PHYSICAL REVIEW B VOLUME 58, NUMBER 2 1 JULY 1998-II

Linear-mixing model for shock-compressed liquid deuterium

Marvin Ross
Lawrence Livermore National Laboratory, Livermore, California 94551

(Received 23 September 1997)

A model has been developed for the equation of state of deuterium that builds in the correct limiting behavior for the molecular fluid at low pressure and extends smoothly through dissociation to the very high-density monatomic-metallic fluid. The key assumption is that the Helmholtz free energy of the dissociating mixture is a function that can be approximated by the composition average of the free energy of the pure molecular and metallic hydrogen equations of state. The composition is determined by minimizing the free energy. In comparison to earlier studies this model leads to an enhancement of molecular dissociation and a lowering of shock temperatures and pressures. Calculations for shock-compressed liquid deuterium are in agreement with experiments to a pressure of 2.1 Mbar. At about 1 Mbar and 20 000 K liquid deuterium is 90% dissociated and is a nearly degenerate metal. The model predicts that molecular dissociation will lead to negative values of $(\partial P/\partial T)_V$ in the range 4000 to 10 000 K and volumes below 7 cc/mol. This feature suggests the formation of covalently bonded species in the partially dissociated mixture. [S0163-1829(98)05825-1]

I. INTRODUCTION

An accurate knowledge of the equation of state (EOS) of fluid hydrogen at extreme conditions is of considerable scientific interest, but it is essential for designing deuterated capsules for inertial confinement fusion (ICF) (Refs. 1 and 2) and for modeling Jovian planets and brown dwarfs.[3,4] Shock wave experiments have been the most reliable source of EOS data for hydrogen at such conditions, and deuterium has been the favored isotope because its higher mass permits the attainment of higher final pressures and densities.

ICF is a scheme in which hydrogen fusion is realized by impinging an intense laser light on a target to generate a shock wave in a liquid deuterium tritide (DT) sample that will achieve a density of $\sim 10^3$ times solid density at a thermal temperature of $kT \sim 10$ keV.[2] The shock path in an optimized capsule would first track this Hugoniot and be designed to follow an isentropic compression from the point of maximum compression to higher density. By following an isentrope the temperature rise is limited, and this permits the sample to achieve the density and temperature necessary for fusion. Since the efficient performance of deuterated ICF capsules relies heavily on achieving a maximum compression, the design of such a capsule depends critically on an accurate EOS for predicting the Hugoniot. Given the complexity of the physics, experimental shock data becomes indispensable for developing an accurate EOS model. While the isotherm for solid hydrogen has been measured in a diamond-anvil cell[5] up to a pressure of 1.2 Mbar at room temperature, the considerably higher temperatures achieved by shock compression are more nearly in the range of interest to ICF and astrophysics.

Shock experiments achieve states at high compression and temperature by introducing a rapid impulse into a substance through the detonation of a high explosive, the impact of a high-speed projectile propelled by a two-stage gun or the absorption of an intense pulse of radiation as with a high-powered laser. High-speed optical and electronic methods are necessary to measure certain dynamic variables; the shock and piston velocities that determine the final pressure, density, and energy.[6] The pressure (P), volume (V) and energy (E) behind the shock front is related to the initial conditions (P_o, V_o, E_o) through the Hugoniot equation:

$$E - E_o = \tfrac{1}{2}(P + P_o)(V_o - V). \tag{1}$$

The Hugoniot curve is the locus of final states that are attainable by a series of experiments with different shock intensities each starting from the same initial state. The temperature of the final shocked state cannot be obtained from the Hugoniot equations. It can be measured if the optical emission from the shock front is sufficiently high, but it is usually obtained from calculations of the Hugoniot using a theoretical equation of state.

Deuterium starting from the liquid, at $V_o = 23.6$ cc/mol and $T_o = 20.3$ K, has been shock compressed using the LLNL two-stage light gas gun to 210 kbar using single shocks and to about 850 kbar with reflected (or double) shocks.[7–9] More recently, a series of laser-generated shock wave experiments have been made to measure the Hugoniot of liquid deuterium over the pressure range from 0.25 to 2.1 Mbar (Ref. 10) with the maximum compression to 3.85 cc/mol, a density of 1.05 g/cc. This is the highest pressure measured in a shock experiment with a liquid hydrogen isotope and greatly extends the data available for examining the equation of state. Prior to these experiments theoretical estimates of the maximum density were lower by 20 to 40 %.

In Sec. II a linear-mixing model is described for dense dissociating hydrogen. The model has built in the correct limiting behavior for the low-density molecular fluid and the high-density monatomic-metallic fluid and the equation of state interpolates smoothly between these limits. The calculated results are presented in Sec. III. Section IV is concerned mainly with interpreting the results in hopes of gaining some new insight into the nature of the partially dissociated fluid. The section also includes a comparison with quantum Monte Carlo calculations. Section V is a summary.

0163-1829/98/58(2)/669(9)/$15.00

II. THE MODEL

A. Theoretical background

A major barrier to the construction of an accurate EOS for deuterium at simultaneously very high pressures and temperatures is the lack of information describing the chemical structure of the dissociating mixture. For example, it is unknown whether the mixture consists only of molecules and atoms such as in a dissociating dilute gas or whether more complex chemically bonded species are present. Molecular bonds may be destroyed by thermally exciting or pressure delocalizing electrons to create molecular chains and electrons may become itinerant as in a metal. One of the few bits of information comes from an analysis of the atomic arrangements found in both quantum Monte Carlo (QMC) (Ref. 11) and quantum molecular-dynamics,[12] calculations that suggests that the structure of the reacting mixture is a complicated arrangement of molecules and strings of atoms that implies the presence of chemical bonding in the mixture.

In the regime of relatively low shock pressure and temperatures, up to 210 kbar and about 4500 K, the fraction of molecules dissociated is only a few percent. Up to this pressure the Hugoniot has been calculated using fluid perturbation theory with the Ross, Ree, and Young (RRY) H_2-H_2 pair potential that was fitted to the shock data.[13] Calculations of the solid isotherm and the melting curve made with this potential are also in good agreement with experiment. At higher pressure and temperature theoretical models must contend with a rapidly increasing degree of dissociation. Attempts to model the EOS in this regime have been made by Saumon and Chabrier[14,15] using the RRY H_2-H_2 potential and potentials for the H-H and H-H_2 interactions that were determined from molecular orbital calculations for the isolated pairs. These potentials are characterized by short-ranged exponential repulsions. They predict second shock temperatures near 0.8–0.9 Mbar that are too high by about 40%.[9] The conclusion drawn from these results is that while theoretical pair potentials may be useful for modeling the low-density gases, they are apparently too repulsive to accurately model the interactions present in a dense, partially dissociated, fluid.

One explanation for the limited usefulness of simple pair potentials for dissociated fluids is the possibility that species other than atoms and molecules will be present. For example, consider the simple H_4 system. Much of the interest in this system has centered around the $H_2+D_2\rightarrow 2HD$ exchange reaction studied in shock tube experiments and by quantum-mechanical calculations and in H_4 as a prototype for the infinite antiferromagnetic chain and as a crude model for metallic hydrogen. Figure 1 shows the results of calculations made by full configuration interaction calculations for linear H_4 and taken from the tables of Bender and Schaefer.[16] In order to place these calculations more clearly within the context of the present discussion, the data has been plotted in terms of the volume occupied by an inner atom of the equidistant H_4 chain for equal linear lengths of H_4 and H_2-H_2. The ground-state energy of the linear H_2-H_2 interaction is repulsive, except for the small van der Waals attraction at low density. In contrast, the energy of the linear equidistant H_4 is predicted to have an energy minima at 1.67 Bohr lying 7.1 eV below the exact energy of four atoms but 1.9 eV above a pair of H_2 molecules. Similar curves exhibiting energy minima have been calculated for H_4 squares, rectangles, rhomboids, and tetrahedrons, but these configurations have higher energies, lying nearer -2.1 Ry.[17] Energy surfaces for the ground and excited states of the H_3 system also show energy minima.[18]

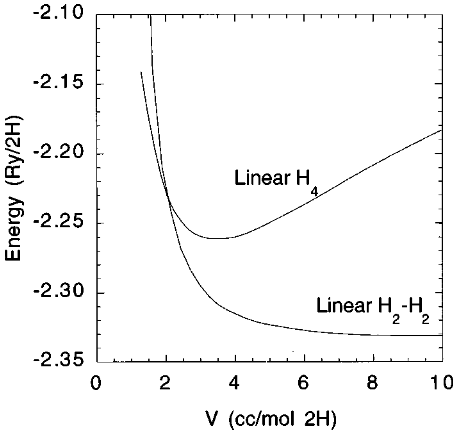

FIG. 1. Configuration interaction calculation of the total energy for H_2-H_2 and linear H_4 taken from the tables of Bender and Schaefer (Ref. 16). The data has been plotted in terms of the volume approximated as the sphere occupied by an inner atom of the equidistant H_4 chain for equal linear lengths of H_4 and H_2-H_2.

In the case of the solid, hydrogen has been found to remain molecular to at least 2.3 Mbar.[19] First-principles total-energy calculations predict the transition to a monatomic-metal at some higher pressure, widely believed to be above 3 Mbar.[20] Similar results are obtained from predictions made with models in which the energy of the molecular solid (lower curve in Fig. 2) is determined by an empirical potential (such as RRY) obtained by fitting experimental data and the energy of a monatomic bcc metal (middle curve) calculated by local-density approximation (LDA) electron band theory.[21] These two curves in Fig. 2 show a striking resemblance to the two plotted for H_2-H_2 and H_4 in Fig. 1. In particular, the energy minimum in the metal and H_4 string occur at about the same interatomic spacing, suggesting that there exists a fundamental relationship between pairs of molecules to strings and solids.

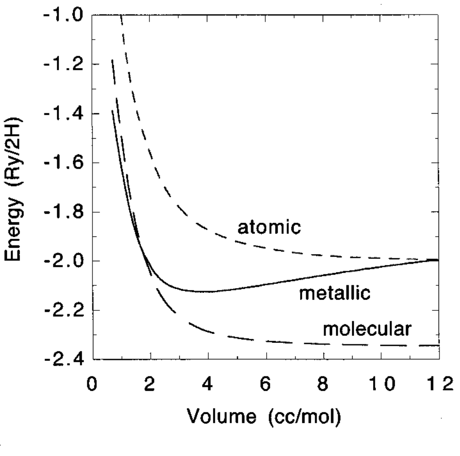

FIG. 2. Energy vs volume/(2H atoms) for lattices of molecular (lower curve), metallic (middle curve), and atomic hydrogen (upper curve).

With increasing density the energy of the molecular phase rises exponentially while the energy of the metallic structure decreases to a minimum at very nearly the same volume. At much higher densities the metallic structure becomes more stable than the molecular, leading to a first-order insulator-metal transition. This is not the case for the uppermost curve in Fig. 2. This curve represents the energy of a close-packed lattice in which hydrogen atoms interact by the short range H-H potential of Saumon and Chabrier.[14,15] This curve shows no energy minimum.

At low density the energy of the atomic lattice converges to that of the metal (middle curve) and both are offset from the molecular energy by the dissociation energy. With increasing compression, the energy of the atomic lattice parallels that of the molecular phase and never crosses into an insulator-metal transition. However, a transition can be created for the dense plasma by adding an attractive polarization potential to describe interactions in a partially ionized mixture between charged and neutral species.[15]

If we naively transfer the theory of chemical equilibrium for a dissociating gas to that for the dissociation of a shocked liquid, then we should expect the partially dissociated fluid to be some hybrid mixture made up, principally, of the lowest energy states; the molecular and metallic phase. Since we know that the electrons in H_2 are highly localized and the electrons in the metal are itinerant, it then follows that a partially dissociated mixture will be characterized by states of intermediate energy with intermediate fractions of localized and itinerant bonding. At very high temperature, when kT is comparable or greater than the metal Fermi energy, hydrogen will be a dense, partially ionized, plasma of atoms, ions, and electrons and outside the scope of the present model.

B. The linear mixing approximation

The linear-mixing model assumes that the Helmholtz free energy of the dissociating mixture is a functional that can be approximated by the composition average of the free energy of the pure molecular and metallic hydrogen equations of state. The composition is determined by minimizing the free energy. This approximation has the important practical feature that it interpolates the equation of state smoothly from the normal molecular liquid to the metallic fluid at extreme conditions that closely tracks the trajectory of the shock experiments. To quantify the model we write the Helmholtz free energy (per two particles) as

$$F=(1-x)F_{\mathrm{mol}}+xF_{\mathrm{met}}-TS_{\mathrm{mix}}, \tag{2}$$

where F_{mol} is the free energy of the molecular fluid and F_{met} is the free energy of the metallic fluid. x is the fraction of dissociated molecules and is determined by minimizing F. S_{mix}, is the entropy of mixing of H_2 and H,

$$S_{\mathrm{mix}}=-k\{(1-x)\ln[(1-x)/(1+x)]+2x\ \ln[2x/(1+x)]\}.$$

For the purpose of equation of state calculations, the energy of mixing is generally a small term and is neglected. Lengthy Monte Carlo simulations for the equation of state of binary ionic mixture fluids in a uniform negative background show that deviations from the linear-mixing rule are small.[22] The pressure and energy of the fluid are obtained by differentiating the free energy:

$$P=(1-x)P_{\mathrm{mol}}+xP_{\mathrm{met}} \tag{3}$$

and

$$E=(1-x)E_{\mathrm{mol}}+xE_{\mathrm{met}}. \tag{4}$$

The linear-mixing approximation does not imply that the mixture consists of clumps of molecular fluid and clumps of metallic fluid, nor does it assume that atoms and molecules are homogeneously mixed, but rather that the free energy of the entire system is a functional that can be expressed as the composition average of these two states of the element. The approximation is equivalent to assuming that the energy of interaction ϕ_{12} between particles 1 and 2 can be written as the average of ϕ_{11} and ϕ_{22}, the interaction between the particles in the pure components,

$$\phi_{12}=(\phi_{11}+\phi_{22})/2. \tag{5}$$

Thus, linear mixing has the attractive feature in that it allows us to avoid specifically defining the interaction energy between unlike species, which includes the effects of chemical bonding, a subject of which we lack sufficient knowledge to model. In many respects, the present model is similar to Landau's two-fluid model for liquid ^{4}He in which the mixture is presumed to consist of thermal excitations of phonons and rotons.

The free energy of the molecular fluid is calculated using soft-sphere fluid variational theory,[13]

$$F_{\mathrm{mol}}=F^0_{\mathrm{mol}}+F_{\mathrm{ref}}+F_{\mathrm{int}}. \tag{6}$$

The first term is the free energy of the ideal gas, and includes the translational, vibrational, rotational terms, and the dissociation energy. F_{ref} is the free energy of the soft-sphere reference system and F_{int} is the contribution of the free energy due to molecular interactions and is calculated using the RRY potential obtained by fitting the theory to the shock data below 210 kbar. The general equations for F_{mol} and F_{met} are summarized here for ease of presentation, but the specific expressions are given in Holmes and co-workers.[9]

The free energy of the metallic fluid is written in terms of the liquid metal, nearly free-electron, perturbation theory using a one-component plasma (OCP) reference system:[23]

$$F_{\mathrm{met}}=F^0_{\mathrm{trans}}+E_{\mathrm{bcc}}+F_{\mathrm{thocp}}+F_1. \tag{7}$$

F^0_{trans} is the H-ion translational free energy. E_{bcc} is the lattice energy of bcc metallic hydrogen,[21] and F_{thocp} is the thermal free energy of the OCP.[24] F_1 is the first-order correction to the Helmholtz free energy due to electron-ion screening. An expression for this term has been derived by Galam and Hansen,[25]

$$F_1=\frac{NkT}{3\pi}\int_0^\infty S(q)w(q)q^2dq,$$

where $S(q)$ is the structure factor of the ionic fluid, and $w(q)$ is the perturbation potential due to electron screening. $w(q)$ is written in terms of the form factor for the electron-ion interaction and the dielectric constant. F_1 is negative definite and acts to lower the free energy.

Experience has shown that for the purpose of calculating accurate liquid metal properties at high pressure using perturbation theory, $w(q)$ must be fitted to data. Rather than attempt to calculate $S(q)$ and fit $w(q)$, we have treated F_1 as an empirical function and fitted it to the shock temperature measurements of Holmes and co-workers.[9] For simplicity, we assumed that $F_1 = \delta ekT$. The value of $\delta e = -2.0$/atom was determined by impedance matching the pressure and shock particle velocity (Up) of the model against the P-Up curve of the LiF or sapphire optical window. δe was adjusted to fit the shock temperature measurements[9] and predict the final volume and pressure. δe was not readjusted to fit the laser shock compression experiments that were carried out afterward.[10] Since F_1 is linear in T, it is effectively an entropy or reference free-energy term and does not appear in the pressure or energy. Viewed as an entropy term, F_1 can also be interpreted as a weighting to the density of states to account for the large number of fluctuating chemical configurations that appear in the fluid and needs to be properly included in a statistical counting.

It should be apparent that any attempt to accurately characterize the properties of a system as complex as a partially dissociating mixture at extreme conditions will require some degree of chemical intuition and empirical approximations. However, by starting with a metalliclike fluid we have a more realistic model and one that simplifies the fitting procedure. By fitting F_1 to a single data point, we obtain an effective interatomic potential that is, in effect, the correction to the free energy for all the inadequacies of the model. Other modeling approaches to this problem, such as those employing H-H_2 and H-H repulsive potentials, would find it necessary to fit several parameters to the experimental data in order to obtain an accurate EOS. The calculated values of F_1 are comparable to those for the screening correction to the free energy extrapolated to higher density from the Monte Carlo results of Hubbard and Dewitt.[26]

Minimization of F with respect to x leads to an expression for the fraction dissociated:

$$x = \sqrt{q}/(4+q),$$

where

$$q = \mathrm{Exp}(-(F_{\mathrm{met}} - F_{\mathrm{mol}})/kT).$$

This expression may be written as

$$q = (Q_{\mathrm{H}}^2/Q_{\mathrm{H2}})\mathrm{Exp}(-D_e/kT), \tag{8}$$

where the effective dissociation energy is

$$D_e = (E_{\mathrm{bcc}} - E_{\mathrm{mol}})_{T=0} + \Delta F_{\mathrm{th}}. \tag{9}$$

The Q's are the ideal gas translational, rotational, and vibrational partition functions of the atom and molecule and ΔF_{th} is the change of the thermal free energy. At $T = 0$ K, D_e is equal to the difference in the energy between the metal and molecular phases. D_e reduces to the gas phase value at low density and with increasing density it decreases monotonically and goes to zero at the insulator metal to metal transition that for this model is near 3.6 Mbar.

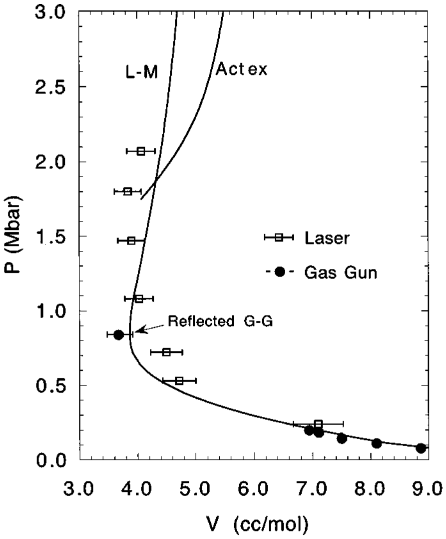

FIG. 3. Summary of shock experiments and linear-mixing model $(L$-$M)$ and Actex calculations for shock-compressed liquid deuterium. Single shock liquid experiments (Refs. 7–9) made with the LLNL two-stage gas gun are shown as black circles. The gas-gun points plotted are representative of a much larger data set. Initial conditions are at atmospheric pressure and $V_o = 23.6$ cc/mol and $T_o = 20.3$ K and reach final pressures of up to about 210 kbar with reflected shock gas-gun experiments to 0.8 to 0.9 Mbar. Laser driven shock experiments (open squares) extend the experimental range to 2.1 Mbar (Ref. 10).

III. RESULTS

The experimental results and model calculations obtained for shock-compressed deuterium are plotted in Fig. 3. For ease of presentation the data is reviewed in chronological order.

(1) Single shock experiments made on the LLNL two-stage light gas gun,[7–9] starting from the liquid, reach final pressures up to about 210 kbar. These points are summarized by the black circles. They represent the sampling of a much larger data set. Up to 210 kbar the fraction of dissociation is small (2% and less). The data was fitted using soft-sphere fluid theory to obtain the RRY H_2-H_2 pair potential.[13] This model provides the molecular contribution (F_{mol}) to the free energy of the linear-mixing model.

(2) Double shock experiments in which the liquid is reshocked from near 210 kbar to about 0.8–0.9 Mbar.[7,8] These points are represented by a single black circle with an error bar. Calculations using the soft-sphere theory modified to include H-H_2, H-H interactions[13–15] are in agreement with P-V measurements. However, no temperature measurements were then available with which to validate predictions in the 7000 K range.

(3) The first shock temperature measurements on deuterium were carried out by Holmes and co-workers.[9] Measurements were made for single shocks up to 210 kbar and 4500 K and reflected shocks to about 0.8–0.9 Mbar. The reflected shock temperatures were found to be near 5000 K. This is lower than predicted by previous models by about 2000 K and lead to the development of the linear-mixing model. The F_1 term in the free energy [Eq. (7)] was determined by impedance matching the theoretical equation of state to the

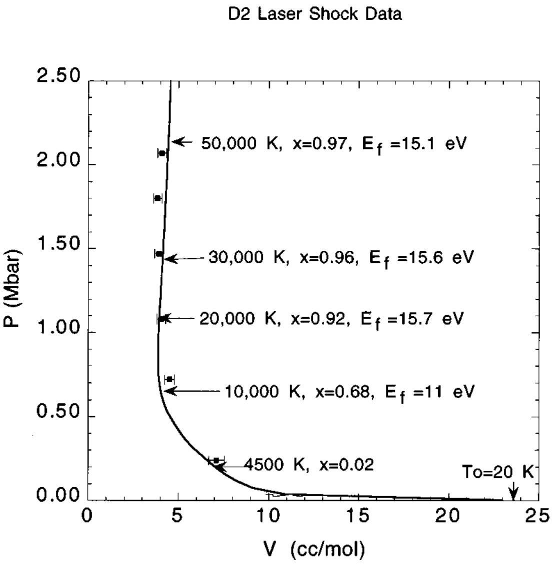

FIG. 4. Experimental laser shock data for deuterium with calculated, Hugoniot, shock temperatures, dissociated fractions (x), and Fermi energies (E_f) at selected pressures.

pressure and particle velocity of the reflecting anvils as described in Sec. II B.

(4) Laser shock experiments extended the experimental range to 2.1 Mbar.[10] These measurements, shown by error bars with open circles, are in reasonable agreement with prior predictions made by the linear-mixing model. The success of the model is at least partly due to the fact that the volume of the reflected shock data point of Holmes near 0.84 Mbar overlaps the volume at maximum compression attained by the laser generated Hugoniot.

Although the temperature has as yet not been measured along the portion of the Hugoniot generated by the laser, the calculated values provide some insight to the nature of fluid at these conditions. Figure 4 shows a plot of the Hugoniot and the calculated temperatures, dissociated fractions (x), and Fermi energies at selected pressures. The temperature rises from 4500 K at 0.21 Mbar to 10 000 K near 0.65 Mbar with 68% of the molecules dissociated. In the region of calculated maximum compression, near 0.9 Mbar, the temperature is about 15 000 K with 90% of the molecules dissociated. The degree of dissociation increases continuously to about 97% at 2.1 Mbar, the highest pressure achieved experimentally. The calculation of the Fermi energy (E_f) is based on the atom density in the dissociated fluid and leads to values of 11 eV at 0.65 Mbar and 15.7 eV at 1.1 Mbar. These energies are an order of magnitude greater than kT. Therefore, deuterium at these conditions can be considered a nearly fully degenerate liquid metal and thermal corrections due to electronic excitations can be treated as negligible.

At temperatures above 50 000 K (above 2.2 Mbar) the thermal energy becomes a significant fraction of the Fermi energy and corrections for nondegeneracy and plasma effects such as charge transfer, highly excited electrons, and electron shell ionization may all occur. Above this temperature the validity of the condensed matter approach taken by the linear-mixing model becomes questionable. While the problems associated with dense, high-temperature matter have not been solved in a comprehensive way, a partial solution can be found in the activity expansion (ACTEX) method which approximates the quantum-mechanical partition function of a mixture of atoms, ions and electrons.[27] The ACTEX method is exact in the weakly-coupled plasma limit of high temperature, but becomes progressively less accurate as the temperature is lowered and molecular states are formed. In the case of deuterium its region of validity extends down to about 60 000 K. Recently, Rogers and Young[28] reported the Hugoniot calculations made with ACTEX shown in Fig. 3. The agreement between ACTEX and the present model is good, but mixed. Although the pressures calculated by the two models are in agreement near 2 Mbar, they begin to diverge at higher pressure. Calculated temperatures for the two models agree to within 10% over the pressure range 2 to 4 Mbar.

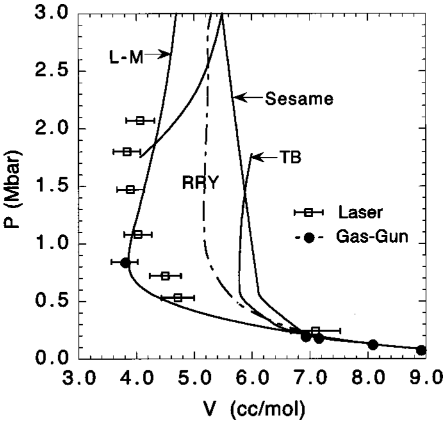

FIG. 5. Experimental shock data for deuterium with calculations from several models: linear-mixing (Fig. 3), RRY (Ref. 13), Sesame (Ref. 31), and tight-binding (TB) (Ref. 30).

A number of Hugoniot calculations have been made for deuterium using very different models. Some of these are shown in Fig. 5. In addition to the present results, these include RRY,[13] Sesame,[29] and the tight-binding molecular-dynamics calculations of Linofsky.[30] Saumon and Chabrier[14,15] have examined the EOS of deuterium but we are not aware of any reported single shock Hugoniot calculations to megabar pressures by these workers. However, unpublished results[31] place the Saumon and Chabrier Hugoniot between the present model and RRY. All the models are in agreement with the Hugoniot data over the pressure range up to 0.21 Mbar where the fluid is molecular. Above this pressure dissociation occurs and the different models demonstrate considerable disagreement. Of these, the tight-binding Hugoniot differs most dramatically. Starting from 0.21 Mbar, the Hugoniot rises steeply and reaches the perfect gas limit $(V/V_o \sim 4)$ near 0.5 Mbar, indicating complete dissociation.

IV. DISCUSSION

Now that comparisons with experimental data have demonstrated the utility of the model, let us consider some insights regarding the nature of the fluid that follow directly. In this regard, a very interesting property is $(\partial P/\partial T)_V$, the variation of pressure with temperature. This derivative depends sensitively on the temperature dependence of the composition.

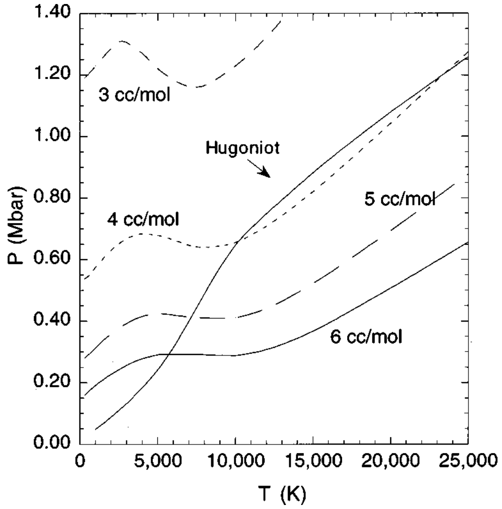

FIG. 6. Calculated isochores and the liquid deuterium Hugoniot plotted as pressure vs temperature.

Figure 6 shows a plot of isochores predicted by the linear-mixing model over the range of volume of greatest interest to the present study. The calculations show that the pressure increases with increasing temperature up to about 4000–5000 K. Further increases in temperature leads to a rapid increase in dissociation, Fig. 7, accompanied by a lowering of the pressure with values of $(\partial P/\partial T)_V < 0$. At about 10 000 K the dissociation is 80% completed and above this temperature the pressure increases again. This feature has important consequences for the Hugoniot, which passes directly through the range of negative or small values of $(\partial P/\partial T)_V$.

In the Grüneisen model, the pressure at some reference state, T_1, V, is related to the pressure at a second state, T_2, V, by

$$P(T_2,V)=P(T_1,V)+\gamma[E(T_2,V)-E(T_1,V)]/V.$$

The second term is the thermal pressure and γ is the Grüneisen parameter

$$\gamma=(V/C_V)(\partial P/\partial T)_V=V(\partial P/\partial E)_V.$$

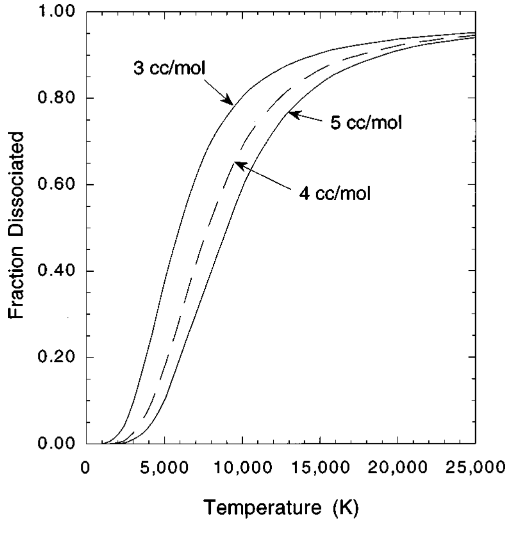

FIG. 7. Calculated fractions of D_2 molecules dissociated vs temperature at several volumes.

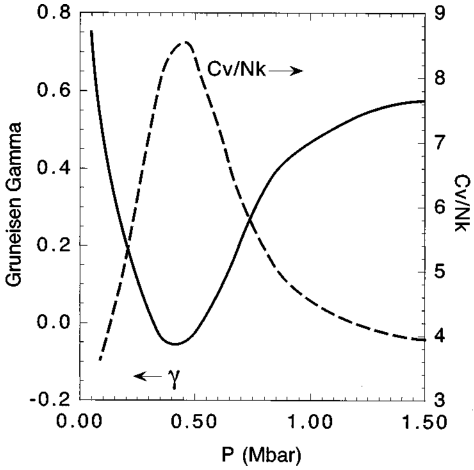

FIG. 8. Gruneisen Gamma (γ) and reduced heat capacity (C_V/Nk) vs pressure calculated along the Hugoniot.

Figure 8 shows a plot of γ and C_V/Nk, the reduced constant volume heat capacity, as a function of pressure along the Hugoniot. Since C_V/Nk peaks near 0.5 Mbar and 7500 K, and $(\partial P/\partial T)_V$ is small or negative, this leads to small or negative changes in the thermal pressure as illustrated by the Grüneisen model, making the fluid more compressible and increasing the maximum density to which deuterium can be shocked.

Plotted in Fig. 9 are isochores, at a volume of $V=6$ cc/mol, predicted by the linear-mixing model and path-integral quantum Monte Carlo.[11] QMC predicts that, starting from 5000 K, the pressure decreases with increasing temperature, reaching a minimum near 10 000 K, and then increases with increasing temperature. Over this temperature range, 5000 to 10 000 K, the linear-mixing model predicts that the dissociation fraction rises from 6% to 70%. Unpublished QMC (Ref. 32) calculations show the same qualitative features persist to higher densities. It is noteworthy that the QMC calculations are unable to converge correctly to the

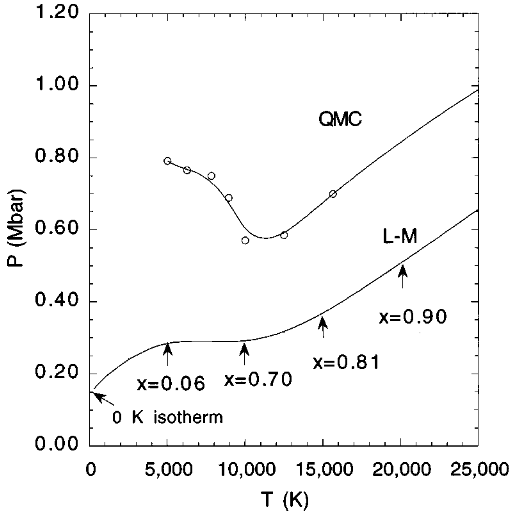

FIG. 9. Comparison of isochores calculated by the linear-mixing model and quantum Monte Carlo method (Ref. 11) for hydrogen at $V=6$ cc/mol ($r_s=2.0$). Listed at several temperatures are the linear-mixing predictions for the fraction of H_2 dissociated. The linear-mixing isochores converge to the low-temperature experimental solid isotherm.

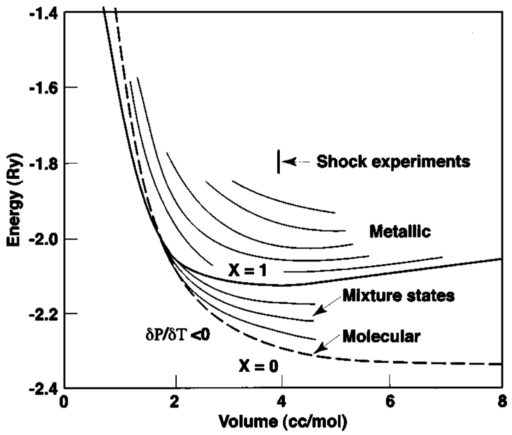

FIG. 10. Schematic description of the energy states of the linear-mixing model. The lower solid line is the energy of the molecular solid ($x=0$). The upper solid line is energy of the bcc metal obtained by an LDA electron band theory calculation ($x=1$). The difference in energy between the two curves at any volume is the effective dissociation energy, D_e at $T=0$ K. The intermediate curves represent energies for states with a dissociation fraction x, with x increasing in the vertical direction. Shock wave experiments extend down to about 3.8 cc/mol near the minimum energy of the metal.

low-temperature limit of the experimental 0 K isotherm. This points to the fact that QMC is currently in a developmental stage, and its validity to accurately predict the equation of state for hydrogen has not yet been benchmarked by a comparison with shock experiments. In addition, we can find no evidence in our calculations for the presence of the critical point reported by Magro near 11 000 K.[11] Over this temperature range linear-mixing model isotherms cross because $(\partial P/\partial T)_V<0$. But, van der Waals-like loops in the isotherm, indicative of a critical point, do not appear.

The physical origin for negative values of $(\partial P/\partial T)_V$ is described schematically in Fig. 10. The lower solid line is the energy of the molecular solid ($x=0$) calculated with the RRY potential. The upper solid line is energy of the bcc metal obtained by an LDA electron band theory calculation and which represents the completely dissociated limit ($x=1$). The intermediate curves represent partially dissociated states with energy $E(x)$, with dissociation fraction x, which increases in the vertical direction. At temperatures above complete dissociation ($x=1$), the increase in energy is the result of thermal ion motion. For the conditions considered here, the Fermi energy is sufficiently large compared to the temperature so that the effects of electron excitation are negligible.

Since the energy of the molecular curve ($x=0$) is continually increasing with decreasing volume, its pressure is always positive. In contrast, the binding energy of the metal curve decreases slowly with decreasing volume and reaches a minimum near 4 cc/mol before increasing at smaller volumes and intersecting the molecular curve near the insulator-metal transition. The point of maximum shock compression is near the minimum of the metal binding energy curve. Since all of the partially dissociated states lying between the molecular and metallic phases are composition averages, they will have intermediate values of the pressure. Since $P_{\text{met}}<P_{\text{mol}}$, then for each molecular fraction (δx) that is dissociated at constant volume a negative contribution, $\delta P=(P_{\text{met}}-P_{\text{mol}})\delta x$, is made to the total pressure, and $\delta P/\delta T\sim(\partial P/\partial T)_V$.

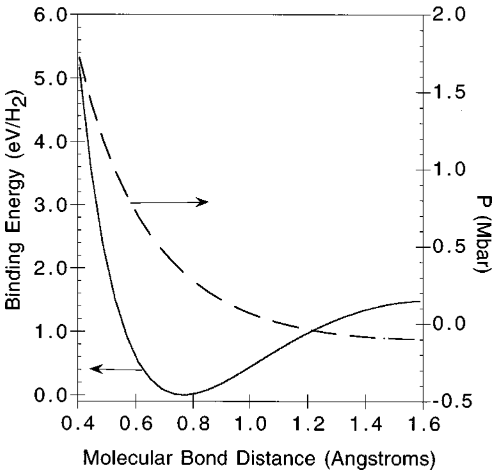

FIG. 11. LDA calculation of the total energy and pressure of an hcp lattice of hydrogen molecules at 0 K (Ref. 33) as the intramolecular bond distance is varied at a constant volume of 4 cc/mol.

Further evidence that dissociation is accompanied by a decrease in pressure, can be drawn from an LDA calculation of the total energy of an hcp static lattice of hydrogen molecules in which the intramolecular bond distance is varied while the volume is held constant.[33] The results of the calculation are shown in Fig. 11. They were made at 4 cc/mol. This is near the maximum compression of the Hugoniot and represents a vertical cut in Fig. 10 at this volume. As the H_2 bond length is shortened from the position of minimum vibron energy, the pressure and energy of the lattice increase. However, expansion of the bond leads to an increase in the energy that flattens near the cell boundary as the metallic state is reached, but the pressure decreases continuously to near zero at the cell boundary. The decrease in pressure reflects the change in electron bonding in going from a localized state in the molecule to an itinerant one in the metal with an accompanying decrease in the electron kinetic energy. It takes only a small leap of intuition to identify the increase in bond distance in going from the molecular to metallic state with the increase in the composition averaged atom-atom separations in the dissociating mixture.

This interpretation is consistent with QMC results[11] that show that, like the pressure, the total electron kinetic energy decreases with increasing temperature and reaches a minimum near 10 000 K before rising again near 60 000 K. This rise is likely due to thermal excitation of conduction electrons in the metal phase. The initial reduction of kinetic energy indicates that in a dense dissociating fluid the electrons are shared by a larger grouping of atoms, thereby extending their wave function in space and lowering the kinetic energy. If a molecule dissociated directly to atoms in the repulsive $^3\Sigma_u$ state, the electron kinetic energy would rise, and not drop. This is the origin of the repulsive H-H interatomic potential.[34]

In contrast to QMC and the present work, Linofsky[30] find that the tight binding EOS is smooth and featureless, and, in particular, $(\partial P/\partial T)_V$ is positive everywhere. Their use of a limited basis set of a single 1s orbital on each atom excludes the additional bound states that can act as a thermal sink to absorb some of the shock energy. These additional states limit the temperature rise and reduce the dissociation. Instead, the molecules dissociate into the repulsive $^3\Sigma_u$ state and the Hugoniot rises rapidly to the monatomic gas limit. Such a model is consistent with the stiff, relatively incompressible, Hugoniot (TB) they calculated, as is shown in Fig. 5.

While the present model differs from other approaches to hydrogen it is consistent with our current understanding of matter at extreme conditions. For example, local-density calculations for solid nitrogen predict the presence of a number of polymeric structures with total energies intermediate between the molecular and metallic crystal[35] and the presence of such states in the dissociating mixture are believed to be responsible for the softening of the liquid Hugoniot and shock cooling.[36,37] Thermal pressure effects analogous to those found in hydrogen, but due instead to electron excitation, are also known to occur in the shock-compressed inert gas liquids. For example, in the case of argon[38] and xenon,[39] the energy of the highest filled p-like valence band increases with compression and intersects the empty d-like conduction band resulting in an insulator to metal transition at megabar pressures. Schematically, the inert gas electron energy diagram is similar to Fig. 10. The filled valence band is the analog of the rapidly rising molecular curve and the empty d-like conduction band is the analog of the nearly flat metallic binding curve. The electron band gap, which is analogous to the dissociation energy, decreases with decreasing volume, leading to enhanced thermal excitation and introduces a negative contribution to the pressure. This results in a considerable softening of the liquid inert gas Hugoniot.

V. SUMMARY

The linear-mixing model is based on the assumption that the thermodynamic properties of the dissociating mixture can be described by the free energy of the composition average of the molecular and metallic hydrogen phases. This ansatz builds in the correct limiting behavior for the molecular phase at normal liquid density and interpolates smoothly to the monatomic-metallic fluid at high density. Model calculations are in agreement with all the available shock measurements for liquid deuterium. Recent measurements of the Hugoniot and sound speed of deuterium up to 276 kbar further confirm the predictions of the model.[40]

There are several reasons for the success of the model and these involve some mixture of theory and phenomenology. First, the model leads to negative values of $(\partial P/\partial T)_V$ in the range 5000 to 10 000 K. This implies that it does in fact mimic some of the changes in chemical bonding described by the fully quantum mechanically based QMC method.

The quantitative success is at least partially due to the fact that the reflected shock data points of Holmes and coworkers near 0.8–0.9 Mbar and about 5000 K, which are used to fit the F_1 term in the free energy, is at the volume of the maximum compression attained by the laser generated shock experiment. This point overlaps both the gun and laser experiments. The good agreement of the theory with both data sets argues for the consistency of the two experimental methods. Another reason for the practical success of the model is that molecular dissociation along the Hugoniot occurs over a relatively narrow range of conditions and linear mixing provides a reasonable interpolation scheme.

Finally, the combined results of the linear-mixing model and QMC calculations suggests the following picture for shock-compressed deuterium. In the temperature range below 10 000 K, partial dissociation leads to the formation of strings and clusters of atoms characterized by a decrease in the electron kinetic energy resulting in a small or negative $(\partial P/\partial T)_V$. With increasing temperature, above 1 Mbar, the clusters, strings, etc., are dissociated to form a nearly degenerate monatomic-metallic fluid. At about 2.5 Mbar and 60 000 K, the temperature is a substantial fraction of the Fermi energy and thermal excitation of electrons leads to a rise in the electron kinetic energy and an approach to the dense plasma regime.

ACKNOWLEDGMENTS

We are grateful to Dr. Lin H. Yang for carrying out the LDA calculations in Fig. 11 and to the many colleagues in H-Division/Physics Dept. for their valuable contributions. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

---

[1] J. D. Lindl, Phys. Plasmas **2**, 3933 (1995).

[2] S. Nakai and H. Takabe, Rep. Prog. Phys. **59**, 1071 (1996).

[3] D. J. Stevenson, Annu. Rev. Earth Planet Sci. **10**, 257 (1982).

[4] G. Chabrier, D. Saumon, W. B. Hubbard, and J. I. Lunine, Astrophys. J. **391**, 817 (1992).

[5] P. Loubeyre, R. LeToullec, D. Hauserman, M. Hanfland, R. J. Hemley, H. K. Mao, and L. W. Finger, Nature (London) **383**, 702 (1996).

[6] M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6, pp. 1–63.

[7] M. van Thiel, L. B. Hord, W. H. Gust, A. C. Mitchell, M. D'addario, K. Boutwell, E. W. Ibarger, and B. Barrett, Phys. Earth Planet. Inter. **9**, 57 (1974).

[8] W. J. Nellis, A. C. Mitchell, M. van Thiel, G. J. Devine, and R. J. Trainor, J. Chem. Phys. **79**, 1480 (1983).

[9] N. C. Holmes, M. Ross, and W. J. Nellis, Phys. Rev. B **52**, 15 835 (1995).

[10] L. B. Da'Silva, P. Cellers, G. W. Collins, K. S. Budil, N. C. Holmes, T. W. Barbee Jr., B. A. Hammel, J. D. Kilkenny, R. J. Wallace, M. Ross, and R. Cauble, Phys. Rev. Lett. **78**, 483 (1997).

[11] W. R. Magro, D. M. Ceperley, C. Pierleoni, and B. Bernu, Phys. Rev. Lett. **76**, 1240 (1996).

[12] I. Kwon, L. A. Collins, J. D. Kress, N. Troullier, and D. L. Lynch, Phys. Rev. E **49**, R4771 (1994).

[13] M. Ross, F. H. Ree, and D. A. Young, J. Chem. Phys. **79**, 1487 (1983).

[14] D. Saumon and G. Chabrier, Phys. Rev. A **44**, 5122 (1991).
[15] D. Saumon and G. Chabrier, Phys. Rev. A **46**, 2084 (1992).
[16] C. F. Bender and H. F. Schaeffer, J. Chem. Phys. **57**, 217 (1972).
[17] M. Rubenstein and I. Shavitt, J. Chem. Phys. **51**, 2014 (1969).
[18] H. H. Michels and R. H. Hobbs, Astrophys. J. **286**, L29 (1984).
[19] H. K. Mao and R. J. Hemley, Rev. Mod. Phys. **66**, 671 (1994).
[20] V. Natoli, R. M. Martin, and D. M. Ceperley, Phys. Rev. Lett. **70**, 1952 (1993).
[21] T. W. Barbee and M. L. Cohen, Phys. Rev. B **44**, 11 563 (1991).
[22] H. DeWitt, W. Slattery, and G. Chabrier, Physica B **228**, 21 (1996).
[23] D. A. Young and M. Ross, Phys. Rev. B **29**, 682 (1984).
[24] W. L. Slattery, G. D. Doolen, and H. E. DeWitt, Phys. Rev. A **21**, 2087 (1980).
[25] S. Galam and J. P. Hansen, Phys. Rev. B **14**, 816 (1976).
[26] W. B. Hubbard and H. E. DeWitt, Astrophys. J. **290**, 388 (1985).
[27] F. J. Rogers, in *The Equation of State in Astrophysics*, edited by G. Chabrier and E. Schatzman (Cambridge University Press, New York, 1994).
[28] F. J. Rogers and D. A. Young, Phys. Rev. E **56**, 5876 (1997).
[29] G. I. Kerley, Los Alamos Scientific Report No. LA-4776, 1972 (unpublished).
[30] T. J. Linofsky, J. D. Kress, and L. A. Collins, Phys. Rev. B **56**, 5164 (1997).
[31] J. D. Johnson (private communication).
[32] W. R. Magro and D. M. Ceperley (private communication).
[33] L. H. Yang (private communication).
[34] M. Vos and I. McCarthy, Am. J. Phys. **65**, 544 (1997).
[35] C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14 419 (1992).
[36] H. Radousky, W. J. Nellis, M. Ross, D. C. Hamilton, and A. C. Mitchell, Phys. Rev. Lett. **57**, 2419 (1986).
[37] M. Ross, J. Phys. Chem. **86**, 7110 (1987).
[38] M. Ross, W. J. Nellis, and A. C. Mitchell, Chem. Phys. Lett. **68**, 532 (1979).
[39] M. Ross, Phys. Rev. **171**, 777 (1968).
[40] N. C. Holmes, W. J. Nellis, and M. Ross (unpublished).