

Molecular Dynamics in Dense Hydrogen

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We present *ab initio* molecular dynamics simulations for high-density hydrogen ($r_s=1.78-1.31$, $P \approx 35-150$ GPa). Protons are treated as classical point charges and electrons in local density functional theory. The basic structural entity in this density range is still the hydrogen molecule but applying pressure changes the molecular ordering drastically. Molecules line up to form filaments and eventually planes, where intermolecular distances become comparable to the H₂ bond length. The phase diagram is strongly temperature dependent, and many different structures with very similar stability exist.

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The phase diagram, structure, and properties of condensed hydrogen have been under scrutiny for several decades. High-density hydrogen in particular is still under much debate because of inherent theoretical and experimental difficulties [1]. The current experimental state of knowledge can be summarized as follows. Hydrogen is stable in the molecular form (H₂) under normal conditions and solidifies at 14 K to form a molecular solid with hexagonal-close-packed structure (hcp, $r_s=3.13$, relative density $\rho/\rho_0=1$). The molecular hcp structure is stable up to 38 GPa ($r_s=1.76$, $\rho/\rho_0=5.6$) [2] but definitive structure determinations are missing beyond this point. Low-frequency Raman spectra suggest that hexagonal order persists at pressures up to and above 150 GPa ($r_s=1.5$, $\rho/\rho_0=9$) [1]. The vibron frequency shows a major discontinuity (~ 100 cm⁻¹) around 150 GPa [3] when plotted against pressure linked possibly to a *molecular* phase transition. Increasing the pressure further it appears that near 250 GPa the optical properties and the Raman spectrum of hydrogen change drastically, signaling the possible onset of molecular dissociation [1], but most measurements beyond 150 GPa are hampered by substantial experimental uncertainties.

On the theory side a large number of structure studies with diverse methods exists. With increasing sophistication of the energy method they remain more and more confined to an ever smaller number of (usually highly symmetric) structures. Early studies of the *atomic* phase [4] have shown a prominence of anisotropic structures with low coordination up to very high pressures (~ 100 Mbar). More sophisticated calculations using density functional theory (DFT) confirm this trend and find simple hexagonal ($c/a < 1$) and related structures most stable [5]. Monte Carlo (MC) calculations treating electrons and protons quantum mechanically find isotropic albeit low coordinated structures more stable [6,7]. Of the *molecular* structures hcp emerges more stable than cubic ones [5,7]. One explanation of the 150 GPa phase transition was therefore metallization by band overlap

and orientational ordering within hcp [8]. Lowering the symmetry, however, increases the band gap and stability, and the band gap closure pressure depends sensitively on the specific molecular orientations [9,10]. In both molecular and atomic phases a multitude of structures exists with very close energies ($\Delta E \lesssim 1$ mRy [10]), and current predictions for the transition pressure range from 200 up to 600 GPa.

It becomes clear that a more comprehensive structure search with a reliable energy method and little bias would be desirable. In this Letter we report the results of unified molecular dynamics and density functional (MD-DF) [11] calculations at three different densities ($r_s=1.78$, 1.5, and 1.31, corresponding to pressures $P \sim 35$, 150, and 300 GPa [12]). We use a periodically repeated cube with 64 atoms, a pseudopotential representation for the electron-ion interaction [13], and a plane wave basis with cutoff energy $E_{\text{cut}} = 60$ Ry for a single k point (Γ). A full account with details of these and subsequent calculations will be published separately [14]. Two important approximations should be borne in mind when interpreting our results: (i) The local density approximation (LDA) for electron exchange and correlation. Its effects can be estimated from diffusion MC calculations [6,7], distorting relative energies for hydrogen crystal structures less than 0.1 eV/atom and typically $\lesssim 0.03$ eV/atom. The LDA is therefore well suited for calculations in the hydrogen system. (ii) 64 atoms in a unit cell sampling only Γ is adequate in insulating hydrogen phases, but finite size effects can become larger than LDA errors in atomic metallic hydrogen structures (as large as 0.5 eV/atom comparing the stabilities of the diamond and simple cubic structure at $r_s=1.31$, the worst case we have encountered). Comparing atomic crystal energies, however, is not the goal of our work.

Our main goal is to sample the energy surface of the system with all available details using classical thermal motion. The need to invoke stringent symmetry restrictions or harmonic phonons known for their varying suc-

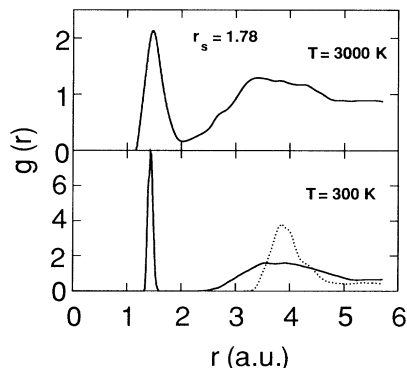


FIG. 1. H-H pair correlation functions $g(r)$ in the simulation with $r_s=1.78$. Atomic starting geometries are unstable and collapse forming H_2 molecules. The ensuing molecular material is stable up to at least $T=3000$ K (top) and forms a disordered solid upon cooling [bottom, the dotted line is the sharper $g(r)$ function between the molecular centers].

cess in structure predictions does not arise. Figure 1 shows how the H-H pair correlation function develops with time and temperature at $r_s=1.78$. Started from arbitrary atomic lattices, all particles pair up into H_2 molecules in only a few thousand time steps independent of the initial geometry of the simulation ($\Delta t = 0.57$ a.u.). Obviously a molecular state is preferred at $r_s=1.78$. At 3000 K the sample is clearly in a liquid state, the individual molecules diffuse freely but remain intact (Fig. 1, top). The position of the first peak in $g(r)$ (3000 K: 1.47 a.u.; 300 K: 1.44 a.u.) differs little from the free molecule equilibrium bond length [15]. The small temperature shift and the asymmetric shape of the peak reflect the anharmonic character of the intra- H_2 potential. The second peak in $g(r)$ centered near $r=3.8$ a.u. represents the weak inter- H_2 interaction. It is substantially broadened by disorder in the orientation of the individual molecules (see Fig. 1, bottom). Cooling the system slowly to 300 K we can observe the molecules form a (distorted) lattice that bears signs of a close packing of spheres [14] but with no particular ordering of molecular axes.

Increasing the density changes the picture. Figure 2 shows how the pair correlation function of the $r_s=1.5$ system changes with temperature. Starting the simulation from atomic initial structures, H_2 molecules form in the first few thousand MD steps with $T < 1000$ K (Fig. 2, top). The position of the first peak in $g(r)$ is practically unaffected by the increase in density but the broad second, inter- H_2 peak fell to ~ 3.3 a.u. Compression affects primarily the intermolecular spacing. Increasing the temperature to 3000 K the two peaks merge (Fig. 2, second from top). The pair correlation function assumes a very peculiar shape without the usual density depletion following a well-defined shell of first neighbors in liquids. Such behavior is known from plasmas [17]. The changes

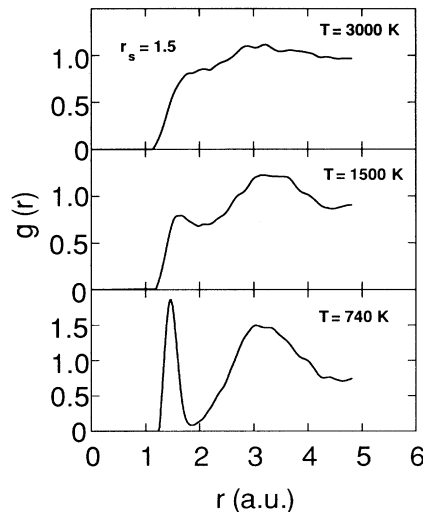


FIG. 2. $g(r)$ for the cooling phase of the simulation at $r_s=1.5$. Above ~ 1000 K $g(r)$ becomes increasingly featureless by overlap of intra- and inter- H_2 peaks (top and center) involving dissociation of molecules. Below 1000 K a strictly molecular phase is stable (bottom).

in $g(r)$ are entirely reversible (Fig. 2, lower two graphs), intramolecular and intermolecular peaks separate again below about 1000 K, with the molecules eventually close packing as before at $r_s=1.78$. As expected for higher compression we observe a more distinct ordering of the molecular axes [14]. Interestingly the dominant structural entities above ~ 1000 K are strings of atoms (see Fig. 3). The mechanism for string formation is via collision, dissociation, exchange of atoms, and renewed formation of H_2 molecules. Each molecule remains intact on average only a few hundred time steps at 3000 K.

The highest density sample we have investigated

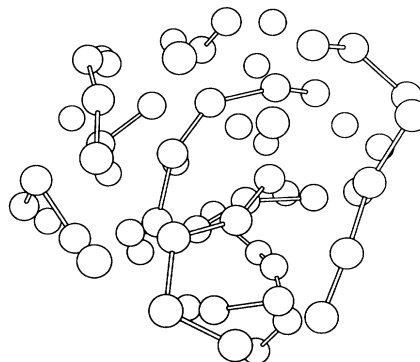


FIG. 3. Snapshot of a geometry at $r_s=1.31$ and $T=1500$ K. Such strings of atoms are typical for the samples with $r_s=1.5$ and 1.31. Bonds are drawn between atoms less than 1.78 a.u. apart, the maximum bond stretch in a free molecule at comparable internal thermal energy.

($r_s=1.31$, $\rho/\rho_0=13.6$) shows an even more pronounced tendency towards dissociation and filament formation. Starting from a compressed *molecular* structure the intra- and inter- H_2 peaks in $g(r)$ at 1.44 and near 2.8 a.u., respectively, overlap substantially already at 500 K (Fig. 4, top). This is sufficient thermal activation energy to initiate dissociation of H_2 molecules. The merging of the peaks is complete at 1200 K and $g(r)$ assumes the peculiar plasmlike shape again. From its highly diffusive behavior ($D \sim 10^{-3}$ cm²/s) we know that the sample is in a liquid state, but a precise melting temperature cannot be derived from MD simulations like ours. On average about half of the H_2 molecules have dissociated, and filamentary objects like in Fig. 3 dominate the microscopic picture. To characterize these further and remove bonding ambiguities we have performed several instantaneous quenches by relaxing the ionic positions to the next local minimum on the energy surface. The strings remain stable, but become zigzag chains of atoms with alternating bond distances ... s - l - s - l ... ($s \sim 1.5$ a.u., $l \sim 1.9$ a.u.) [18]. The sample at this stage is still best described not as “atomic” but as “partially molecular” in character. The transition to an entirely atomic form of hydrogen requires even higher densities [14].

Cooling the sample slowly (overall simulation length 110 000 time steps), two peaks separate again, finally leading to a well-ordered structure (Fig. 4, bottom). Each atom has on average three close neighbors, one at $d=1.53$ a.u., another one at $a=1.83$ a.u., and a third one at $b=2.15$ a.u. The next atoms are clearly further away. A schematic diagram of the structure neglecting numerous defects is shown in Fig. 5. H_2 molecules with

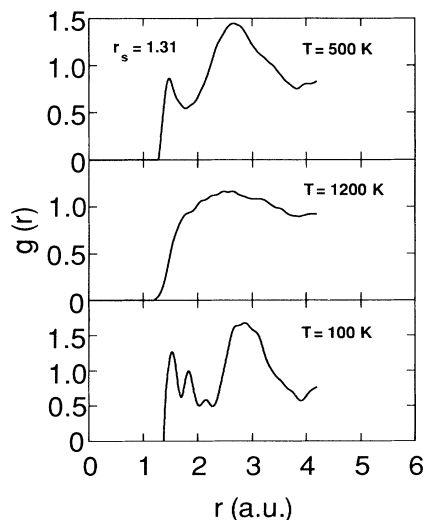


FIG. 4. $g(r)$ for $r_s=1.31$ in a run starting from a compressed *molecular* geometry (top). Heating the sample intramolecular and intermolecular peaks merge as in Fig. 2 (center), but a distinct molecular structure with zigzag chains in layers emerges upon annealing (bottom, see text and Fig. 5).

a large bond distance d form zigzag chains (spacing a) that interact with one another at slightly larger distances b to form weakly interacting layers (see Fig. 4, bottom). The molecular axes are all approximately parallel and tilted out of the planes formed by the molecular centers by $\Theta \sim 8^\circ$. Neighboring molecules form parallelograms with angle $\phi \sim 50^\circ$ (see Fig. 5). This geometry, although less symmetric, is qualitatively very similar to the most stable hcp molecular orderings reported in Refs. [9,10] and it is also close to the most stable alignment of two isolated molecules [19]. This structure is ~ 0.2 eV/atom more stable than the most stable *atomic* structure (simple cubic) commensurate with the cubic MD cell.

The vibrational density of states from our MD trajectory sheds some light on the nature of the vibron shifts observed experimentally with pressure. At 300 K the $r_s=1.78$ simulation shows a clear signal at 4250 cm⁻¹. This is in good agreement with experiment. Moderate compression leads to a slight *decrease* of bond length [20] and corresponding *increase* in the vibron frequency ([1], 30 GPa at 77 K: ~ 4500 cm⁻¹) with respect to the free molecule value. The calculated vibron frequency $\nu = 3750$ cm⁻¹ at $r_s=1.5$ is *lower* than its free-molecule and $r_s=1.78$ value. At $r_s=1.31$ finally it becomes so low [14] that overlap with other modes near 3000 cm⁻¹ prohibits quoting a precise value. The intramolecular and intermolecular distances become comparable, not only through isotropic compression but also through the particular molecular ordering brought about by it. The notion of a “molecular vibron” is losing meaning. We conclude that the structural changes laid out above can naturally account for the general behavior of the vibronic frequency with pressure [20]. Whether they are accompanied by metallization is a difficult to answer question for us, but trends on the basis of the electronic density of states (EDOS) at $\mathbf{k} = 0$ can be given. The EDOS for the *liquid* samples [14] at $T \sim 1500$ K with $r_s = 1.78, 1.5$, and 1.31 quite surprisingly still shows substantial gaps re-

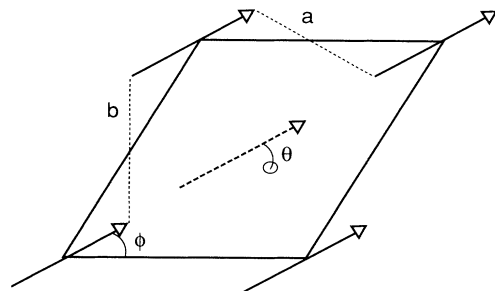


FIG. 5. Schematic diagram of the structure at $r_s=1.31$ and 100 K. Solid lines with arrows indicate hydrogen molecules ($d = 1.53$ a.u.) in the top layer; dashed arrows are the next layer underneath (see text). The molecular axes are approximately parallel ($\phi \sim 50^\circ$) and tilted out of the xy plane by $\theta = 8^\circ$ ($a \sim 1.83 < b \sim 2.15$ a.u.)

maining between the occupied and unoccupied manifolds even in the LDA (~ 3.0 , 2.0 , and 1.3 eV, respectively). This is in agreement with Ref. [9]: More stable structures lead to larger band gaps and structural changes leading to band gap closure are not favored.

In conclusion, our work suggests that the primary structural deformations in hydrogen in the density range investigated here are "dimensionality changes." With increasing pressure H_2 molecules (0D) line up to form filaments (1D). At low thermal energies these order in layers (2D) upon further application of pressure. The same mechanism has been proposed for the two-stage high-pressure transformation in elemental iodine [21]. Energy differences and barriers between low-lying structures are often very small ($O[0.01-0.1$ eV/atom $\equiv O[100-1000$ K]). Classical melting sets in at correspondingly low temperatures. Considering that the (structure dependent) ionic zero-point motion contributes typically $0.2-0.3$ eV/atom ($\sim 2000-3000$ K) over the density range $r_s=1.77-1.31$ [6,7] looking for *the* most stable hydrogen structure is not a meaningful endeavor with classical hydrogen as model. The actual phase diagram will to a large extent be determined by the interplay between the complex electronic energy surface dealt with in this work and the protonic zero-point motion apparently favoring isotropic structures at $T=0$ [6,22].

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