

$$F(V,T) = (1-x)F_{H_2}(V,T) + F_{H+H}(V,T) + TS_{\text{mix}} - (1-x)D^0$$

where  $x$  is the fraction of dissociated molecules and is determined by minimizing the free energy. The dissociation energy of an isolated molecule is  $D^0$ , and the mixing entropy term makes a small contribution. The free energy of the molecular phase,  $F_{H_2}$ , was determined previously using soft-sphere perturbation theory to find the molecular potential that agrees with available experimental shock and static data. Fully dissociated monatomic hydrogen is approximated as a nearly free-electron metal. The free energy of this monatomic phase,  $F_{H+H}$ , combines a density-dependent, nearly free-electron gas, a modified one-component-plasma ion-thermal energy for the fluid, and an adjustable parameter cho-

- sen to agree with all our pressure-temperature and pressure-volume data. We also include a density-dependent function chosen to force agreement at 0 K with ab initio calculations [T. W. Barbee and M. L. Cohen, *Phys. Rev. B* **44**, 11563 (1991)] of the free energy of the body-centered-cubic-phase metal. Thus, the phenomenological model we have adopted builds in the correct limiting behavior for the low-density molecular fluid and high-density monatomic fluid and interpolates smoothly between them.
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## Ab Initio Calculation of the Sound Velocity of Dense Hydrogen: Implications for Models of Jupiter

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First-principles molecular dynamics simulations were used to calculate the sound velocity of dense hydrogen, and the results were compared with extrapolations of experimental data that currently conflict with either astrophysical models or data obtained from recent global oscillation measurements of Jupiter. Excellent agreement with the extrapolated experimental data was obtained. These results strongly support the notion that the existing models for the jovian interior need to be revised.

Although hydrogen is the simplest of all elements, its properties at high pressures (in the 100-GPa regime) and temperatures (several thousand kelvin) are not well understood. Hydrogen in such physical regimes occurs in abundance in astrophysical bodies such as stars and the giant planets, and thus its properties are of fundamental importance in understanding the physical properties of these bodies. A number of recent experimental and observational breakthroughs may lead to a much better understanding of the properties of hydrogen at these conditions. In particular, Duffy *et al.* (1) have measured the sound velocity of dense hydrogen up to pressures of 24 GPa. These measurements were preceded by observations of global oscillations of Jupiter (2), from which the planet's "equidistance" has been inferred. The equidistance is the inverse of twice the time it takes for a ray to travel from the planet's center to the surface. In the context of a model for the pressure profile of Jupiter

(3), this equidistance can be used to obtain an estimate of the sound velocity of hydrogen under the conditions prevailing in the interior of the planet (1).

The global oscillation data, combined with a reliable interior model, may provide a convenient way to probe the interesting intermediate temperature regime in which the electron gas is partially degenerate. However, the sound velocities that have been obtained in this way are in substantial disagreement with the measured sound velocities (1). At present, the source of disagreement is not clear. To make meaningful comparisons, researchers have extrapolated experimental data (by means of fitting the data to empirical potentials) from 25 to 300 GPa, but this procedure is fraught with uncertainty because in this high-pressure regime hydrogen is expected to undergo a variety of transitions (both first-order and continuous), including a molecular-to-atomic transition (3) and a metal-insulator transition. Empirical potentials for  $H_2$ , fitted to lower density data, tend to overestimate the repulsive wall of the molecules (1). The result is an underestimate of the compressibility of dense hydrogen or, equivalently, an overestimate of the sound velocity. Indeed, the extrapolated "low-pressure" experimental data predict sound velocities in dense hydrogen that are much greater than those inferred from the global oscillation data. However, it cannot be concluded that the extrapolation

procedure to estimate the high-pressure sound velocity is in error; the assignment of the global oscillation spectra in (2) has been controversial, and the results of the data analysis depend strongly on the choice of the model for the interior of Jupiter. Thus, the apparent disagreement between the jovian global oscillation data and the extrapolated terrestrial results may also signal the need for a revision of the existing models of Jupiter (1, 2). A completely independent measurement of the sound velocity in dense, hot hydrogen would help to clarify these issues. Here, we present ab initio calculations of the sound velocity of hydrogen and compare our results with the above findings.

The prediction of sound velocities over such a broad range of pressures presents a formidable theoretical problem for a number of reasons. First, in this pressure regime the nature of the effective interaction between the protons changes from a completely molecular state to an increasingly dissociated one. A parameter-free model that can consistently describe hydrogen throughout this regime necessitates a proper quantum mechanical treatment of the electrons. In addition, the thermal fluctuations of fluid hydrogen must be properly sampled, which requires a statistical treatment of the protons, and, furthermore, dynamical information is necessary to compute sound velocities. An approach that combines quantum and statistical mechanics is the method of ab initio molecular dynamics (Car-Parrinello method) (4), which has recently been successfully applied to the hydrogen plasma (5).

The method we used is different in one basic respect from the usual Car-Parrinello method, namely, that it is based on finite temperature density functional theory, as developed in (6), rather than ground state ( $T = 0$ ) density functional theory; this enabled us to check the effect of electronic temperature on the approach to the metallic phase. In our calculations two approximations remain, namely the electronic exchange-correlation functional, which we treat in the local density approximation (LDA) (7), and the neglect of the zero-point motion (ZPM) of the protons.

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The combined error introduced by these two approximations will be judged wherever possible by comparison with  $T = 0$  diffusion Monte Carlo (DMC) calculations (8), which treat both the ZPM exactly and electronic correlation beyond the LDA.

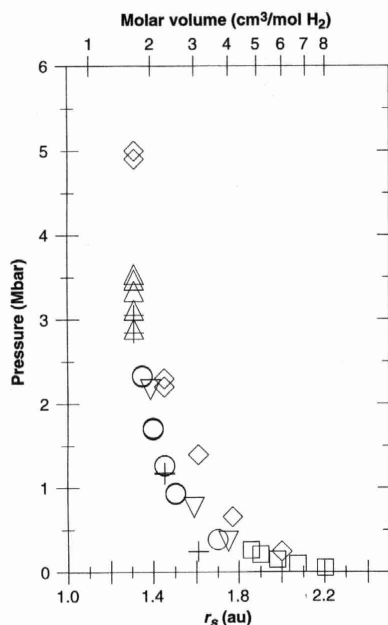
We considered systems consisting of 64 atoms at a temperature of  $T = 1000$  K at five densities ranging from 3.673 to 1.840  $\text{cm}^3/\text{mol H}_2$  (9). In terms of the ion-sphere radius  $r_s = (3/4\pi\rho)^{1/3}$  (where  $\rho$  is the density), this range spans  $r_s = 1.7$  to 1.35 (in units of the Bohr radius) and covers a pressure regime of  $\sim 30$  to 300 GPa. For a given configuration of protons, the electronic density  $n(\mathbf{r})$  was computed (10) by minimizing the free-energy functional  $\mathcal{F}$  of the electron gas, defined as

$$\mathcal{F} = \Omega + \mu N + E_{II} \quad (1)$$

$$\Omega[n(\mathbf{r})] = \frac{2}{\beta} \log \det\{1 + \exp[-\beta(\mathcal{H} - \mu)]\} - \int d\mathbf{r} n(\mathbf{r}) \left[ \frac{\phi(\mathbf{r})}{2} + \frac{\delta\Omega_{xc}}{\delta n(\mathbf{r})} \right] + \Omega_{xc} \quad (2)$$

(6), which reproduces the exact finite temperature density of the Mermin functional (11). In these equations,  $N$  is the number of electrons,  $\beta^{-1}$  is the electronic temperature,  $\mu$  is the electronic chemical potential,  $\mathcal{H} = -(1/2)\nabla^2 + V(\mathbf{r})$  is the one-electron Hamiltonian with potential  $V(\mathbf{r}) = \sum_i V_{ei}(\mathbf{r} - R_i) + \phi(\mathbf{r}) + \delta\Omega_{xc}/\delta n(\mathbf{r})$ ,  $\phi(\mathbf{r})$  is the Hartree potential of an electron gas of density  $n(\mathbf{r})$ ,  $V_{ei}$  is the electron-proton interaction (10),  $R_i$  are the instantaneous positions of the protons,  $\Omega_{xc}$  is the exchange correlation grand potential energy (7), and  $E_{II}$  is the classical coulomb energy of the protons. The value of  $\mathcal{F}$  was optimized for each ionic configuration by means of a self-consistent diagonalization method, as in (6). The electronic density thus computed, together with the Hellmann-Feynman theorem, enables the calculation of the ionic forces. The ionic degrees of freedom were integrated with a time step of 20 atomic units ( $\approx 0.48$  fs), which gave rise to a conservation in total energy of 1 part in 5000. Simulations of duration 0.5 ps per density were performed; this time length was found to be adequate for equilibration of both pressure (12) and temperature, and it allowed the computation of time-correlation functions. During equilibration, the temperature was thermostated at 1000 K, but the production runs, in which time-correlation functions were computed, were done in the microcanonical ensemble (constant total energy), in which the average temperature remained close to 1000 K.

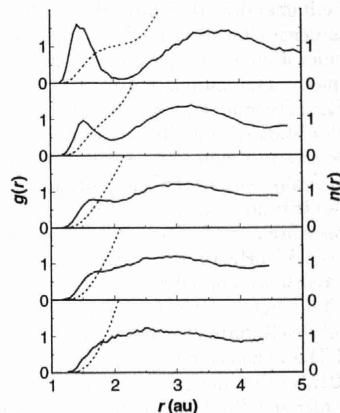
To obtain the sound velocities as a function of pressure, we first calculated the equation of state (EOS). This is shown in Fig. 1, along with similar results from experimental (13) and theoretical work (8, 14, 15). Com-



**Fig. 1.** EOS of dense hydrogen as obtained from our calculations ( $\circ$ ), experimental data at 300 K ( $\square$ ) (13), DMC calculations of (8) ( $\Delta$ ) and (15) ( $\diamond$ ), molecular structures; +, atomic structures), and LDA calculations including ZPM in a harmonic approximation (14) ( $\nabla$ ).

parison with DMC calculations and experimental data provides a stringent test of the validity of our calculations. Our results for the high-pressure regime agree well with recent DMC results (8), whereas at lower pressures they are consistent with the available experimental data. The absolute error in the pressures is estimated to be  $\sim 5\%$  (12). The calculated pair correlation functions (Fig. 2) show a gradual disappearance of the molecular peak as a function of increasing pressure. As the molecular phase disappears, no discontinuities in pressure, indicating a strong first-order transition, are observed. Inspection of the atomic configurations reveals that, with increasing density, short-lived anisotropic filamentary structures with percolative character build up instantaneously. They are not stable with respect to the thermal motion, however, and disintegrate rapidly (on the order of a few femtoseconds, substantially less than a molecular vibron).

The question of the importance of ZPM has been the subject of studies that used  $T = 0$  DMC (8, 15) and LDA calculations at both  $T > 0$  and  $T = 0$  (5, 14). These studies showed that at  $T = 0$ , where ZPM has its greatest influence, the primary effect of the neglect of ZPM is to overstabilize anisotropic structures; ZPM favors more isotropic structures. The magnitude of this overstabilization, however, is less than the  $kT$  (16) in our work; the motion in the fluid



**Fig. 2.** Pair correlation functions  $g(r)$  (solid lines) and coordination numbers  $n(r)$  (dotted lines).  $T \approx 1000$  K in all cases. From top to bottom:  $r_s = 1.7, 1.5, 1.45, 1.4,$  and  $1.35$  au.

is not frozen into such structures. The samples were fluid and strongly diffusive throughout the density regime of interest. Because at  $T > 0$  the effect of ZPM is intrinsically reduced, the overall effect of ZPM in the fluid can be expected to be rather small. The effect of the finite electronic temperature is to increase the band gap by approximately  $kT$  relative to the  $T = 0$  LDA. Even at  $r_s = 1.35$  the hydrogen, although dissociated, is not yet metallic.

The adiabatic sound velocity  $c_S$  can be obtained indirectly from the molecular dynamics simulations in several ways. The first method derives  $c_S$  from the isothermal sound velocity  $c_T$ , which can be obtained from the EOS (Fig. 1) by means of the thermodynamic relation

$$c_T^2 = (dP/d\rho)_T \equiv 1/(\rho K_T) \quad (3)$$

where  $K_T$  is the isothermal compressibility. The value of  $c_S$  can then be obtained from  $c_S = \sqrt{\gamma} c_T$ , where  $\gamma = C_p/C_v$ , the ratio of the specific heats at constant pressure and volume, respectively. The value of  $\gamma$  is not directly available from the simulations, but a reasonable estimate can be obtained from the dynamic structure factor  $S(k, \omega)$  (16) as follows. In the small  $k$  limit,  $S(k, \omega)$  should exhibit the characteristic Rayleigh-Brillouin form of a Rayleigh peak centered at  $\omega = 0$  and two Brillouin peaks at finite  $\omega$ . The ratio of areas under the Rayleigh and Brillouin peaks  $J_R/J_B$  is the Landau-Plazcek ratio (17), which is related to  $\gamma$  by  $J_R/2J_B = \gamma - 1$ . The value of  $\gamma$  thus obtained, combined with  $c_T$ , enables the calculation of  $c_S$ . The value of  $c_S$  can also be obtained from the small  $k$  limit of the dispersion curve  $\omega(k)$  of the Brillouin peak by means of the relation  $\lim_{k \rightarrow 0} \omega(k) = c_S k$ . However, the rather small system sizes used in our study do not allow comfortable extrapolation to  $k = 0$ ; this is especially true

of the higher densities. Nevertheless, for the lower densities, this method of computing  $c_S$  provides a useful independent check of the thermodynamic estimate of  $c_S$ .

The dynamic structure factors for the smallest wave vectors (Fig. 3) were found to exhibit very convincingly the Rayleigh-Brillouin form, from which the Landau-Plazek ratios (18) can be estimated. The values of  $\gamma$  decrease from  $\gamma \approx 1.45$  at  $r_s = 1.7$  to  $\gamma \approx 1.16$  at  $r_s = 1.35$ . [The values of  $\gamma$  for  $H_2$  gas at 300 and 400 K at atmospheric pressure are 1.38 and 1.40, respectively (19). Increasing the pressure to 100 atm increases  $\gamma$  on the order of 1%.] The estimated error in  $\gamma$  is on the order of 10%, so that the error in  $c_S$  should be on the order of  $\sim 5\%$ . Figure 4 shows  $c_T$  computed from the EOS (3) and the resulting thermodynamic estimate of  $c_S$ , as well as the  $c_S$  values obtained from the dispersion curves. For the three lower densities, the two methods yield very similar estimates for  $c_S$ , whereas at the highest two densities the dispersion estimate is markedly lower. This reflects the fact that  $\omega(k)$  at the large wave vectors necessarily probed at the higher densities shows a significant deviation away from the limiting linear form, which results in an underestimation of the limiting slope. At these two densities, therefore, the thermodynamic estimate of  $c_S$  is more realistic.

In any event, our ab initio estimates of the sound velocity in dense hydrogen are in excellent agreement with the extrapolated experimental (terrestrial) data, particularly with those of Ross *et al.* (20) that were based on shock compression data. Our sound velocities are marginally higher than the extrapolations of Duffy *et al.*, but the discrepancy is within the statistical errors of the present calculations. The fact that our simulation results support the extrapolated data of (1) and (20) necessarily implies that our data are incompatible with the sound velocity estimates that result from the current interpretation of the jovian global oscillation data. Given the parameter-free nature of the present calculation, this agreement removes much of the earlier doubt as to the validity of the extrapolations and strengthens the case (1) for a revision of

either the current jovian models or the global oscillation spectra themselves.

Current models of Jupiter depend crucially on the EOS  $P(\rho)$  of H and H-He mixtures, and they are based on free-energy models (3) in which a number of simplifying assumptions are made. In particular, pair interactions between  $H_2$ , H, and  $H^+$  enter as necessary input. Ideal mixing between the H and He components is also assumed. On the basis of currently available data, it is difficult to assess the effect of these various approximations on the overall EOS. An indication of anomalous behavior is that the value of  $\gamma$  they yield for the jovian adiabats (3) exceeds 2, which is in excess of the value of  $5/3$  for an ideal gas. Our calculations indicate that the value of  $\gamma$  should decrease from roughly 1.4 at low densities, approaching unity at higher pressures. This would suggest that the construction of free-energy models built on our EOS data and similar work may yield more accurate models, which may ultimately remove the present discrepancies. More interesting, however, is the assumption of ideal mixing of the two components. In particular, close to the critical point that signals the onset of phase separation between H and He, the behavior of  $c_S$  will be anomalous because both  $K_T$  and  $\gamma$  are divergent (with similar exponents) (21). In such conditions  $c_S$  may be attenuated. These effects would be in line with our calculations; if this is indeed the case, it goes against the current orthodoxy that He is fully miscible in H under the conditions prevailing in Jupiter. In either case, the present discrepancy be-

tween the sound velocity of pure dense hydrogen and the jovian sound profiles remains unexplained. The resolution of this issue may lead to an improved model of the planet and to a better understanding of H-He mixtures at high pressures and temperatures.

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10. The electronic density was expanded in plane waves up to an energy cutoff of 40 rydbergs. The self-consistent density was computed so that the error in the forces per atom was less than 1 part in  $10^5$ , which enables the propagation of stable atomic trajectories. A smooth electron-proton pseudopotential was used [F. Gygi, *Phys. Rev. B* **48**, 11692 (1993)].
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16.  $S(k, \omega)$  is defined as

$$F(\mathbf{k}, t) = (1/N) \langle \rho_{\mathbf{k}}(t) \rho_{-\mathbf{k}}(0) \rangle$$

$$\rho_{\mathbf{k}} = \sum_i \exp(-i\mathbf{k} \cdot \mathbf{R}_i) \quad (4)$$

$$S(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt F(\mathbf{k}, t) \exp(-i\omega t) \quad (5)$$

- where  $\omega$  is the angular frequency. For isotropic systems the dynamic structure factor is rotationally invariant and can be averaged over angles to give  $S(k, \omega)$ , where  $k$  is the modulus of the wave vector  $\mathbf{k}$ .
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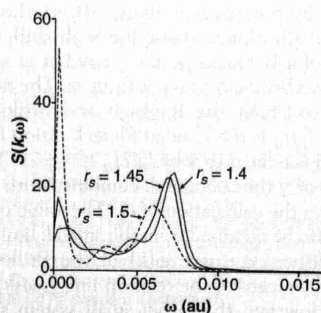


Fig. 3. Dynamic structure factors for the lowest wave vectors at three densities.

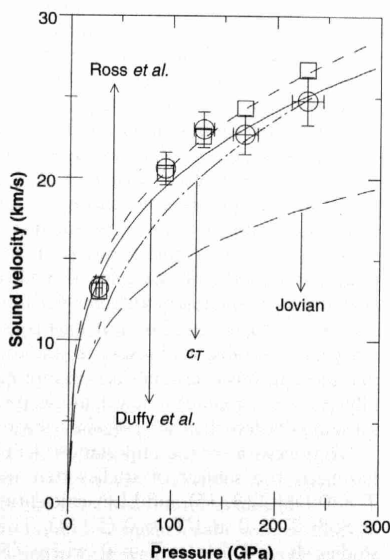


Fig. 4. The sound velocities.  $\square$ , Thermodynamic estimate of  $c_S$ ;  $\circ$ , dispersion estimate of  $c_S$ ; dot-dashed line,  $c_T$  computed from the EOS; solid line, extrapolation of Duffy *et al.* (1); dashed line, extrapolation of Ross *et al.* (20); and long dashed line, jovian profile from (1).