obtained from the best fit and C_j and S_j are the values of C and S obtained by varying the jth value of u_{s3} by its experimental uncertainty. Standard deviations in C and S are relatively large because all terms in these sums are positive.

For our purpose, however, uncertainties in C an S are not important. Rather, it is the uncertainty in the Hugoniot of deuterium calculated from the fit that is important. The uncertainty in u_s calculated from the fit at a given u_p varies with u_p because data points at the extremes of u_p have the largest effect on the fit and these points also have larger error bars.

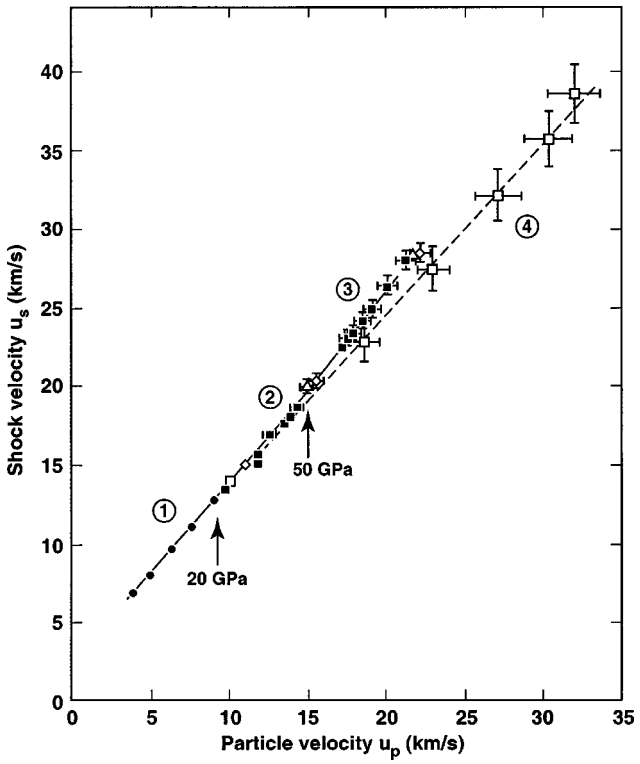

FIG. 1. Shock velocity u_s versus mass velocity u_p for deuterium: open diamonds (this work), open triangles (Refs. 7 and 8), solid squares (Refs. 2–4), solid circles (Ref. 9), open squares (Ref. 1). Solid curve is least-squares fits in regions 1–3; dashed curve in region 4 is linear fit to Ref. 1.

The standard deviation in u_{s3} as a function u_p is given by $\sigma[u_s(u_p)]=[\Sigma_j(\delta C_j+u_p\delta S_j)^2]^{1/2}$.[19] This technique was also used to analyze Hugoniot data of Al, Cu, and Ta.[12] Uncertainties in shock velocity calculated with the fit at a given u_p are relatively small because δC_j and δS_j have opposite signs. For 19 CS and PC points in the range $15<u_p<22$ km/s, $\sigma[u_s(u_p)]=(3.216-0.3301u_p+0.008487u_p^2)^{1/2}$. $\sigma[u_s(u_p)]/u_s$ has a minimum of 0.4% at $u_p=19.5$ km/s and 85 GPa, which is precisely the regime in which high accuracies are needed. Experimental uncertainties in our shock velocity measurements at $\sim$100 GPa are 1.4%.

In the second region, $9<u_p<15$ km/s, the combined CS-PC data have a small curvature. The shock pressures corresponding to these velocities are 20 and 50 GPa, respectively. This is the same shock pressure range in which optical reflectivity experiments indicate that deuterium undergoes a transition from a diatomic insulator below 20 GPa to a monatomic, strong-scattering metal above 50 GPa.[20] This reflectivity data justifies treating the small curvature in this region as physical in nature. Thus, in the region $9<u_p<17$ km/s a cubic polynomial was used to fit 15 CS and PC points: $u_{s2}=A_1+A_2u_p+A_3u_p^2+A_4u_p^3$, where A_1, A_2, A_3, and A_4 are constants, the simplest form to represent the universal behavior of low-Z diatomics.[5] This expression represents an initial softening in u_{s2} caused by dissociation, followed at higher u_p by a stiffening in u_{s2} caused by completion of the temperature-driven nonmetal-metal transition from Maxwell-Boltzmann statistics for the diatomic insulator to Fermi-Dirac sta-

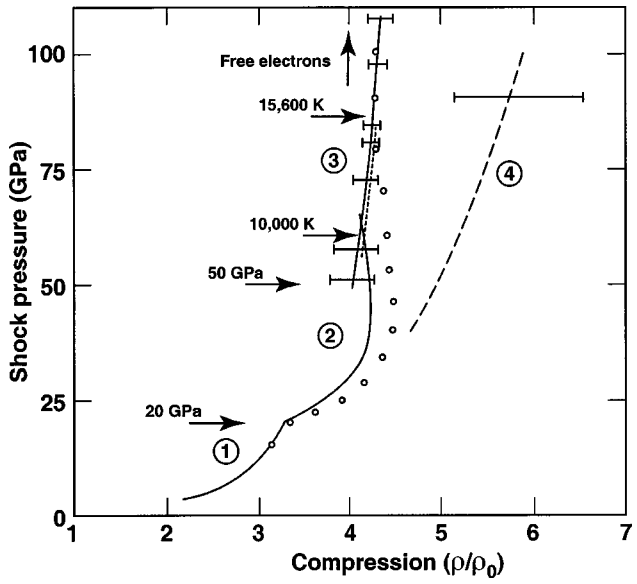

FIG. 2. Pressure (P) versus compression (ρ/ρ_0) calculated with Hugoniot equations and u_s-u_p fits in Fig. 1. Solid and dashed curves correspond to solid and dashed curves in Fig. 1. Error bars are standard deviations of fits calculated from uncertainties in measured shock velocities. Dotted curve and temperatures were calculated with PIMC (Ref. 22). Open circles calculated with DFT (Ref. 23).

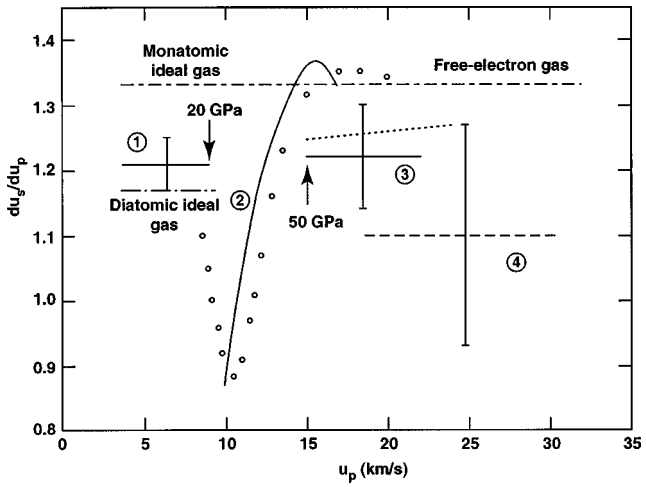

FIG. 3. du_s/du_p versus u_p. Solid curve: 1 is from Ref. 9; 2 is derivative of solid curve in Fig. 1 for $9<u_p<17$ km/s; 3 is linear slope of solid line above $u_p=15$ km/s in Fig. 1. Dissociation occurs between $u_p=\sim 9$ and ~ 15 km/s, which corresponds to 20 and 50 GPa (Ref. 20). Dashed line is slope of dashed line in region 4 of Fig. 1. Error bars are standard deviations of slopes S of linear fits caused by uncertainties in shock velocity measurements. Dot-dash lines are slopes corresponding to limiting compressions of monatomic and diatomic ideal gases and free-electron gas, as indicated.

tistics for the monatomic metal.[21] This cubic fit is the solid curve in the range $9<u_p<15$ km/s, region 2 in Fig. 1.

The laser data (L) are linear ($u_{sL}=C_L+S_L u_p$) in the range $18<u_p<32$ km/s,[1] the dashed line in region 4 of Fig. 1. Our experimental results (CS) are in excellent agreement with the PC data and the error bars of the CS and PC data sets are less than half those of the L data. Figure 1 shows that the CS-PC and the L data agree at the extremes of the error bars of each individual data point in u_s-u_p space. Thus, on the basis of the error bars of the individual data points all the data sets agree. However, the significantly smaller error bars of the fits caused by all the error bars of all the individual points show that the CS-PC data should be used for comparison of experiment with theory.

The u_s-u_p fits to the CS-PC, L, and GG data were transformed to P versus compression (ρ/ρ_0). The results are shown in Fig. 2 as the solid (segments 1–3) and dashed (4) curves, respectively. Thus, relatively small differences in u_s-u_p space (solid and dashed curves in Fig. 1) cause substantial differences in P-compression. The error bars of compression for the solid and dashed curves in the range 50 to 110 GP are their standard deviations calculated from the uncertainties in the u_s-u_p fits, which are caused by uncertainties in all the measured shock velocities. No effort was made to obtain a smooth join in $P-(\rho/\rho_0)$ space between regions 2 and 3, which occurs within the error bars of the two fits.

The fits to the experimental data are now compared to theories in the two extreme limits, the cases in which all interactions are taken into account (PIMC and DFT computations) and the case in which all interactions are neglected (free electrons). The Hugoniot calculated with the path integral Monte Carlo (PIMC) method,[22] which uses no adjustable parameters, is the dotted curve in Fig. 2. The PIMC results are essentially coincident with the fit to the CS-PC data. PIMC assumes that interactions between charged particles are Coulombic ($1/r$), that all particles are in thermodynamic equilibrium, and that nodal surfaces may be used to solve the fermion sign problem. This method is valid above 5000 K, where shock-compressed deuterium is assumed to be monatomic.

Density functional theory (DFT) has a spatial criterion for the existence of molecules, namely, two atoms form a molecule when they are mutually nearest neighbors or nearest neighbors for a minimum of two or more vibron periods. In calculations between shock pressures of 20 and 100 GPa, ~ 80 and ~ 100 % of D_2 molecules dissociate into atoms at 50 and 100 GPa, respectively,[23] which is consistent with experiment.[20] These calculations, the open circles in Fig. 2, are in excellent agreement with Refs. 2–4.

Both PIMC and DFT are in excellent agreement with experiment and say that deuterium is monatomic or nearly so above 50 GPa on the Hugoniot. Other calculations[24–27] approach limiting compressions of essentially 4.3-fold, as well.[28] Thus, limiting compressions of the fit to the CS-PC data and of several calculations are essentially the same and are relatively close to the limiting shock compression of 4.0 of an initially degenerate free-electron gas.[21]

Slopes of u_s-u_p fits to experimental data are now compared to PIMC and DFT calculations and to results for free electrons and ideal gases of D and D_2. Comparison of these slopes, is more stringent than comparisons of the data itself. Also, this comparison gives an estimate of the effect of temperature.

Slopes du_s/du_p derived from the fits to the GG-CS-PC data in Fig. 1 and their error bars are plotted in Fig. 3. These slopes are constants in the first and third regions. In the sec-

ond region, du_s/du_p is the derivative of the cubic fit to the data in this range. Between 9 and 17 km/s the slope of the fit to the CS-PC data has an initial sharp minimum, ~25% less than that of the molecular phase, followed by a broader maximum. The open circles are obtained from DFT calculations. The slope of the PIMC results (dots) was calculated by transforming published P-ρ results to u_s-u_p. Values of du_s/du_p obtained from fits to the experimental data are in good agreement with PIMC and DFT results. For comparison, limiting slope $S_{\lim}$ ($C \ll S u_p$) is 1.33 for both a free electron gas and an ideal monatomic gas of deuterons; limiting slope of a diatomic ideal gas is 1.17. The latter three are the dot-dash lines, as indicated.

Also plotted in Fig. 3 is the slope of the u_s-u_p data of Ref. 1, $S_L = 1.10 \pm 0.17$ for $18 < u_p < 32$ km/s (long dashes). The relatively low value of this slope for $u_p > 18$ km/s is inconsistent with dissociation proposed in Ref. 1, which is observed experimentally to be essentially complete by $u_p = 15$ km/s.[20] Mass velocity of the L data was obtained by an absolute determination of u_p by transverse radiography. In contrast, the CS, PC, and GG data obtained u_p with the shock-impedance match method with Al. Experimental issues with the two techniques have been discussed.[5]

Several conclusions can be drawn from these results: (i) When error bars of each point are taken into account, all three u_s-u_p data sets are in agreement. (ii) The CS-PC u_s-u_p data are in excellent mutual agreement, their error bars are less than half those of the L data, and the standard deviations of their joint fit are quite small. Thus, to compare experiment to theory, the u_s-u_p fit to the combined CS-PC data should be transformed to P-ρ space. (iii) $u_s(u_p)$ is weakly sensitive to dissociation; its slope du_s/du_p is sensitive to the onset of dissociation at 20 GPa and less sensitive to its completion above 50 GPa. (iv) Limiting compression of the fit to the CS-PC experimental data is 4.30 ± 0.10 at 100 GPa. The corresponding value of limiting compression calculated with PIMC and DFT is essentially 4.3 and it is 4.0 for an initially degenerate free-electron gas. The associated limiting slopes $S_{\lim}$ are 1.30 and 1.33, respectively. The slope of the CS-PC data is $S_3 = 1.22 \pm 0.08$. D_2 Hugoniot data at 100 GPa pressures can barely resolve the presence of interactions. (v) Thus, kinetic thermal energy dominates potential energy at 100 GPa shock pressures. (vi) Because interparticle potential energies become even smaller relative to thermal kinetic energies at higher shock pressures, it is expected that the deuterium Hugoniot agrees with PIMC and DFT calculations at higher shock temperatures and pressures, as well.

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[28] Of particular note is the work of Kerley (Ref. 24), who predicted the stiffer D_2 Hugoniot over thirty years ago before there were any experimental data available for shock-compressed liquid D_2.