Shock Compression of Quartz to 1.6 TPa: Redefining a Pressure Standard

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Evaluation of models and theory of high-pressure material response is largely made through comparison with shock wave data, which rely on impedance match standards. The recent use of quartz as a shock wave standard has prompted a need for improved data. We report here on measurements of the quartz Hugoniot curve from 0.1–1.6 TPa. The new data, in agreement with our *ab initio* calculations, reveal substantial errors in the standard and have immediate ramifications for the equations of state of deuterium, helium, and carbon at pressures relevant to giant planets and other high-energy density conditions.

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The high-pressure response of materials is critical to several areas of physics, including geophysics, planetary astrophysics, inertial confinement fusion, and *ab initio* modeling. For example, structure of the giant planets, and therefore our understanding of their formation, depends sensitively on the equations of state of hydrogen and helium at several 100 GPa [1]. Evaluation of models and theory at these conditions is predominantly made through comparison with shock compression data, which necessarily rely on impedance match (IM) standards. Thus the quality of the IM standard is crucial: errors in the standard propagate as systematic errors in the inferred density and pressure in shock wave experiments. This is particularly pertinent for highly compressible materials such as deuterium and helium.

Quartz has recently become an IM standard of choice in the several 100 GPa regime [2]. Above melt on the Hugoniot curve, at ~5000 K and ~100 GPa [3], liquid silica is a conductive fluid [4,5]. Thus strong shock waves exhibit substantial reflectivity, allowing precise determination of the shock velocity by measuring the Doppler shift of reflected laser light using velocity interferometry (VISAR) techniques [6]. This significantly reduces random measurement error in comparison to transit time measurements. Several recent studies on materials including deuterium [7], helium [8], and diamond [9] have used this technique, with significant improvement in measurement precision. However, we show the quartz standard used in these studies is in error, in part due to the large pressure range over which disordering and dissociation of the fluid occurs, which extends from melt to ~1–1.2 TPa. We demonstrate that the error in the IM standard produces systematic errors up to ~12% and ~23% in the density of deuterium and helium in the 100–200 GPa pressure regime, respectively.

Plate-impact shock wave experiments were performed on z-cut, α quartz (single crystals obtained from Argus) using the Sandia Z Machine [10], a pulsed-power accelerator that produces currents and magnetic fields exceeding 20 MA and 10 MG, respectively. These current and field densities result in substantial magnetic pressures (up to ~650 GPa) capable of propelling the outer electrodes of the load outward at high velocity. With proper shaping of the current pulse, macroscopic metal plates (17 mm by 40 mm by 0.85 mm thick) can be launched to velocities approaching ~40 km/s [11].

For the experiments reported here, aluminum (6061-T6) and copper (OFHC) flyer plates were accelerated to ~7–40 km/s and ~9–18 km/s, respectively. VISAR was used to optically measure velocity. Transparency of the quartz allowed laser light to initially reflect from the flyer plate, providing a measurement of the velocity from rest to impact with the window v_f. Upon impact, measurement transitions to the shock velocity U_s. The shock trajectory was determined by integration of the velocity profile, enabling a comparison with the measured thickness of the window (typically 0.75–1.5 mm in thickness). These comparisons typically agree to better than 1%, eliminating any possible 2π phase shift ambiguity in the quartz U_s.

Typical measurements are shown in Fig. 1. The shock velocity profile in the quartz provides an indication of the density profile of the plate at impact. In particular, previous analysis of the aluminum flyer plate launch, using 2D magnetohydrodynamic simulations [11], indicates that in all cases the impact side of the plate corresponds to solid density aluminum, and that the subsequent drop in shock velocity is associated with the melt transition within the flyer plate. The copper impactors were composite flyer plates composed of 0.15 and 0.7 mm of copper and aluminum on the impact and power flow side of the plate, respectively. In these cases, the abrupt drop in shock velocity seen in Fig. 1 is due to the large impedance mismatch between copper and aluminum. Further details of the condition of the flyer plates at impact can be found in Ref. [11].

The bulk of these measurements (100 total) used a high bandwidth VISAR diagnostic, capable of recording better than 0.5 GHz fringe frequency. This enabled a low velocity per fringe (typically ~500 m/s per fringe), and therefore high velocity sensitivity, resulting in uncertainties of ~0.2–0.5% in both v_f and U_s. Earlier measurements used a less sensitive system with corresponding uncertainties of ~0.5–1% in both v_f and U_s [12]. The particle

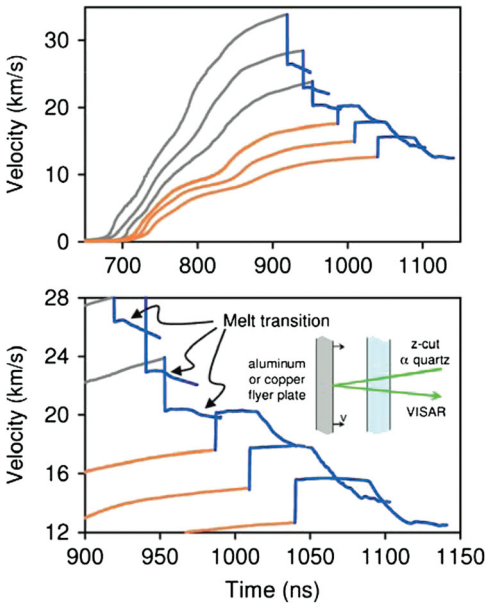

FIG. 1 (color). Typical VISAR data. Gray (orange) lines, the aluminum (copper) flyer plate velocity; blue lines, the quartz shock velocity. Bottom plot shows detailed view of the quartz shock velocities.

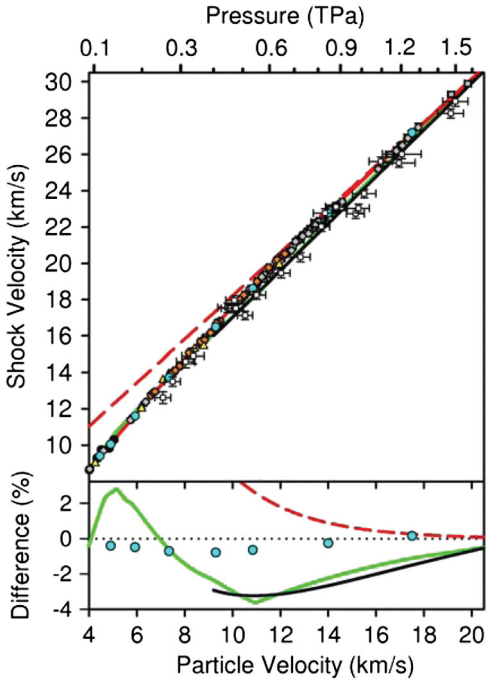

FIG. 2 (color). Quartz U_s-u_p Hugoniot curve. Diamonds (squares) VISAR (transit time) measurements where gray (orange) correspond to aluminum (copper) impacts, this work; black circles, Ref. [3]; yellow triangles, Ref. [17]; white squares, Ref. [2]; blue circles, QMD calculations this work; green solid line, SESAME 7360 [18]; black solid line, Hugoniot curve fit from Ref. [2]; red solid line, Hugoniot curve fit this work; red dashed line, Hugoniot curve fit this work with $c = 0$. Bottom plot, U_s residuals with respect to Hugoniot curve fit from this work.

velocity u_p was determined through IM with the aluminum and copper flyer plates [13–15]. The Hugoniot curves of both materials are well known and represented as piecewise functions, $U_s = C_0 + Su_p$, with different C_0 and S values for the solid and liquid regions of the Hugoniot curve [16]. Uncertainties in the inferred particle velocities were determined through a Monte Carlo analysis method, and were slightly larger than that of the measured flyer velocity.

The resulting 122 Hugoniot curve measurements obtained from 43 individual Z experiments are shown in the U_s-u_p and P-ρ planes in Figs. 2 and 3, respectively. Also shown are data obtained using gas guns [3], explosive and nuclear drives [17], the Ω laser [2], and the predicted response from the SESAME 7360 equation of state [18]. Given the significant curvature in the U_s-u_p plane we chose to fit the data with the functional form $U_s = a + bu_p - cu_p e^{-du_p}$. This form was found to be very robust; in particular, little difference was observed for a weighted and unweighted fit, which is expected for large sample sizes. A least squares, weighted fit of the Z data results in the following values: $a = 6.26 \pm 0.35$ km/s, $b = 1.20 \mp 0.02$, $c = 2.56 \mp 0.15$, and $d = 0.37 \pm 0.02$ $(\mathrm{km/s})^{-1}$.

Residuals of U_s with respect to the Z fit are shown in Fig. 2. Of particular note is the SESAME model [18], which exhibits two abrupt changes in slope at ~100 GPa, caused by melt, and ~550 GPa, due to an abrupt transition from a molecular to atomic fluid. The notion of such an abrupt dissociative transition is in stark contrast to the present results. The dashed red lines in Fig. 2 correspond to the asymptotic linear limit of the Z fit (i.e., $c = 0$). This residual is still significant to pressures approaching 1–1.2 TPa, suggesting that the effects of disordering and dissociation of the fluid persist over a rather larger pressure range.

To investigate dissociation along the Hugoniot curve, quantum molecular dynamics (QMD) calculations were performed using version 5.1 of VASP [19]. Both the local density approximation (LDA) and the recently developed Armiento-Mattsson (AM05) functionals [20] were used, with similar results. In contrast to the generalized gradient approximation, both LDA and AM05 functionals produce an accurate bulk modulus for α quartz at ambient conditions. Our calculations show that, in contrast to LDA, the AM05 functional gives the correct ground state energy ordering of α quartz with respect to stishovite, which is close to the density of the silica liquids considered here. We therefore show the AM05 results in Figs. 2 and 3. Silicon and oxygen atoms were represented with projector augmented wave (PAW) potentials [21], with the PAW LDA potentials used with either functional [22]. A total of 72 atoms were included in the supercell, with a plane wave cutoff energy of 600 eV [23]. Simulations were done in the canonical ensemble, with simple velocity scaling as a thermostat, and typically covered several picoseconds of

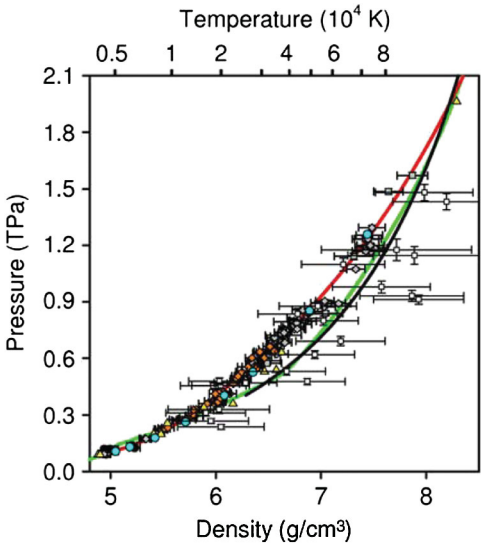

FIG. 3 (color). Quartz P-ρ Hugoniot curve. Lines and symbols as in Fig. 2. Top axis, temperature scale determined from QMD calculations.

real time. Thermodynamic quantities were taken as time averages of the equilibrated portions of the molecular dynamics runs.

Residuals of the QMD Hugoniot curve calculations with respect to the Z fit are less than 1% throughout the entire pressure range investigated. This agreement suggests the QMD accurately describes the hot dense fluid, and can be used to gain unique insight into the thermodynamics in this regime. The calculations indicate the extended region of curvature in the U_s-u_p Hugoniot curve is due to disorder and dissociation of the fluid. The total ion energy, thermal plus potential, is found to rise above the Dulong-Petit value for temperatures above melt, leading to an enhanced specific heat, in agreement with earlier work [4]. However, our results also indicate that at higher pressures and temperatures the ion contribution to the specific heat drops and remains between $2Nk_B$ and $3Nk_B$ to the highest pressures and temperatures considered here. This reflects competition of increasing disorder in the liquid and weaker interactions between the atoms as the O-O and Si-O bond energies drop with increasing electronic temperature. This suggests the energy imprint of disorder and dissociation of the molecular fluid persists to much higher pressures and temperatures than previous thought, and plays a significant role in the extent over which curvature is seen in the U_s-u_p response. A more detailed discussion of the QMD calculations and the insight obtained is beyond the scope of this Letter, and will be the subject of a future publication.

Figure 2 also shows the residuals of the fit to the high-pressure data of Hicks *et al.* [2] (we refer to as the Ω fit), which has recently been used extensively as an IM standard for shock wave experiments in the several 100 GPa regime [7–9]. There is a substantial difference in the Z and Ω fits in this pressure regime. It is instructive to look at the percentage difference (PD) in derived quantities as a function of the observable U_s in quartz. Figure 4 shows the PD in the quartz u_p inferred from the Ω fit [2] with respect to that inferred from the Z fit. The PD peaks at ~4.3% at pressures near ~500–600 GPa. The difference in ρ is somewhat larger, as can be seen by comparing Figs. 2 and 3. It is easily shown that the PDs in ρ and density compression, $\eta \equiv \rho/\rho_0 = U_s/(U_s - u_p)$, are given by the PD in u_p multiplied by the factor $(\eta - 1)$. Since η for quartz exceeds 2 at a pressure of ~150 GPa, the PDs in ρ and η are larger than the PD in u_p over the entire pressure range of interest.

These errors in the quartz u_p also lead to errors in inferred quantities in other materials where quartz was used as an IM standard. As an example we consider the shock response of liquid deuterium, the focus of a recent publication. Figure 5 shows the P-η results to 220 GPa recently published inferred using the Ω fit for quartz [7], these same experiments reanalyzed using the Z fit for quartz, and the results of flyer plate experiments performed on Z to 180 GPa [24]. The apparent increase in η at ~100 GPa, as inferred in Ref. [7], has been interpreted as possible evidence for a plasma phase transition (PPT). However, our reanalysis suggests that the apparent increase in η is likely an artifact of the quartz Hugoniot curve used in the IM analysis. The PD in η, inferred using the Ω fit versus the Z fit for quartz, peaks at about 12%–13% near ~100 GPa in deuterium, which corresponds to ~600 GPa in the quartz, the pressure at which the Z and Ω fits exhibit the largest difference. The PD in $\eta/(\eta - 1)$ is quite close to the PD in u_p for quartz, indicating that the error in u_p for deuterium is caused by, and essentially equal to, the difference in the Ω fit with respect to the Z fit. The large error in η results from the high compressibility of deuterium, with $(\eta - 1)$ approaching 3.4–4 as inferred in Ref. [7].

Even larger errors result in the case of helium, where a peak compression of $\eta \approx 6.33$ has been reported [8]. In this case the large compressibility results in an error in density of ~23%. This correction would reduce η to ~5.1,

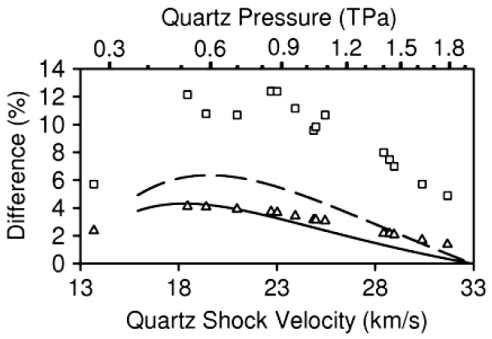

FIG. 4. Percent differences as a function of U_s in quartz. Solid black line, quartz u_p (Ω fit versus Z fit); dashed black line, quartz ρ (Ω fit versus Z fit); squares, deuterium η (from Ref. [7] inferred using Ω fit versus that inferred using Z fit for quartz); triangles, deuterium $\eta/(\eta - 1)$. Top axis, pressure scale for quartz.

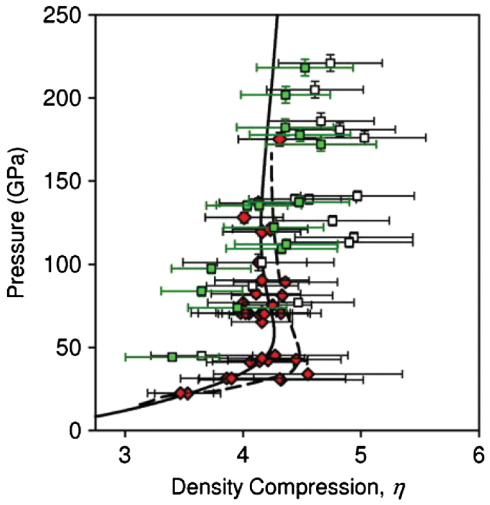

FIG. 5 (color). Liquid deuterium P-η Hugoniot curve. Red diamonds, Ref. [24]; white squares, Ref. [7]; green squares, data from Ref. [7] corrected using the Z fit for quartz. Solid line, Ref. [28]; dashed line, Ref. [26].

which is in reasonable agreement with *ab initio* modeling of Militzer [25]. In the case of carbon, which is considerably less compressible, the error in density is somewhat less. Over the pressure range of 0.6–2 TPa, η ranges between 1.75–2.5 [9] resulting in an error in density of ~4%.

We have performed an extensive study of the shock response of z-cut, α quartz in the pressure range of 0.1–1.6 TPa. This work lays the foundation for the use of quartz as a high precision standard for use in IM shock wave experiments. In particular, the present results indicate the need for reanalysis of several recently published data sets, which have immediate ramifications for the modeling of gas giant planets and other high-energy density conditions. The volume and precision of this data set also provide a benchmark for theoretical modeling of high-energy density conditions in which disordering, dissociation, and ionization dominate. These processes have hindered the modeling of high-energy density systems to date. As an example, we call attention to the decade-long debate over a proposed PPT in the vicinity of the deuterium Hugoniot curve at several 100 GPa ([7,24,26,27] and references therein), whose presence or absence has profound implications to the structure of the giant planets [1]. The present work suggests the absence of such a PPT.

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