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Equation of state of molecular hydrogen and deuterium from shock-wave experiments to 760 kbar

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We have carried out single-shock experiments with liquid deuterium to 210 kbar ($T \approx 4800$ K) and reflected experiments to 760 kbar ($T \approx 7000$ K) as well as single-shock experiments with liquid hydrogen to 100 kbar ($T \approx 3300$ K). These data enable us to determine a theoretical spherically symmetric, effective intermolecular pair potential. Calculated solid isotherms are compared with recent static measurements.

The high-pressure equation of state of molecular hydrogen and its transition to the metallic state is currently a subject of intense interest. In this paper we report accurate, new shock-wave results on the liquid up to a pressure of 760 kbar and a calculated temperature of about 7000 K. The high final temperatures and pressures achieved in the shock process allow us to determine an effective pair potential for molecular hydrogen valid at small intermolecular separations. We have used this potential to calculate solid isotherms for comparison with recent static measurements, and to predict the molecular-metallic phase transition.

For these experiments shock waves were generated by accelerating a planar projectile to a velocity in the range 3.9–6.7 km/s using a two-stage light-gas gun[1] and impacting the projectile onto a target containing liquid H_2 or D_2. The experiment is based on the Rankine-Hugoniot relations which relate measured kinematic parameters to thermodynamic variables. The diagnostic system was described previously.[2] Liquid-D_2 specimens were also double shocked by reflecting a shock wave off an aluminum (alloy 1100) anvil to achieve pressures four times higher than could be achieved by a single shock. The technique has been described previously.[3] For the double-shock D_2 experiments the mixing circuit used to multiplex two detector signals onto a single oscilloscope was modified somewhat because of the short shock transit times being measured (~110 ns). The cryogenic targets have also been described.[4] The coolant was liquid H_2 for all experiments. The cryogenic design was modified because the heat of vaporization per unit volume is significantly less for liquid H_2 than for coolants used previously, such as liquid N_2 or Ar. The initial state was close to the saturation curve at 20.2 K. Au-Fe versus chromel thermocouples were calibrated in place. Sample temperature was used to obtain initial sample density.[5,6] The Hugoniot equation of state for the metal impactors and walls or base plates were published earlier,[7] as was the calculation of the release isotope of the aluminum base plate.[4] Small corrections were made for thermal contraction as previously noted.[4] The error analysis has also been published.[2,7] Changes in experimental details from our other experiments will be published elsewhere.

The data are plotted in Figs. 1 and 2 and are compared with earlier work of van Thiel *et al.*[8–10] and Dick and Kerley.[11] Figure 1 shows the D_2 principal (single-shock) Hugoniot up to 0.21 Mbar and the reflected D_2 or (double-shocked) Hugoniot data near 0.76 Mbar. These higher-pressure points were re-

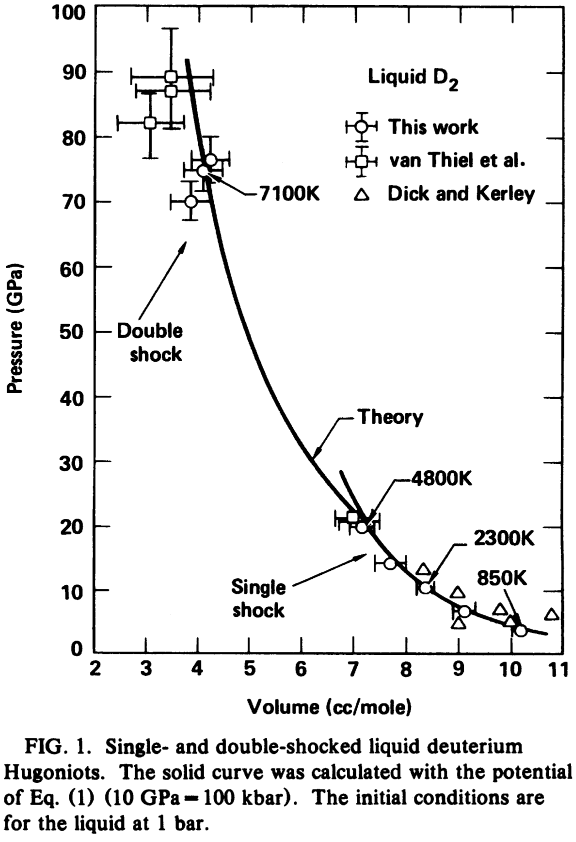

FIG. 1. Single- and double-shocked liquid deuterium Hugoniots. The solid curve was calculated with the potential of Eq. (1) (10 GPa = 100 kbar). The initial conditions are for the liquid at 1 bar.

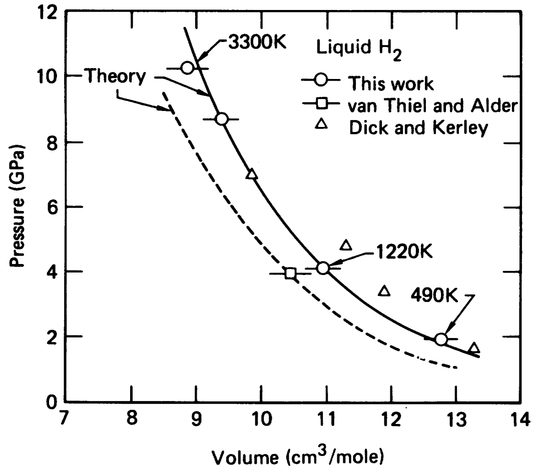

FIG. 2. Single-shocked liquid-hydrogen Hugoniot. The solid curve was calculated with the potential of Eq. (1). The dashed curve was calculated using the exponential-six potential fitted to Shimizu *et al.*'s isotherm (Ref. 22) (10 GPa =100 kbar). The initial conditions are for the liquid at 1 bar.

flected from the lower point at 0.21 Mbar. Our three double-shock points are for impact velocities in the range 6.62–6.73 km/s. Only the three points of van Thiel *et al.*[10] with an impact velocity in the range 6.82–6.88 km/s are plotted in Fig. 1. Figure 2 shows the H_2 principal Hugoniot points. We note that the earlier van Thiel-Alder result for hydrogen appears to be too soft. The present shock-wave experiments have the highest accuracy of any to date on H_2 and D_2.

One goal of our work has been to determine a spherically symmetric, effective intermolecular potential which can be used with accurate theoretical models to calculate the equation of state of condensed hydrogen. In 1978 Silvera and Goldman[12] (SG) carried out a very careful theoretical study of the deuterium isotherm at 4 K and up to 26 kbar using self-consistent photon theory and determined an intermolecular potential that best fit these data. Subsequently we showed[13] that their potential would also predict the fluid isotherms of H_2 and D_2 from 75 to 300 K up to 20 kbar[14] and the melting curves to 57 kbar in agreement with experimental data.[15] In these calculations we used soft-sphere perturbation theory for the fluid properties and lattice dynamics for the solid with anharmonic corrections. The melting curves were computed by equating the Gibbs free energies and pressures of the two phases. However, this limited data base is insufficient to determine the short-range intermolecular repulsions that dominate the high-temperature–high-pressure shocked states, and as a result the SG potential predicts Hugoniot curves that are too steep. We found that if this potential was modified for $r < 2.55$ Å it was possible to compute the theoretical Hugoniots shown in Figs. 1 and 2, and still maintain the excellent fit to the lower-pressure fluid, solid, and melting data. Our new potential is

$$\phi=\begin{cases}\phi_{\mathrm{SG}}\,, & r>r_c \qquad \text{(1a)}\\ A\exp[-B(r-r_c)-C(r-r_c)^2-D(r-r_c)^3-E(r-r_c)^3(r-r_1)]\,, & r<r_c \qquad \text{(1b)}\end{cases}$$

where $A=3.98823\times10^{-14}$ erg, $B=4.76940$ Å^{-1}, $C=2.25457$ Å^{-2}, $D=0.955189$ Å^{-3}, $E=0.248158$ Å^{-4}, $r_1=1.2$ Å, and $r_c=2.55$ Å.

The potential given by Eqs. (1a) and (1b) can also be described by a simpler (exponential-six) potential, i.e.,

$$\phi=\frac{\epsilon}{\alpha-6}\{6\exp[\alpha(1-r/r^*)]-\alpha(r^*/r)^6\}\ , \tag{2}$$

where the magnitude (ϵ/k) and range (r^*) of the attractive minimum is given by 36.4 K and 3.43 Å, respectively. These values are consistent with the experimental molecular-beam data of Bauer *et al.*[16] and differ only slightly from the values $\epsilon/k=34.3$ K and $r^*=3.41$ Å given by Silvera and Goldman for their "pair" interaction potential. In Eq. (2) the parameter α which characterizes the stiffness of the exponential repulsion is chosen to be 11.1 to make it compatible with the quantum mechanical *ab initio* calculations.[17] The value $\alpha=11.1$ means that the intermolecular repulsion of molecular hydrogen is much softer than that of most other simple molecules or atoms which have $\alpha=13$.[18] Satisfactory agreement with static and shock data can be achieved using Eq. (2).

The calculation of the theoretical Hugoniot curves for deuterium in Fig. 1, and for hydrogen in Fig. 2, and the statistical mechanical theory used to compute the thermodynamic properties are described in previous publications.[13,18,19] In Fig. 1 there are two theoretical curves. The lower one is the calculated single-shock Hugoniot. The upper, or double-shocked curve, begins in the liquid but is reflected at 21 GPa. At the temperatures and densities along the Hugoniots hydrogen and deuterium are classical and we expect the same potential to be valid for both fluids. In these calculations the vibrational properties and the bond dissociation energy were assumed to be unaffected by compression. The actual change in the vibrational frequency under compression to pressure up to 600 kbar at 300 K reported by Sharma *et al.*[20] is too small to be observed along the Hugoniot. This agrees with our detailed *ab initio* study[17] which showed that the intermolecular vibration of H_2 depends very weakly on the intermolecular separation between two H_2 molecules. Although it is expected that some hindrance to molecular rotation will occur at high density, it has been shown that the barriers are small compared to the Hugoniot temperature and hydrogen may be considered a free rotor.[21] This feature also justifies our approximating the effective potential as being spherical. Molecular dissociation was included. It was found to be negligible at and below 210 kbar and led to a softening of less than 1% at 800 kbar.

The theoretical Hugoniot curves were calculated with fluid perturbation theory and Monte Carlo calculations. Perturbation theory is particularly useful in a study of this type in which a best-fit pair potential is sought and fast calculational methods are desirable. To check the accuracy of the perturbation theory we carried out Monte Carlo calculations and determined that the predicted Hugoniots were generally softer than perturbation theory by about 1% in volume, but well within the ±3% experimental error. The theoretical curves shown in Figs. 1 and 2 are based on Monte Carlo results. Also indicated on the figures are some of the calculated temperatures. The high temperatures achieved in these experiments provide information about the pair potential down to molecular separations of about 1.6 Å, or comparable to separations at which the molecular-metallic transition is believed to take place.

Pressure versus volume measurements, made using diamond anvils, have been reported by Shimizu *et al.*[22] up to 200 kbar at 300 K, and by van Straaten *et al.*[23] up to 370 kbar at 5 K. These two sets of data, shown in Fig. 3, are in disagreement. The disagreement is somewhat worse than it appears since the 300-K isotherm is below the 5-K curve. The solid curve in Fig. 3 is a theoretical 5-K isotherm calculated using lattice dynamics with Eq. (1) and is in very good agreement with the results of van Straaten *et al.* In addition our calculated isotherm up to 6 Mbar is also in excellent agreement with the extrapolation of their data as given in Ref. 23. We also reversed our procedure and fitted the 300-K solid isotherm of Shimizu *et al.* with an exponential-six potential ($\alpha = 10.7$, $r^* = 3.44$ Å, and $\epsilon/k = 32.2$ K) and used it to calculate liquid Hugoniots. This potential has the same minimum and well depth as the Silvera-Goldman potential. The result for hydrogen is shown as the dashed curve in Fig. 2 and lies outside the experimental error bars. Similar results, not shown, were obtained for deuterium. Thus our theoretical results based on the shock data are not consistent with the work of Shimizu *et al.*

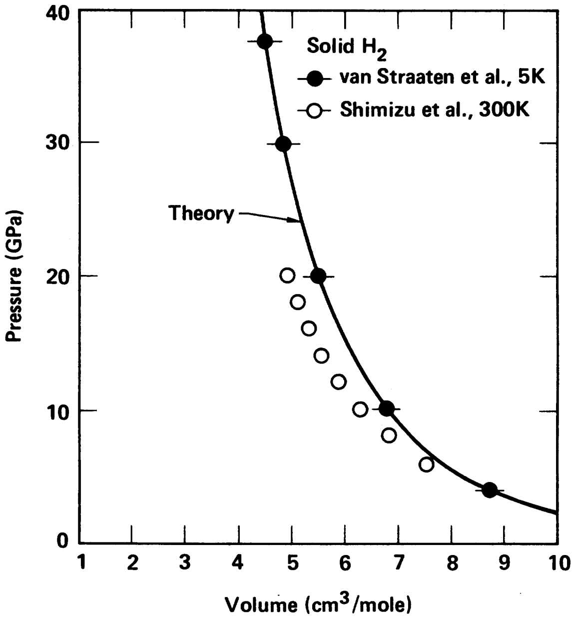

FIG. 3. Solid hydrogen isotherms. The solid curve was calculated with the potential of Eq. (1) (10 GPa = 100 kbar).

We have calculated the molecular-to-monatomic metal transition using our H_2 equation of state and metal equations of state calculated by the augmented-plane-wave (APW) method[24] and third-order perturbation theory.[25] Zero-point properties and electron correlation energy were included. These calculations predict metallic transitions at 3.1 Mbar (APW) and 3.6 Mbar (third order) and do not differ substantially from earlier theoretical work[26] based on the experiments in Refs. 8–10. The results assume metallization will occur by molecular dissociation but recent experimental work on iodine[27] has demonstrated that a molecular crystal can also become conducting, as a result of the crossing of the filled valence band of the molecule with its empty conduction band. Some preliminary theoretical calculations for a solid at 0 K indicate that hydrogen may undergo the same transition.[28–30]

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