Fluid Hydrogen at High Density: The Plasma Phase Transition

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We apply a new model equation of state, based on realistic interparticle potentials and a self-consistent treatment of the internal levels, to fluid hydrogen at high density. This model shows a strong connection between molecular dissociation and pressure ionization. We consider the possibility of a first-order plasma phase transition for which we give both the evolution in temperature and the critical point.

The equation of state (EOS) of dense hydrogen has been a subject of great interest for years because of its astrophysical importance and its theoretical novelty. Current studies of giant planets and low-mass stars, which consist mostly of hydrogen under high pressure, require of an accurate hydrogen EOS.[1] There has also been considerable interest in the possibility of an insulator-metal phase transition in hydrogen at high pressure. Theoretical predictions give a transition pressure[2-6] in the 1-5 Mbar range, approached by recent static compression experiments.[7] At high temperature ($T \approx 6000$ K), shock-wave experiments have confirmed the stability of the molecular phase up to 0.8 Mbar.[2] This Letter gives new results for molecular dissociation and pressure ionization, and it predicts a realistic plasma phase transition as well as a critical point.

We have developed a very detailed model EOS which covers a wide temperature and density regime for fluid hydrogen. We adopt a "chemical picture," in the sense that we assume the existence of independent, bound configurations such as H atoms and H_2 molecules, interacting with pair potentials. At densities corresponding to pressure ionization, however, such a scheme has dubious validity, and the concept of a pair potential fails,[8] requiring the use of a quantum-statistical many-body theory. In such a "physical picture," only fundamental particles (electrons and nuclei) exist. Although the physical picture is formally exact, in practice numerical calculations must be based on expansions which converge only at low density and high temperature. The calculation of an EOS for practical applications is rendered nearly impossible by the formidable complexity of these theories. For such reasons, the chemical picture remains a powerful alternative.

Our EOS consists of a neutral and a fully ionized model, which represent, respectively, the low-density, low-temperature and the high-density, high-temperature limits of a general model applied in the partial ionization zone. Full details of the calculations will be published elsewhere.[9]

(a) Model for neutral species.—For densities $\rho \lesssim 1$ g cm^{-3} and temperatures $T \lesssim 10^4$ K, hydrogen is adequately treated as a neutral mixture of atoms and molecules. The ions H^- and H_2^+ have negligible concentrations[10] and are ignored. The chemical equilibrium concentrations of H_2 and H are obtained by numerically minimizing the Helmholtz free energy of the mixture. Assuming a factorization of the partition function, the adopted free energy is

$$F(N_H, N_{H_2}, V, T) = F_{id} + F_0 + F_{int} + F_{qm}, \quad (1)$$

where F_{id} is the ideal-gas contribution, and the other terms are discussed below.

Computation of the interactions between particles in the binary mixture requires knowledge of three interaction potentials, $\phi_{\alpha\beta}(r)$. For $\phi_{H_2-H_2}(r)$, we use an effective pair potential derived from shock compression experiments.[2] Since no similar experimental data exist for $\phi_{H-H}(r)$ and $\phi_{H-H_2}(r)$, we have fitted *ab initio* calculations[11] with generalized Morse potentials. We treat the spin dependence of the H-H interaction by averaging the interaction potentials of the singlet and triplet states; the resulting $\phi_{H-H}(r)$ has no bound states.

The contribution of the atomic and molecular interactions, the "configurational energy" F_0, is calculated from these potentials using the Weeks, Chandler, and Andersen (WCA) fluid perturbation expansion.[12] The reference system chosen is a hard-sphere mixture, for which the *density- and temperature-dependent hard-sphere diameters σ_{11} and σ_{22}* ($1 \equiv H$, $2 \equiv H_2$) are determined thermodynamically by the WCA criterion.[12] The failure of the WCA expansion scheme at high density is corrected by using new potential separations.[13] Comparison of the excess internal energy and pressure derived from this expansion scheme with Monte Carlo (MC) simulations for the density and temperature range of interest agree within 3%.[13] This *demonstrates the validity of the configuration energy for the H-H_2 mixture* for a given set of potentials.

The effect of near-neighbor interactions on the internal structure of bound species is essential to a correct description of pressure dissociation and ionization. We have used a new approach based on an "occupation probability" formalism,[14] which gives excellent agreement with spectroscopic data.[15] The occupation probability of a bound state, which can be interpreted as a statistical

weight, is expressed in terms of the interparticle interaction. In the internal free energy, F_{int}, this is approximated by a simple excluded-volume factor for the neutral species,[14] using the hard-sphere diameters computed for F_0. This ensures *consistency of both the interaction and its effect on the internal partition function*. This procedure yields convergent internal partition functions and ensures continuity of the free energy by providing a smooth cutoff of the sum over eigenstates, and therefore a *physically plausible pressure-ionization effect*.

The term F_{qm} in Eq. (1) is due to quantum diffraction effects and has been calculated to first nonvanishing order in the Wigner-Kirkwood $\hbar^2$ expansion.

To our knowledge, this model represents the most sophisticated treatment of the thermodynamics of neutral hydrogen in the fluid phase currently available. When applied to hydrogen and deuterium, Hugoniot curves computed from this model are in excellent agreement with single- and double-shock compression experiments.[16,17]

(b) *Model for fully ionized hydrogen.*— For $kT \gtrsim 1$ Ry or $\rho \gtrsim 2$ g cm^{-3} (corresponding to $r_s \approx 1$, where r_s is the mean interionic spacing in units of the Bohr radius), the atoms retain no bound states, and the fluid is fully ionized. At densities high enough so that $r_s < 1$, the ion-electron interaction is sufficiently weak that the plasma is adequately described as a linearly screened ionic fluid[18] and a partially degenerate electron gas. Under these conditions, the free energy can be written in the form

$$F = F_{\text{id}}^i + F_{\text{id}}^e - NkT \ln \int e^{-\beta U^{\text{eff}}} d\mathbf{r}_N + F_{\text{xc}} + F_{\text{qm}}, \quad (2)$$

where F_{id}^i and F_{id}^e denote the ionic and electronic perfect-gas contributions. F_{xc} is the exchange and correlation free energy of the finite-temperature electron gas evaluated with an accurate fit.[19] The third term on the right-hand side of Eq. (2) is the free energy of the ionic fluid, calculated in the framework of the hypernetted chain theory for a *temperature- and density-dependent* screened Coulomb potential, using the finite-temperature Lindhard dielectric function with a local-field correction.[20] This ionic contribution is in excellent agreement with existing MC calculations.[21] The quantum correction F_{qm} for the ions is again calculated to leading order in $\hbar^2$, using a Wigner-Kirkwood expansion for a screened ionic fluid.

The main sources of uncertainty in this model are the fit for F_{xc} and the exclusion of nonlinear contributions to the ion-electron interaction. We estimate the resulting maximum error in the total plasma free energy to be $\approx 3\%$. The thermodynamics derived from Eq. (2) is *as reliable as the results of more detailed theories*,[20,22] over the whole range of electron degeneracy. At intermediate densities ($r_s > 2$ and $kT > 1$ Ry), the free energy is interpolated smoothly to the low-density limit, calculated with a semiclassical two-component plasma model.[23] This treatment is computationally convenient and

covers the whole density and temperature range for fully ionized hydrogen.

(c) *Partial ionization.*— The behavior of hydrogen in the regime of pressure ionization constitutes a challenging problem. Whether the transition from an insulating molecular or atomic state to a metallic state occurs smoothly or via a first-order phase transition is still an open question. The two models described above enable us to explore these two possibilities.

Below the regime of thermal ionization ($T < 15\,000$ K), the degree of ionization of dense hydrogen is negligible ($< 10^{-3}$) up to $\rho \approx 0.2$ g cm^{-3} (see below). Conversely, starting from high densities, electronic bound states are predicted to develop at densities $\lesssim 2$ g cm^{-3}.[24] Outside this density range, we believe that the two models we have used provide the most accurate EOS for fluid hydrogen currently available. Thus, pressure ionization can be treated as a *continuous* process by interpolating between these two limits.

A better approach, which also provides a description of temperature ionization, is to use an appropriate combination of the two model free energies described previously. Because the pair potentials become meaningless at high densities, the chemical picture fails to describe adequately complete pressure ionization. Nevertheless, it remains a powerful tool for the study of partial ionization and molecular dissociation. To correct for the extreme softness of the potentials, we have introduced repulsive cores at $r < 2a_0$ for $\phi_{\text{H-H}}$ and $r < 2.7a_0$ for $\phi_{\text{H}_2\text{-H}_2}$ (a_0 is the Bohr radius). We find that these repulsive cores do not appreciably affect either the comparison with experimental Hugoniots or the characteristics of the plasma phase transition discussed below.

In this mixed calculation, we treat the interaction between charged and neutral particles through a *polarization potential*.[25] We approximate this by a hard-core interaction inside the atomic or molecular radius and by a screened potential outside the core. The hard-core contribution amounts to reducing the volume employed in the calculation of the ionic and electronic ideal terms. The second contribution has been calculated using the exact temperature- and density-dependent screened potential U^{eff} [Eq. (2)] and introduces an additional polarization term in the final free energy. Having imposed the electroneutrality condition, we minimize the free energy in a two-dimensional concentration space to obtain the chemical equilibrium of the four-component mixture (H_2, H, H^+, e^-). The resulting abundances and pressure are in good agreement with activity expansion calculations, which have been carried up to 0.03 g cm^{-3}.[26]

(d) *The plasma phase transition (PPT).*— We calculate the limit of stability of the mixed-model free energy described in (c) as a function of the density along an isotherm. The characteristics of the related first-order phase transition are given in Table I. Since temperature ionization does *not* occur via a phase transition, the pressure ionization phase transition must end in a critical

TABLE I. Characteristics of the plasma phase transition. For each temperature T, we give the pressure P, the density of each phase $(\rho^{\mathrm{I}}, \rho^{\mathrm{II}})$, the degree of ionization in the partially ionized phase χ^{II}, and the entropy discontinuity ΔS.

T (10^3 K)	P (Mbar)	ρ^{I} (g cm^{-3})	ρ^{II}	χ^{II}	$\Delta S = S^{\mathrm{II}} - S^{\mathrm{I}}$ (10^7 ergs K^{-1}g^{-1})
8	1.88	0.66	0.80	0.53	2.70
10	1.32	0.55	0.66	0.52	2.34
12	0.964	0.45	0.54	0.46	1.99
14	0.725	0.37	0.42	0.35	1.57
14.8	0.664	0.34	0.39	0.32	1.37
15	0.646	0.36		0.20	0

point. We find the parameters of this point to be P_c =0.646 Mbar, T_c =15000 K, and ρ_c =0.36 g cm^{-3}. The phase transition line from this mixed-model calculation is shown in Fig. 1, where it is compared with existing experimental and theoretical results. The use of various charged-neutral interactions does not affect either the existence of the PPT or its qualitative features. We estimate the uncertainty in our PPT calculation to be much smaller than the range between MH and ER in Fig. 1. The latter calculations represent two extreme approximations. In one case, a PPT is forced between a pure H_2 and a fully ionized phase. In the second, the neutral-species interactions are unrealistically harsh (pure hard-sphere potentials). In addition, we have
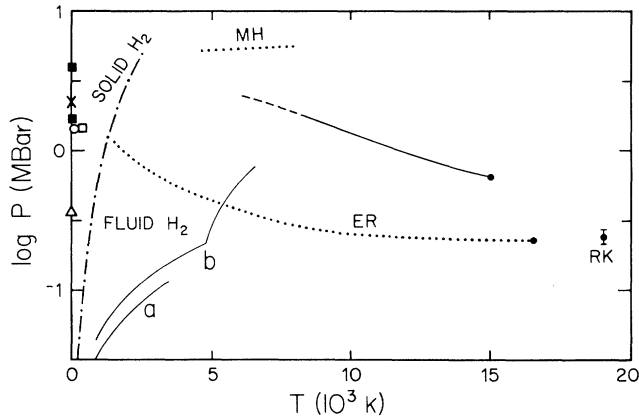

FIG. 1. P-T diagram for hydrogen in the pressure-ionization regime. Heavy solid line: mixed-model PPT and critical point. Other theoretical estimates for the PPT and the critical point are labeled MH (Ref. 1), RK (Ref. 5), and ER (Ref. 6). The zero-temperature calculations of Ref. 3 ($\times$) and Ref. 4 ($\blacksquare$) for the phase transition are indicated. Dash-dotted curve: theoretical melting curve of H_2 from Ref. 2. The curves labeled a and b are experimental single- and double-shock Hugoniots of H_2 and D_2, respectively (Refs. 17 and 2). Open symbols indicate the highest pressures reached in static compression experiments: $\square$, Ref. 7(a); $\bigcirc$, Ref. 7(b); and $\triangle$, Ref. 7(c).

verified by explicit *ex post facto* calculations that the band structure in the H_2 molecule has little effect on the PPT: Using the density-dependent band gap calculated at zero temperature,[3] we estimated the fraction of thermally excited electrons to vary from less than 10% at 8000 K to 2% at the critical point. Figure 2 shows the concentrations of atoms, molecules, and charged particles as functions of density for two isotherms above and below the critical temperature.

We draw the following conclusions.

(i) The system undergoes a first-order phase transition from a *neutral phase* $(x_e \leq 10^{-3}$ for $T < T_c)$ to a *partially ionized phase* $(x_e \leq 0.5)$ as ρ increases. Although the degree of ionization depends on the hard-core radius in the charged-neutral interaction polarization potential, the qualitative features remain unaffected.

(ii) The degree of ionization increases drastically and discontinuously at the transition pressure, corresponding to an insulator-conductor transition. The most striking feature of the model is that *molecular dissociation and pressure ionization occur at almost the same density.*

(iii) Above the critical density, the system reaches complete ionization *very gradually.* The sharp rise in the ionization curve at high density is a consequence of the repulsive cores introduced in the interaction potentials between neutral species. This points out the qualitative difference found when treating pressure ionization with realistic, albeit flawed, potentials and with pure hard-sphere interactions. Even though our model for the neutral species is highly questionable above the transition density, our calculations do suggest that full ionizations may occur much more gradually than indicated by previous studies using pure hard-sphere potentials.[6]

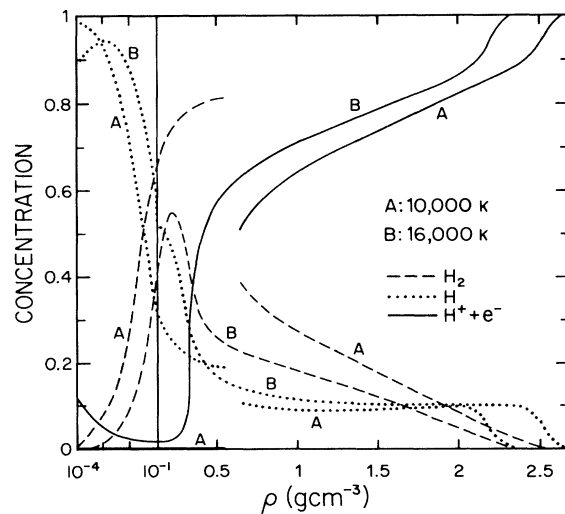(iv) Molecules are the dominant neutral species at

FIG. 2. Concentration of H_2, of H, and of charged particles $(H^+ + e^-)$ along two isotherms on either side of T_c. Left panel: The low-density behavior on a log-density scale.

high density. The fact that the concentration of atoms is low in the ionized phase (< 10%) adds credibility to our results since the hydrogen atoms lose their identity in a dense plasma.

In summary, we have applied an improved EOS, the validity of which has been assessed by comparison with experimental results and Monte Carlo simulations, to the high-density domain of fluid hydrogen. The interatomic and intermolecular interactions are based on realistic potentials, although they are the principal source of uncertainty in the model at high densities. The influence of these interactions on the internal levels is calculated self-consistently with an occupation probability formalism. Finally, a complete model of four interacting neutral and charged species is generated in the domain of partial ionization. Pressure ionization is handled using two different assumptions, either (a) continuous ionization over a narrow density range or (b) a plasma phase transition. Moreover, the model gives new information concerning molecular dissociation and its eventual connection with pressure ionization. To our knowledge, the treatment of the microphysics presented in this paper is the most complete proposed so far for detailed numerical EOS calculations over a broad range of temperatures and densities. We believe this picture to give realistic estimates for the partial ionization zone and the hypothetical PPT and to form a good basis for an improved treatment. The PPT occurs at temperatures and densities characteristic of giant planets and low-mass brown dwarfs and has a major effect on their thermal structure.[27] In view of these results the possibility of H-He separation in Jovian planets should be reexamined. In addition, our model provides a useful guide for high-pressure experiments which hold the promise of pressure ionizing hydrogen in the near future.

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