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Isentropes and Hugoniot curves for dense hydrogen and deuterium

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Multiple-shock experiments with fluid hydrogen have shown that a transition from semiconducting behavior to metal-like conductivity occurs at pressures (p) of about 140 GPa and temperatures (T) near 3000 K. We model the p-T pathway by Hugoniot curves (initial shock) and isentropes (subsequent shocks). For the calculation of these curves we apply an expression for the free energy developed recently for dense hydrogen and deuterium plasma in the regions of partial dissociation and partial ionization. Furthermore, we discuss the relations between Hugoniot curves, isentropes and the coexistence line of the plasma phase transition.

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I. INTRODUCTION

The behavior of fluid hydrogen and deuterium derived from recent shock-wave experiments shows distinct features at Mbar pressures (1 Mbar=100 GPa) and finite temperatures. While metallization of solid hydrogen near $T=0$ K has not been verified up to 300 GPa so far, metallic-like conductivities have been observed in shock-compression experiments using a two-stage light gas gun in the fluid domain around 140 GPa and 3000 K [1]. Furthermore, significant discrepancies between the Hugoniot curves derived from laser-driven shock-wave experiments [2,3] and theoretical equations of state such as the Sesame tables [4] have been found in the Mbar region where fluid hydrogen shows a higher compressibility than predicted. New results from molecular dynamics simulations within the generalized gradient approximation of density functional theory [5,6] and from path-integral Monte Carlo simulations [7] are closer to the Hugoniot curve derived from the Sesame tables. Both effects, the transition to metallic-like behavior and the increased compressibility, would change our present understanding of the behavior of hydrogen at ultrahigh pressures relevant for models of planetary and stellar interiors and inertial confinement fusion studies.

In the present Rapid Communication we start from a recently derived expression for the free energy [8,9] and calculate the isothermal equation of state (EOS), the isentropes and the Hugoniot curve. We assume that isentropes and Hugoniot curves are theoretical idealizations of the real compression process. While single-shock compression as well as the initial shock of a multishock compression are described by Hugoniot curves, the subsequent multishock compression process is close to an isentrope. As is well known, the pressure along isentropes increases much faster with the temperature than along Hugoniot curves. Therefore, the calculation of a set of Hugoniot curves and isentropes gives an orientation how the real multishock compression process proceeds in the pressure-temperature plane.

Nearly isentropic parts of the compression curve may also cross the coexistence line of the plasma phase transition (PPT), which has been predicted to follow almost an isobar; see Refs. [8,9]. Multishock compression experiments are, therefore, candidates to verify the existence or nonexistence of this phase transition.

II. EQUATION OF STATE AND ISENTROPES

This paper is based on an approach to the free energy of dense hydrogen plasmas which was applied to temperatures between 2000 and 10 000 K [8,9]. The effects of pressure dissociation, $H_2 \rightleftharpoons 2\mathrm{H}$, and ionization, $H \rightleftharpoons e+p$, are taken into account so that the transition from a molecular fluid at low temperatures and pressures through a partly dissociated, warm fluid at medium temperatures of some thousand Kelvin to a fully ionized, hot plasma above 10 000 K can be explained.

The free energy expression for a two-component system of neutral (F_0) and charged particles ($F_{\pm}$),

$$F(V,T,N)=F_0(V,T,N)+F_{\pm}(V,T,N), \tag{1}$$

combines results for the fully ionized plasma domain [10] with improved data for the dense, neutral fluid calculated within a dissociation model [11,12]. Both contributions to the free energy are split into ideal and interaction parts. We take into account the interactions in the neutral and in the charged subsystem, respectively, whereas the interaction between charges and neutrals is accounted for by the reduced-volume concept.

We have performed classical Monte Carlo simulations for partially dissociated, fluid hydrogen for a grid of temperature and density points in the region of $T=(2-10)\times 10^3$ K and $\varrho=(0.2-1.1)$ g/cm^3. Effective pair potentials of the exponential-6 form have been used to model the interactions between the molecules and atoms in the dense fluid. The dissociation equilibrium $\mathrm{H}_2 \rightleftharpoons 2\mathrm{H}$ has been solved taking into account the correlation parts of the chemical potentials using fluid variational theory. The Monte Carlo data for the interaction contribution can be interpolated accurately within an eight-parameter fit with respect to density and temperature leading to an analytical expression for the free-energy density; see Ref. [8].

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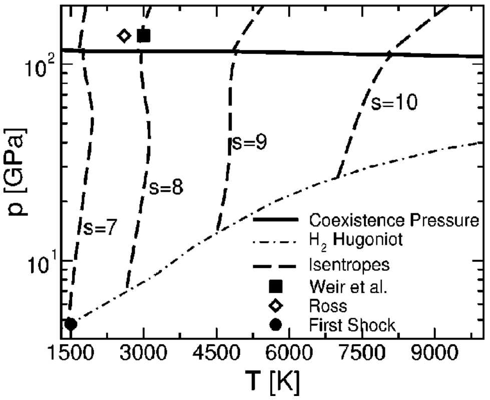

FIG. 1. Isentropes for different values of the specific entropy s, single-shock Hugoniot curve, and coexistence line of the PPT for hydrogen. The square (■) marks the location of the insulator-to-metal transition as found in the multishock experiments [1]. Insulator-to-metal transition (diamond, ◇) and final state of the first shock (closed circle, ●) according to the linear mixing model [14], respectively.

The interaction contributions of the charged component account for correlations and exchange in the electronic and ionic subsystem, and the electron-ion screening. They are treated in terms of Padé approximations which are based on analytical results for the quantum virial expansion. The ionization equilibrium of the plasma was calculated by minimizing the total free energy. The hydrogen EOS is also used for deuterium applying mass scaling; i.e., it is assumed that the same particle numbers for hydrogen and deuterium lead to the same degree of dissociation and to identical interaction contributions to the thermodynamic function of the neutral fluid for a given temperature.

Other thermodynamic functions can be calculated from free energy (1) by derivatives. For instance, the isothermal EOS follows by derivation with respect to the volume, and the entropy by derivation with respect to the temperature:

$$p=-\frac{\partial F(V,T,N)}{\partial V}, \quad S=-\frac{\partial F(V,T,N)}{\partial T}. \tag{2}$$

Combining these two expressions we get the pressure along an isentrope $p=p(s=\text{const},T)$, where $s=S/N_p k_B$ is the specific entropy per proton (N_p is the total number of protons in the plasma, including the protons bound in H and in H_2). Simple expressions for the isentropes were already calculated in Ref. [13]. Here we have used the expressions for the free energy given in Ref. [8].

Figure 1 shows a set of isentropes calculated for different values of the specific entropy s together with the single-shock Hugoniot curve and the coexistence line of the PPT for hydrogen within the present approach. The most interesting result is the completely different derivative $\partial p/\partial T$ of these three theoretical lines. The coexistence line is weakly decreasing with temperature and, therefore, almost an isobar. The Hugoniot curve is increasing with temperature, but rather slowly, and the derivative is decreasing with temperature. The isentropes are steeply increasing. We mention that the temperature decreases slightly along the low-temperature isentropes ($s=7$ and $s=8$) in the region between 60 and 110 GPa. A reliable discrimination of this behavior from an almost vertical slope is beyond the accuracy of our theory. The most important conclusion from Fig. 1 [14] is that according to our calculations single-shock Hugoniot curve and coexistence line of the PPT are well separated, while isentropes may cross the coexistence line due to their high slope.

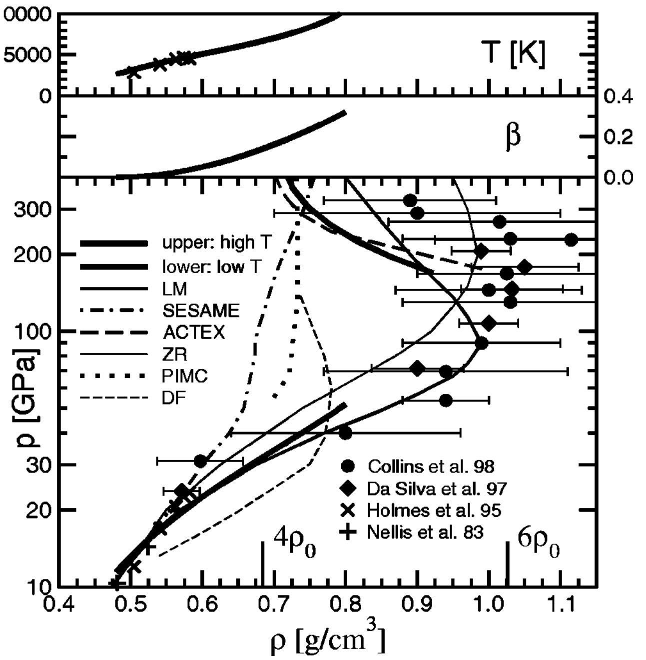

FIG. 2. Pressure along a single-shock Hugoniot curve of deuterium versus density (initial state; see text). Experimental data from laser-driven shocks (◆, ●) [2,3] and gas-gun experiments (×, +) [17] are compared with the present results in the low- and high-temperature branch, the linear-mixing model (LM) [15], the SESAME tables [4], density functional (DF) [5] and path-integral Monte Carlo (PIMC) simulations [7], the activity expansion method (ACTEX) [19], and a modified linear-mixing model (ZR) [16]. The temperature T and the degree of dissociation β are shown in the upper panels.

III. SINGLE AND MULTIPLE SHOCKS

In order to compare with experimental results, we have calculated the single-shock Hugoniot curve of deuterium D_2 with initial conditions (label 0) taken from the experiments, i.e., liquid deuterium with a density of $\rho_0=0.171$ g/cm^3 corresponding to a specific volume of $v_0=0.391\times10^{-25}$ cm^3 per molecule. The initial temperature is $T_0=19.6$ K, and the initial pressure is below 10^5 Pa. Figure 2 shows the resulting Hugoniot curve together with experimental data as well as with other theoretical calculations.

Along the single-shock Hugoniot curve temperatures of $T=(2-10)\times10^3$ K correspond to total D_2 mass densities of about $\varrho=(0.4\text{–}0.8)$ g/cm^3. In this range the proposed model (lower thick curve: low T) is in good agreement with the experimental data, the linear-mixing model (LM) of Ross [15], and a modified version of Zinamon and Rosenfeld (ZR) [16]. The calculated final-state temperatures (upper frame) are in good agreement with other estimates [17]. The increase in compression is associated with the onset of dissociation (middle frame), while the degree of ionization remains lower than 10^{-4} in the considered temperature range. At high pressures and temperatures, the Hugoniot curve enters the region of highly ionized plasma. There, the employed EOS reduces to a previous model (upper thick curve: high T) which describes thermodynamic properties by Padé approximations in the chemical picture (PACH) as introduced in Ref. [8]. The activity expansion method (ACTEX) of Rogers and Young [19] is also indicated in that region.

Even for very strong shocks the compression ratio $\eta = v_0/v_1 = \rho_1/\rho_0$ between initial and final state (label 1) cannot exceed a certain value; see Ref. [18]. The maximum compression for an ideal monoatomic gas is $\eta_{\max}=4$, while ideal diatomic gases can be compressed by a factor of 6 if the vibrational modes are frozen, and by a factor of 8 if these modes can be excited. Because compression is always accompanied by heating, increasingly strong shocks will eventually create temperatures where dissociation and ionization occur and $\eta=4$ is approached asymptotically. From the Hugoniot relation we derive a compression ratio

$$\eta = 4\frac{U_{\mathrm{kin},1}+U_{\mathrm{int},1}}{U_{\mathrm{kin},1}+\frac{1}{2}U_{\mathrm{int},1}} + \frac{3U_{\mathrm{bind},1}}{U_{\mathrm{kin},1}+\frac{1}{2}U_{\mathrm{int},1}} \qquad (3)$$

in this range by choosing $U_0=0$ and separating the internal energy $U=U_{\mathrm{kin}}+U_{\mathrm{int}}+U_{\mathrm{bind}}$ into a kinetic part (label kin), an interaction part (label int), and the binding energy (label bind) of atoms and molecules including energies of internal excitation. $U_{\mathrm{bind},1}$ denotes the difference in binding energy between final and initial state.

Equation (3) shows that dissociation and ionization energies lead to an increase in the density ratio while Coulomb interaction reduces the accessible compression range, i.e., the two effects tend to compensate each other. Note that for increasing final-state temperature T_1 the interaction energy $U_{\mathrm{int},1}$ decreases and $U_{\mathrm{bind},1}$ remains constant once complete dissociation and ionization is achieved. Since $U_{\mathrm{kin},1} \sim T_1$ the ideal gas value $\eta=4$ is approached again as $T_1 \to \infty$.

The above considerations impose a strong constraint on the Hugoniot curve at high pressures. Figure 3 depicts the Hugoniot curves according to the present EOS, the ACTEX method [19], and the Debye approximation together with the highest experimentally obtained pressures. The ACTEX and PACH curves separate below 4000 GPa corresponding to a temperature of about 600 000 K and a coupling parameter of $\Gamma_{\mathrm{ion}} \approx 0.25$ in a region of almost complete ionization. The Debye model and ACTEX coincide down to pressures of approximately 1000 GPa and temperatures of about 200 000 K, where the coupling parameter is almost 1.

Dissociation and ionization effects prevail for weakly coupled and partially ionized and dissociated plasma, hence $\eta > 4$. The dotted line in Fig. 3 (labeled ideal) corresponds to the Hugoniot curve of an ideal plasma model that neglects all interaction effects but includes the difference in binding energy between initial and final state. In the area of complete ionization and for initially molecular deuterium D_2, Eq. (3) reduces to a parametric representation of the ideal Hugoniot curve: $\eta = 4 + 184\,370\,\mathrm{K}/T_1$.

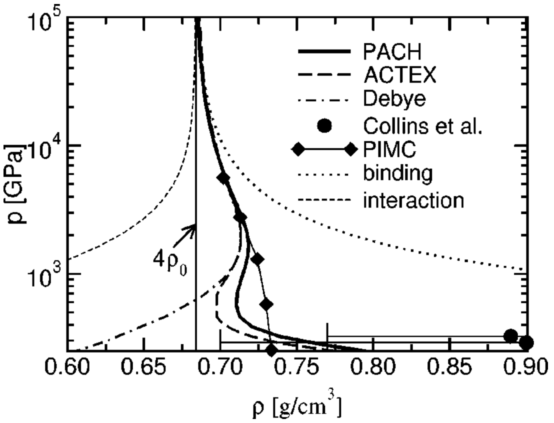

FIG. 3. Deuterium Hugoniot curves for ultrahigh pressures as obtained from the PACH (solid line) and ACTEX methods (dashed line) [19], path-integral Monte Carlo (PIMC) simulations [7], and the Debye approximation (dashed-dotted line). The highest experimental pressures (●) [3] are shown for comparison. The dotted curve (labeled ideal) corresponds to an ideal plasma model that neglects all interaction effects.

Multishock experiments allow one to generate higher pressures at lower temperatures than single-shock experiments. Analysis of the experimental data has shown [14,20] that the first of the reverberating shocks is a strong shock with $p_1/p_0 \approx 50\,000$, while the successive reverberations are much weaker ($p_{n+1}/p_n \gtrsim 1$) and can, therefore, be approximated by an isentrope. For this case, the entropy production during the shock is small and the increase in pressure along the Hugoniot curve is only slightly higher than along the corresponding isentrope. This is due to the fact that the first derivative $\partial p/\partial V$ and the second derivative $\partial^2 p/\partial V^2$ are identical along a Hugoniot curve and along an isentrope. We refer again to Fig. 1, which shows isentropes for different values of specific entropy s together with the single-shock Hugoniot curve and the coexistence line of the PPT in hydrogen. After the first shock, pressure and temperature reach values of about 4.7 GPa and 1450 K, respectively [14]. The isentrope starting at these conditions ($s \approx 7$) reaches a pressure of 140 GPa at a temperature below 2000 K and a density of about 0.9 g/cm^3. These values are based on the extrapolation of the present model to temperatures below 2000 K. The linear-mixing model [14] determines a temperature of 2600 K at a density of 0.7 g/cm^3. The lower temperature in our calculation is consistent with the higher degree of dissociation and the additional ionization found in the PACH approach at these conditions. Results for the electrical conductivity based on the present EOS [21] show a strong increase with the density as observed experimentally [1].

IV. CONCLUSION

We have studied the location and the slopes of Hugoniot curves, isentropes, and of the coexistence line of the PPT for hydrogen (deuterium) in the pressure-temperature plane. In particular we have shown that the derivative $\partial p/\partial T$ of these three theoretical lines is completely different. The coexistence line located at about 140 GPa is weakly temperature-dependent and only slowly falling. The Hugoniot curve is increasing with a relatively small derivative which is a decreasing function of the temperature. The isentropes are steeply increasing and, at small temperatures, nearly vertical in this presentation.

We conclude from Fig. 1 that the Hugoniot curve can hardly cross the coexistence line of the PPT but that isentropes may cross it due to their steep slope. Below temperatures of 10 000 K the coexistence line lies substantially above the single-shock Hugoniot curve for hydrogen. When the pressure along the Hugoniot curve reaches the range of the predicted coexistence pressure, the corresponding temperatures are in the range of the predicted critical temperatures of the PPT. Extrapolation shows that the Hugoniot curve will not cross the coexistence region or, at best, close to the critical point. Having in mind the large error bars of the single-shock experiments and the substantial deviations of the various theoretical predictions for the location of the PPT, these experiments are not particularly suited for probing the existence and location of the PPT. Multishock experiments seem to be more promising in this direction.

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