Shock Compression of Deuterium near 100 GPa Pressures

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(Received 19 February 2002; published 26 September 2002)

The shock-compression curve (Hugoniot) of D_2 near 100 GPa pressures (1 Mbar) has been controversial because the two published measurements have limiting compressions of fourfold and sixfold. Our purpose is to examine published experimental results to decide which, if either, is probably correct. The published Hugoniot data of low-*Z* diatomic molecules have a universal behavior. The deuterium data of Knudson *et al.* (fourfold limiting compression) have this universal behavior, which suggests that Knudson *et al.* are correct and shows that deuterium behaves as other low-*Z* elements at high temperatures. In D_2, H_2, N_2, CO, and O_2, dissociation completes and average kinetic energy dominates average potential energy above ~60 GPa. Below ~30 GPa, D_2, H_2, N_2, CO, and O_2 are diatomic. D_2 dissociation is accompanied by a temperature-driven nonmetal-metal transition at ~50 GPa.

DOI: 10.1103/PhysRevLett.89.165502 PACS numbers: 62.50.+p, 64.30.+t

Hydrogen at high pressures and temperatures in the fluid state is of great interest because of the condensed matter physics of these newly accessible extreme states of matter, for understanding interiors of giant planets in this solar system and the ~90 such planets which have been discovered recently around other stars, as fuel in inertial confinement fusion, and as a possible route to the synthesis of novel materials such as solid metallic hydrogen. Two Hugoniots have been measured recently for deuterium at 100 GPa pressures and temperatures of several 1000 K [1,2]. These Hugoniots have limiting compressions, because as single-shock pressure increases, so too does temperature, which inhibits further compression. The observed limiting compressions differ by ~50%, a substantial discrepancy. This difference has been a subject of great controversy. In addition, minimum metallic conductivity has been observed in tenfold compressed liquid hydrogen at 140 GPa and 3000 K [3]. These conditions were achieved by multiple shock compression, which is quasi-isentropic, lower in temperature than on the Hugoniot, and has no limiting compression. This nonmetal-metal transition under multiple shock compression is density driven in a disordered, highly degenerate fluid. The purpose of this Letter is to assess which of the two single-shock Hugoniots of deuterium is probably correct, to demonstrate universal behavior of low-*Z* diatomics under single-shock compression, to determine if hydrogen behaves as heavier low-*Z* atoms on the Hugoniot, and to determine the conditions of temperature-driven molecular dissociation on the Hugoniot.

The deuterium Hugoniot measurements were performed at two extremely large facilities. Da Silva *et al.* [1] used the Nova laser and Knudson *et al.* [2] used the pulsed-current *Z* machine. Both these experiments focus energy on a sample thickness of a few 100 μm for experimental lifetimes of ~10 ns. Recently, Trunin *et al.* [4] reported a preliminary Hugoniot point using a converging shock wave generated by high explosives.

Shock pressures, densities, and specific internal energies were determined in all the experiments using the Rankine-Hugoniot jump conditions across a thin shock front. These equations relate flow velocities and thermodynamic variables in the shocked state to those of the initial state:

$$P - P_0 = \rho_0 u_s u_p, \tag{1a}$$

$$V = V_0[1 - u_p/u_s], \tag{1b}$$

$$E - E_0 = 1/2(P + P_0)(V_0 - V), \tag{1c}$$

where P is shock pressure, V is specific shock volume, E is specific internal shock energy, u_s is shock velocity, u_p is mass or material velocity behind the shock front, and $\rho = 1/V$ is mass density. Zero-subscripted variables refer to the initial state ahead of the shock front. Shock impedance $Z = \rho_0 u_s$.

Da Silva *et al.* [1] measured the Hugoniot up to 150 GPa using an intense laser pulse to drive a strong shock into an Al baseplate, which was then transmitted into a liquid deuterium sample. A second laser beam produced a soft x-ray source to sidelight shock velocity, material velocity, and compression (ρ/ρ_0). Knudson *et al.* [2] measured the Hugoniot up to 70 GPa using a pulsed current to generate a magnetic field B, which generated a pressure $P \sim B^2$, which accelerated an Al impactor plate to a velocity as high as 21 km/s, which impacted an Al baseplate. The steady impact shock was then transmitted into a liquid deuterium sample. Shock and impact velocities were measured; material velocity was determined by shock-impedance matching. Trunin *et al.* [4] measured a Hugoniot point at 55 GPa by driving a metal impactor to very high velocity and using the shock-impedance-match method. Their point is in good agreement with Knudson *et al.*

The three experimental results for deuterium [5] are shown in Fig. 1. Limiting shock compressions of sixfold [1] and fourfold [2,4] of initial density are reported.

0031-9007/02/89(16)/165502(4)$20.00

Various theories are shown as well [6–10]. Sixfold compression was ascribed to dissociation [9]. High single-shock temperature causes a decrease in compressibility and, at sufficiently high shock pressures and temperatures, a limiting compression. Since limiting shock compression of an ideal monatomic gas is fourfold [11], the data of Knudson *et al.* suggest that D_2 is dissociating into atoms. Higher limiting compression is possible only if the diatomic molecule is maintained intact. Thus, significant insight into the critically important issue of dissociation is available immediately through comparison with other diatomic systems.

The Hugoniots of diatomic molecules have a common, systematic behavior in u_s-u_p space. Data are plotted in Fig. 2 for D_2 [2,4,12], H_2 [12], N_2 [13–15], CO [16], and O_2 [14] up to $u_p = 18$ km/s. The solid line is the fit to deuterium data in the molecular phase [12]; the dashed line is its linear extrapolation into the dissociation region. Figure 2 illustrates that the u_s-u_p data of these diatomic fluids lie on a common line, that dissociation of CO, N_2, and D_2 is observed as a slight decrease in u_s ($\sim 3\%$) relative to this line, and that u_s then increases as dissociation completes. The data of Ref. [1] (not shown) deviate significantly from this universal behavior; values of u_p are in the range 18 to 32 km/s and values of u_s are $\sim$7.5% lower than the dashed line, except for one point on the solid line at $u_p = 10$ km/s. Dissociation commences when shock pressure and temperature are sufficiently high, and this depends on initial mass density ρ_0 [Eq. (1a)]. Figure 2 emphasizes that very high experimental accuracy is required to characterize dissociation.

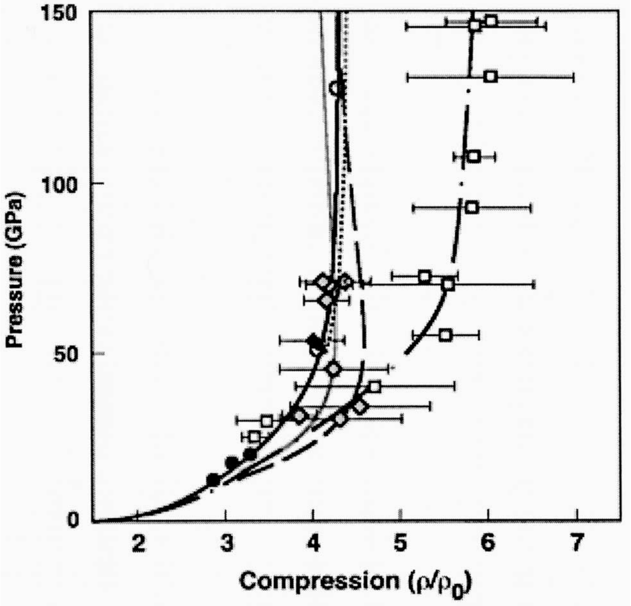

FIG. 1. Deuterium Hugoniots plotted as pressure versus compression, ρ/ρ_0 ($\rho_0 = 0.17$ g/cm^3). Experiments (gray diamonds [2]; open squares [1]; solid diamond [4]; solid circles [12]). Theoretical models (solid curve [6]; gray curve [7]; dashed curve [8]; dot-dashed curve [9]; dots [10]). After [2].

By transforming the u_s-u_p relations in Fig. 2 via Eqs. (1), Hugoniot data of deuterium, hydrogen, nitrogen, carbon monoxide, and oxygen are plotted as shock pressure versus relative compression in Fig. 3. Note that, although oxygen dissociates above 30 GPa, it is not readily apparent because its density change and dissociation energy in going to the monatomic fluid are small relative to those of N_2 [17]. An important point here is that relatively small variations in u_s-u_p space cause substantial variations in P-V space. Hugoniot experiments are performed in u_s-u_p space; theory is performed in P-V space.

Above $\sim$60 GPa, D, N, O, and C + O asymptotically approach fourfold compression, limiting shock compression of an ideal monatomic gas, i.e., a dense fluid in which the only relevant degrees of freedom are momenta of atoms (kinetic energy). At the densities and temperatures of these data, pressures are definitely not ideal. However, the systematic approach to fourfold compression, within 10% for three diatomics, is strong evidence that dissociation to atoms is becoming complete and that average kinetic energy dominates average potential energy above

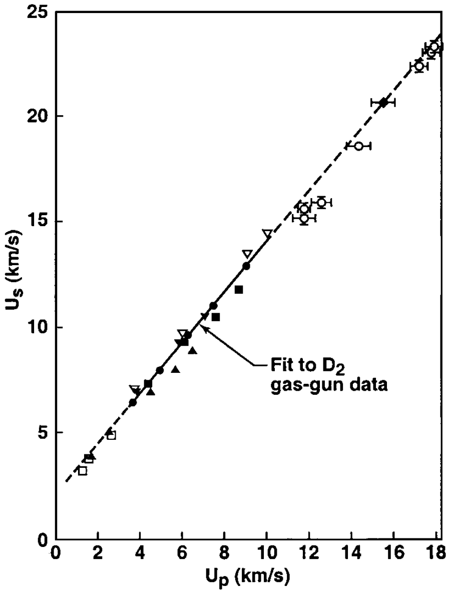

FIG. 2. Hugoniots plotted as u_s versus u_p of deuterium (open circles [2]; solid diamond [4]; solid circles [12]), hydrogen (open inverted triangles [12]; $\rho_0 = 0.071$ g/cm^3), nitrogen (open squares [13]; solid squares [14,15]; $\rho_0 = 0.81$ g/cm^3), carbon monoxide (solid triangles [16]; $\rho_0 = 0.81$ g/cm^3), and oxygen (solid inverted triangles [14]; $\rho_0 = 1.20$ g/cm^3). The solid line is the fit to deuterium data for molecular phase [12]; the dashed line is its extrapolation. Dissociation of D_2, N_2, and CO is observed as a slight decrease in u_s ($\sim 3\%$) from the common line. Deuterium data in [1] (not shown) have values of u_p in the range 18 to 32 km/s and u_s values $\sim$7.5% below the dashed line, except for one point on the solid line at $u_p = 10$ km/s.

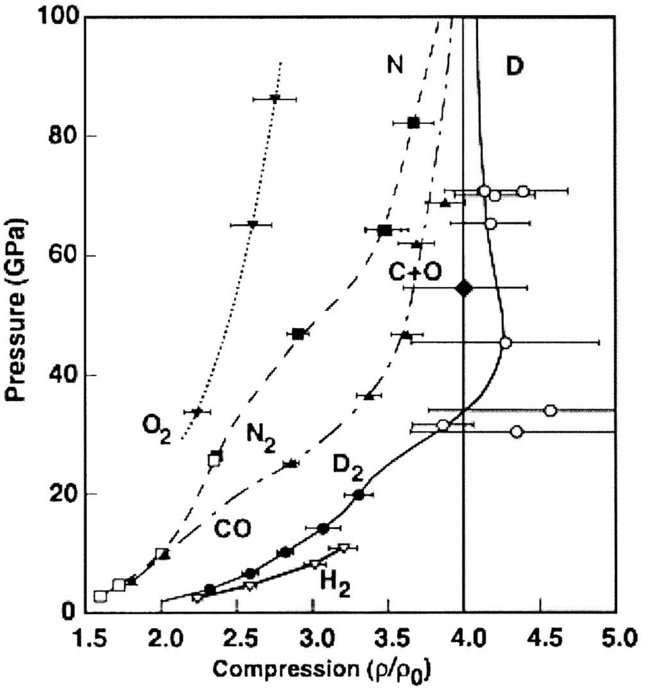

FIG. 3. Hugoniots plotted as pressure versus relative compression (ρ/ρ_0) of deuterium (open circles [2]; solid diamond [4]; solid circles [12]), hydrogen (open inverted triangles [12]), nitrogen (open squares [13]; solid squares [14,15]), carbon monoxide (solid triangles [16]), and oxygen (solid inverted triangles [14]). Curves were calculated with fits to u_s-u_p data in Fig. 2 and Eqs. (1), except for a guide to the eye through the open circles.

~60 GPa, which for deuterium corresponds to a temperature of ~0.5 eV [18]. Because a classical ideal gas has a limiting shock compression and a degenerate electron gas does not [19], the approach to fourfold compression must be a direct consequence of the monatomic character of the species present above ~60 GPa. Below ~30 GPa, D_2, H_2, N_2, O_2, and CO are diatomic and thus dissociate continously between ~30 and ~60 GPa.

Evidence for the complete dissociation of D_2 at a shock pressure of ~50 GPa is provided by the temperature data which plateaus at ~0.5 eV near 50 GPa [18]. A plateau in temperature is characteristic of a latent heat of dissociation, as in nitrogen [15], and indicates that dissociation is temperature driven on the Hugoniot. For both D_2 and N_2, $k_B T_d / E_d \sim 0.1$, where k_B is Boltzmann's constant, T_d is dissociation temperature, and E_d is dissociation energy. That is, at fourfold compression, E_d of D_2 is 4.5 eV [20] and $T_d \sim 0.5$ eV [18]. For N_2, $T_d \sim 0.8$ eV [15] at a dissociation energy of ~7 eV [21].

Optical reflectivities of shocked deuterium also indicate dissociation is complete by ~50 GPa. Reflectivities increase from <0.1 at 20 GPa up to saturation at ~0.5 at shock pressures above 50 GPa [22]. A reflectivity of 0.5 is characteristic of a poor metal and, thus, temperature-driven dissociation to a monatomic state is accompanied by a nonmetal-metal transition. It is very unlikely that the large sixfold compression reported above 50 GPa can be attributed to dissociation.

The above analysis indicates that fluid D_2 undergoes a diatomic-to-monatomic transition at 0.6–0.7 g/cm^3, 5000–10 000 K, and ~50 GPa on the Hugoniot, in excellent agreement with recent predictions [23]. Dissociation does vary with density and temperature, which are different off the Hugoniot.

Three conclusions can be drawn from the published experimental data. First, the data of Knudson *et al.* are probably correct because they agree with the universal behavior of diatomic liquids (Fig. 2). Second, a controlling feature of dissociation is initial mass density, which determines pressure [Eq. (1a)] and thus temperature to satisfy $k_B T_d / E_d \sim 0.1$. The corresponding pressure-compression curves are approaches to monatomic ideal gases. This behavior is remarkably simple in view of the fact that these systems were previously thought to be so complex. Third, the fact that D has no core and is a light, potentially quantum atom is of no consequence on the Hugoniot. D behaves as its heavier neighbors in the periodic table at high temperatures on the Hugoniot.

The question then remains as to possible causes of the larger error bars than expected in the laser experiments. It is important to speculate on such possibilities as bases for obtaining smaller error bars in future experiments. First, the distance-time trajectories of the shock front and motion of the interface between deuterium and Al do not have a common origin in space-time in the streak-camera record [1], as they do in actuality. The offset of the origins of the two trajectories could be caused by a ~1° tilt between the sidelighting soft x rays and the Al interface, which would result in an apparently larger compression than actual. Historically, tilt has been a major issue in Hugoniot measurements and apparently was not taken into account in [1]; general distortion was taken into account in [2]. Second, the use of the sidelighting method, a transverse probe, adds constraints which are not present in the shock-impedance-match method, which uses longitudinal probes [2,4,12,24,25]. The shock-impedance-match method is not very sensitive to alignment of diagnostics and does not require a steady shock for large distances behind the shock front. That is, the governing equations (1) are jump conditions across a thin (~ 100 Å in deuterium) shock front. The sidelighting method requires that measurements of shock and material velocities be done by diagnosing shock-front and interface motions separated by ~20 μm. Achieving a steady shock over such a large spatial scale is difficult, especially when the driving laser pulse is not constant in time. In addition, there should be no changes in the initial conditions caused by the preheat which precedes shock compression, e.g., magnetic flux diffusion in [2] or fast electrons in [1]. Shielding of preheat appears to be the case in [2], but it is not clear this condition is met in [1].

The author acknowledges M. D. Knudson, J. R. Asay, R. F. Trunin, V. E. Fortov, N. W. Ashcroft, N. C. Holmes, R. Chau, and A. C. Mitchell for interesting discussions. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory, under Contract No. W-7405-Eng-48.

Note added.—The slopes in the data in Fig. 2 are readily estimated. Figure 2 indicates that the relation between u_s and u_p is essentially linear; that is, $u_s = C + Su_p$, where C is a constant and S is the slope. The slope S is readily estimated from (i) the Hugoniot relation for specific volume [Eq. (1b)], (ii) the assumption that u_p is large compared to C, and (iii) the limiting shock compression of an ideal gas. The first two conditions yield the relation $S = (\rho/\rho_0)_L/[(\rho/\rho_0)_L - 1]$, where $(\rho/\rho_0)_L$ is ρ/ρ_0 in the limit $u_p \gg C$. For a diatomic ideal gas for which all the vibrational and rotational degrees of freedom are excited, $(\rho/\rho_0)_L = 7$ and $S = 1.17$. The solid line for D_2 in Fig. 2 has a slope $S = 1.21 \pm 0.04$ [12]. For a monatomic ideal gas, $(\rho/\rho_0)_L = 4$ and $S = 1.33$. The value of S measured for He is 1.36 [26]. These values of S are in excellent agreement with the slopes in Fig. 2.

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[1] L. B. Da Silva *et al.*, Phys. Rev. Lett. **78**, 483 (1997).

[2] M. D. Knudson *et al.*, Phys. Rev. Lett. **87**, 225501 (2001).

[3] S. T. Weir, A. C. Mitchell, and W. J. Nellis, Phys. Rev. Lett. **76**, 1860 (1996); W. J. Nellis, S. T. Weir, and A. C. Mitchell, Phys. Rev. B **59**, 3434 (1999).

[4] R. F. Trunin *et al.*, in Proceedings of 6th Zababakhin Scientific Readings (in Russian) (to be published); R. F. Trunin, *Shock Compression of Condensed Materials* (Cambridge Press, Cambridge, 1998), p. 20.

[5] Deuterium in all these experiments is in thermal equilibrium because the time between intermolecular collisions is $\sim 10^{-14}$ s, small compared to experimental resolutions and lifetimes of 10^{-10} s or more and 10^{-8} to 10^{-7} s, respectively.

[6] G. I. Kerley, *Molecular Based Study of Fluids* (American Chemical Society, Washington, D.C., 1983), p. 107.

[7] T. J. Lenosky *et al.*, Phys. Rev. B **56**, 5164 (1997); L. Collins *et al.*, Phys. Rev. E **52**, 6202 (1995).

[8] T. J. Lenosky *et al.*, Phys. Rev. B **61**, 1 (2000).

[9] M. Ross, Phys. Rev. B **58**, 669 (1998); **54**, R9589 (1996).

[10] B. Militzer and D. M. Ceperley, Phys. Rev. Lett. **85**, 1890 (2000).

[11] Ya. B. Zeldovich and Yu. P. Raizer, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena* (Academic, New York, 1966), Vol. 1, p. 52.

[12] W. J. Nellis *et al.*, J. Chem. Phys. **79**, 1480 (1983).

[13] V. N. Zubarev and G. S. Telegin, Sov. Phys. Dokl. **7**, 34 (1962).

[14] W. J. Nellis and A. C. Mitchell, J. Chem. Phys. **73**, 6137 (1980).

[15] W. J. Nellis *et al.*, J. Chem. Phys. **94**, 2244 (1991).

[16] W. J. Nellis *et al.*, J. Chem. Phys. **75**, 3055 (1981).

[17] G. I. Kerley and A. C. Switendick, in *Shock Waves in Condensed Matter*, edited by Y. M. Gupta (Plenum, New York, 1986), pp. 95–100.

[18] G. W. Collins *et al.*, Phys. Rev. Lett. **87**, 165504 (2001).

[19] As shock pressure of an ideal gas increases, so too does temperature, causing a limiting compression. In contrast, thermal pressure of a degenerate electron gas is weakly sensitive to temperature. The electron system remains cold and does not have a limiting shock compression. For deuterium on the Hugoniot, $T/T_F \sim 0.5/10 \ll 1$. Thus, limiting compression is caused by classical ions, and electron pressure can be substantial.

[20] N. W. Ashcroft, Phys. Rev. B **41**, 10 963 (1990).

[21] M. Ross, J. Chem. Phys. **86**, 7110 (1987).

[22] P. M. Celliers *et al.*, Phys. Rev. Lett. **84**, 5564 (2000).

[23] B. Militzer *et al.*, Phys. Rev. Lett. **87**, 275502 (2001).

[24] M. van Thiel *et al.*, Phys. Rev. Lett. **31**, 979 (1973).

[25] R. D. Dick and G. I. Kerley, J. Chem. Phys. **73**, 5264 (1980).

[26] W. J. Nellis *et al.*, Phys. Rev. Lett. **53**, 1248 (1984).