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Ab initio simulations of compressed liquid deuterium

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Using *ab initio* molecular dynamics, we have investigated liquid deuterium under pressure, in a range of densities relevant to recent laser shock experiments. Our results show that between four- and sixfold compression, and temperatures between 5000 and 10 000 K, the liquid goes continuously from a *dissociation/recombination regime*, where a substantial proportion of atoms form D_2 complexes, to a *scattering regime*, where mostly atoms are present. At about 10 000 K and sixfold compression, we find that the liquid is a poor metal. Our simulations point at a compression along the Hugoniot larger than indicated by old data, but smaller than predicted by laser shock experiments.

Recent experiments[1–4] on shock-compressed liquid hydrogen and deuterium have produced interesting and unexpected results for the equation of state and electrical conductivity at pressures near 100 GPa and elevated temperatures. In particular, measurements[1,2] of the electrical conductivity of samples compressed by reverberating shocks indicate that hydrogen becomes metallic at 140 GPa, near 3000 K. Measurements of the deuterium Hugoniot[3,4] using a high-intensity laser to shock liquid samples at 20 K and ambient pressures indicate that fluid deuterium is significantly more compressible (by about 50%) than previously thought. These results raise important questions about our understanding of hydrogen, the most abundant element of the universe.

In spite of the apparent simplicity of hydrogen, the challenges involved in accurate theoretical modeling of the warm, compressed fluid are formidable; indeed significant discrepancies exist between different theoretical approaches and some theories disagree with recent experimental data (see Fig. 1) for the deuterium Hugoniot. Statistical thermodynamics models[5–7] reasonably reproduce the recent data of Collins *et al.*[4]. These models are fitted to gas-gun data and assume mixtures of atoms and molecules in the liquid, their proportion varying with temperature (T) and pressure (P) and being determined by the minimization of free-energy model functions. Fully quantum mechanical approaches.[8] treating both ions and electrons with Path Integral Monte Carlo (PIMC) methods seemed also to indicate a maximum compression of deuterium along the Hugoniot close to that obtained in laser shock experiments. Theoretical approaches developed for strongly coupled plasmas[9] and applicable only at high P and T shows as well a maximum compression along the Hugoniot close to that obtained in recent experiments.[4] On the other hand, molecular dynamics simulations using a tight-binding (TB) model for the electrons,[10] give a pressure/density relationship along the Hugoniot, which substantially deviates from recent experiments, and agree with older models.[11] The same is true for the results of a classical spin Hamiltonian model recently proposed by Rescigno.[12]

In this paper we present the results of *ab initio* molecular dynamics (MD) simulations[13] of compressed liquid deuterium using Density Functional Theory (DFT) to describe electron-electron and electron-deuteron interactions, and classical dynamics to treat the motion of ions. We have considered temperatures sufficiently high ($T \geqslant 5000$ K) so that ion dynamics is expected to be reasonably described by Newtonian equations of motion. We have chosen to investigate the liquid at two densities (0.67 and 1.0 g/cm^3, corresponding to $\simeq$ four- and $\simeq$ sixfold compression,[14] respectively) where new shock laser data[4] significantly deviate from older models.[11] In particular $\rho = 1.0$ g/cm^3 is close to the density at which maximum compression along the Hugoniot was recently observed experimentally.[4] We have used a generalized gradient approximation (GGA) (Ref. 15) for the exchange and correlation energy functional, with no adjustable parameter. In our investigation, we have focused on the structural and electronic properties of the fluid as a function of P and T, and we have estimated its maximum compression along the Hugoniot.

We have performed constant volume MD simulations with periodic boundary conditions and supercells containing 124 atoms.[16] Some runs were performed using 216 atom

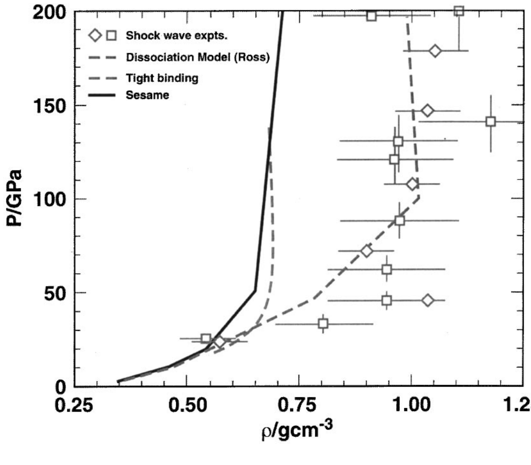

FIG. 1. Comparison of experimental Hugoniot data for deuterium with the results obtained using different theoretical models (see text). Laser shock data (Refs. 3,4) are indicated with open squares (Ref. 4) and diamonds (Ref. 3), corresponding to two sets of experiments. The Sesame (Ref. 11) data are indicated by a solid line. The results of tight-binding calculations (Ref. 10) and of the free-energy model of Ross (Ref. 5) are indicated by dotted and dashed lines, respectively.

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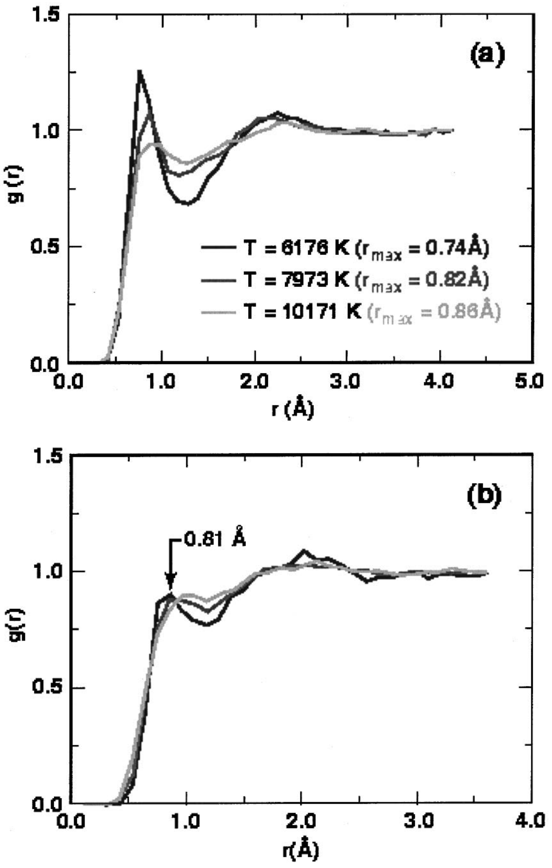

FIG. 2. Deuteron-deuteron pair correlation functions $[g(r)]$ for liquid deuterium at ρ=0.67 (a) and 1 g/cm^3 (b) at three different temperatures [$T\simeq$ 6000 (solid line), 8000 (dotted line) and 10 000 (dashed line) K]. The position of the first maximum (r_{max}) of the $g(r)s$ are indicated, when well defined.

supercells to test size effects. For the purpose of our investigation, size effects were found to be small; for example, at 10 000 K, the values of the pressure are 34 ± 5 GPa and 36 ± 2 GPa at ρ=0.67 g/cm^3, when calculated with 124 and 216 atom cells, respectively and $76\pm$ 5 and 79 ± 2 GPa at ρ=1 g/cm^3. Small size effects were also observed for the potential energy (E_p) of the liquid. For example, at 10 000 K and ρ=1 g/cm^3, the difference between E_p calculated with 124 and 216 atom supercells is 0.044 eV/atom. This difference is slightly smaller at the same temperature and ρ=0.67 g/cm^3. In our simulations, the interaction between electrons and ions was described with a norm-conserving pseudopotential[17] and only the Γ point was used to sample the supercell Brillouin zone. Single-particle electronic states were expanded in plane waves with a maximum kinetic energy cutoff of 45 Ry (a cutoff of 180 Ry was used for the potential and the charge density). The same *reference* MD cell was used at all densities, with the electronic kinetic energy being evaluated as in Ref. 18. This allowed us to have a constant resolution at different volumes and meaningfully compare values of the pressure obtained at different densities. At ρ= 0.67 g/cm^3 and temperatures less than 10 000 K, several annealing cycles were carried out in order to insure that the liquid was properly equilibrated. At high density and temperature (ρ=1.0 g/cm^3 and T=10 000 K), we performed MD runs both by using a Car-Parrinello dynamics and by quenching the electrons in their ground state at each step.[16] This enabled us to compare statistical averages obtained with different tolerances on the energy conservation in the microcanonical ensemble. The results of the two simulations were basically identical. Depending on T and P, the time step used in our simulations varied from 0.5 to 3. a.u. (1. a.u. = 0.0249 fs). Each run lasted about 1 ps, corresponding to $\simeq$ 100 oscillations of the D_2 molecule, whose vibrational frequency in the gas phase (ω_0) is 3112.7 cm^{-1}.

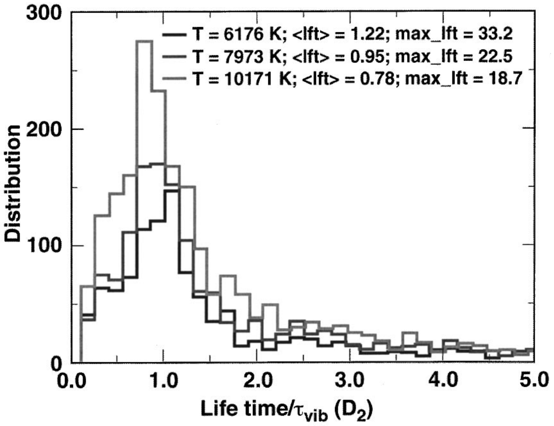

FIG. 3. Distribution of pairs lifetimes at ρ= 0.67 g/cm^3 and $6000\leqslant T\leqslant10000$ K (see text). The lifetime of a pair is defined as the number of times a pair of deuterons undergoes an oscillation at the vibrational frequency of the D_2 molecule in the gas phase, before separation of the two atoms occurs. We have indicated the average and maximum lifetime with <lft> and max_lft, respectively.

Figure 2(a) shows the deuteron-deuteron pair correlation functions $[g(r)]$ calculated for ρ=0.67 g/cm^3 (r_s=$2a_0$) as a function of temperature. The position of the first maximum of $g(r)$ varies from 0.74 Å at 6000 K to 0.86 Å at 10 000 K. These $g(r)s$ are qualitatively similar to those obtained both with TB-MD and PIMC simulations, although quantitative differences are present. For example the position of the first maximum at 10 000 K is 0.95 Å in TB-MD,[19] and 0.75 Å in PIMC (Ref. 8) calculations. The number of atoms forming pairs at a distance less than or equal to r_c=r_s =1.06 Å is about 80% at 6000 K and decreases only by few percent when T is increased up to 10 000 K. The number of atoms involved in pairs is very sensitive to the choice of the cutoff radius and decreases to less than 60% when r_c is decreased to 0.96 Å . Even when at distances close to the bond length of the gas phase D_2 molecule, atoms forming pairs do not necessarily give rise to true molecular states, in the liquid. This is shown, e.g., by the average lifetime of a pair, measured as the number of times a pair undergoes an oscillation at the frequency ω_0, before separation of the two atoms occurs. At r_s=2 a_0, the pair average lifetime is 1.22 at 6000 K and decreases to 0.78 at 10 000 K (see Fig. 3). At all T considered here, the lifetime distribution is very broad, with some pairs having lifetimes up to 33 and 19, at 6000 and 10 000 K, respectively. Consistent with these findings, the computed vibrational spectrum of the liquid $[Z(\omega)]$ at ρ=0.67 g/cm^3 does not show a clear peak centered at ω_0, but rather exhibits a very broad, flat distribution of modes, for T $\geqslant$ 6000 K. We note that even at lower densities, e.g. ρ=0.40 g/cm^3 and 10 000 K, the computed Z(ω) shows a

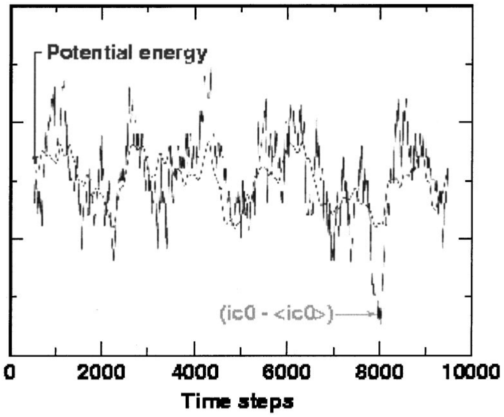

FIG. 4. Fluctuations of the potential energy (dotted curve, arbitrary units) and number of isolated deuterium atoms (ic0) as a function of the simulation time for compressed deuterium at $\rho=$ 0.67 g/cm^3 and $T\simeq6000$ K. The number ic0 has been defined as the number of atoms without a nearest neighbor within a cutoff $r_c=r_s$; the average coordination number $<$ic0$>$ is 25 and the smallest and largest values observed for ic0 are 15 and 30, respectively.

broad peak around the D$_2$ vibron, indicating that molecules lose their gas phase identity already at moderate (about 2.5) compression. At about fourfold compression, the liquid is to be viewed as a dynamical system where pairs of atoms constantly form and break apart, consistent with TB-MD results.[20] We call this a *dissociation/recombination* regime. The changes in atomic coordination as a function of time are directly related to the potential energy (E) fluctuations observed in the liquid; these are shown in Fig. 4 for $T\simeq$ 6000 K, where a clear relationship between the particle coordination and the fluctuations of E can be identified.

The upper panel of Fig. 5 shows the values of P and T computed for the liquid at $r_s=2$ a$_0$. At 10 000 K we report the values obtained with both 124 and 216 atom supercells, indicating that size effects are fairly small on both quantities. The range of computed values of $P(T)$ are similar to those obtained with the linear mixing model.[5] They do not show any change in the slope of $P(T)$ in the temperature range considered here, thus indicating no sign of a phase transition in the liquid at this density. However our simulations show a clear increase of P as a function of T, rather than a flat $P(T)$ curve, as found in Ref. 5. The potential energy contribution to the pressure ($-dE/dV$) is basically constant as a function of temperature in the range 5000–10 000 K, thus giving a slope dP/dT similar to that of an ideal gas at the same density. We note that our $P(T)$ curve is qualitatively similar to that obtained in TB-MD (Ref. 10) simulations, but rather different from the one obtained in PIMC calculations[8]. However PIMC data might be revised, according to recent refined simulations.[21]

The liquid is much less structured at $\rho=1$ g/cm^3 ($r_s=1.75$ a$_0$), as shown by the deuteron-deuteron correlation functions displayed in Fig. 5(b), which at all temperatures between 6000 and 10 000 K have a maximum smaller than 1.0. The position of the first maximum increases in going from $r_s=2.0$ to $r_s=1.75$ a_0, at all temperatures. At 10 000 K the first maximum in g(r) becomes a shoulder, with the first minimum being hardly defined. Geometrical definitions of pairs are thus difficult to apply, due to the lack of meaningful cutoff distances (r_c). Pairs identified with the same r_cs as those used at $r_s=2$ a_0 turn out to have average lifetimes less than 1 at all T, although some of them can persist in the liquid for as long as 10–15 oscillations, depending on the temperature. Most importantly, inspection of electronic eigenstates at $\rho=1$ g/cm^3 and high temperature shows a tendency of the electronic states to become delocalized. Most of the geometrically defined pairs do not correspond to chemically bonded species. In order to substantiate these findings, we have computed the electrical conductivity (σ) of the liquid as a function of frequency (ω) at 10 000 K and $\rho=1$ g/cm^3, using the Kubo-Greenwood formula.[22] From the limit of $\sigma(\omega)$ for $\omega\rightarrow0$, at 10 000 K we found an estimate of the dc conductivity ($\sigma_{\rm dc}$) of 8000 (Ω cm)$^{-1}$, corresponding to a resistivity ($1/\sigma_{\rm dc}$) of 125 $\mu\Omega\cdot$ cm; this is a value typical of a poor metal. The dc conductivity is twice as small at the same temperature and $\rho=0.67$ g/cm^3. The conductivity values obtained in our calculations are consistent with those computed in Ref. 19,23 for TB samples at similar densities. The difference in the values of $\sigma_{\rm dc}$ obtained using integer occupation numbers or Fermi-Dirac distributions is about 5%. But the error associated to the computed values of the conductivity could be as large as 30/50%, because of errors introduced by our GGA approximation and by k-point sampling. However we can conclude that increasing density in liquid deuterium leads to electronic delocalization and increased electrical conductivity; eventually the system becomes a poor metal at $T\simeq$ 10 000 K and in a range of densities $\rho=0.67$-1 g/cm^3. Consistently, in a Mott-Hubbard picture, at 10 000 K the ratio U/W—where U is the Coulomb interaction energy between two electrons on the same atom and W is the one-electron bandwidth—is slightly larger than

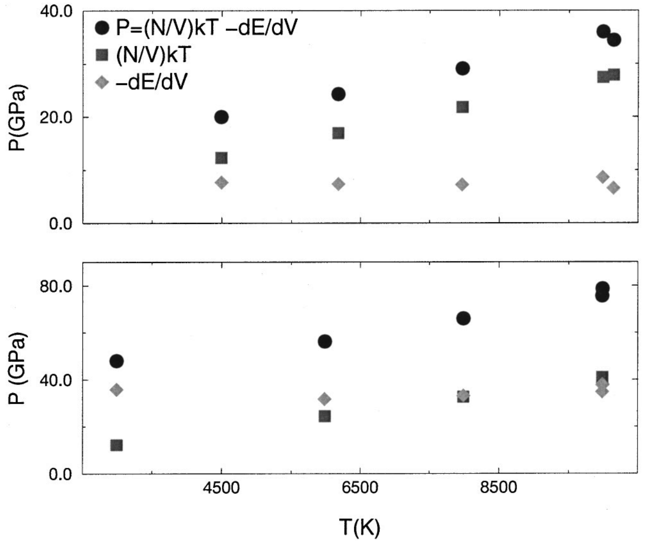

FIG. 5. Pressure (P) as a function of temperature (T) in compressed deuterium ($r_s=2$ and $r_s=1.75$ a_0 in the upper and lower panel, respectively) as obtained in *ab initio* simulations. The total pressure is given by $P=(N/V)kT\text{-}dE/dV$, where N, V, and E are the number of particles, the volume, and the potential energy of the system; k is the Boltzman constant. For $T=10\,000$ K, results obtained with both 124 and 216 atom MD cells are shown. Statistical error bars on the pressure obtained with 124 atom simulations vary from ± 5 to ±8 GPa, those on the temperature from 50 to 75 K and those on the potential energy from 0.05 to 0.08 eV/atom.

one at $\rho=$ 0.67 g/cm^3, and becomes less than 1 at $\rho=1$ g/cm^3. This indicates that $\rho=0.67$-1 g/cm^3 is a transition region from a nonmetallic to a metallic regime. In particular, we have taken $U\simeq$ 17 eV,[24] and W = 16 and 18.5 eV, as calculated from averaging over 7 MD configurations at $\rho=$ 0.67 and 1 g/cm^3, respectively. Our findings on the conductivity of the sixfold compressed liquid are in agreement with recent reflectivity measurements[25] showing that at $\rho=1$ g/cm^3, compressed deuterium becomes a poor metal, at high T.

The lower panel of Fig. 5 shows the computed values of P and T at $\rho=1$ g/cm^3. The pressure is an increasing function of the temperature. Contrary to what was found at the lower density, the kinetic energy contribution to the pressure is smaller than the potential energy contribution in a large temperature range, up to $\simeq$8–9000 K. At 10 000 K the kinetic contribution is again dominant, similar to the lower density.

We used the limited number of (P,T,E) points calculated in our simulation to estimate some (P,ρ) values on the deuterium Hugoniot. Assuming that P will increase with T also for temperatures higher than those considered in our simulations, our estimated maximum compression of the liquid is at $\rho\simeq$ 0.75 g/cm^3 (corresponding to 4.4 compression) and $P \simeq$ 50 GPa. This density is larger than that shown by old data (the so-called Sesame fit,[11]) but smaller than that observed[4] by recent laser experiments ($\rho\simeq1$ g/cm^3, six-fold compression). Similar results for the Hugoniot have been obtained in independent first-principles simulations by Lenosky *et al.*[26]

In conclusion, we have studied compressed deuterium at $5000 \leqslant T \leqslant 10\,000$ K, and densities relevant to recent laser shock experiments. Between four and six fold compression the liquid changes continuously from a *dissociation/recombination* regime, with a considerable proportion of long-lived diatoms, to a scattering regime, where mostly atoms and some short-lived diatoms are present. In the *dissociation/recombination* regime we found a large number of different molecular aggregates with different electronic properties. In the scattering regime most pairs defined according to a distance criterion do not correspond to chemically bonded species. We note that at all densities considered here, using the concept of diatoms (or of transient diamers)[2] is more appropriate than that of molecules; indeed pairs of atoms separated by a distance close to the D_2 bond length can attain a variety of bonding configurations, which are in general different from that of the molecule in the gas phase. The mean-field approximation (DFT/GGA) used here seems to underestimate the maximum compression observed experimentally along the Hugoniot. This could come from an underestimate of the energy difference between fully dissociated metallic states and semiconducting states containing both atomic pairs and isolated atoms, in the liquid. Investigations involving explicit treatment of the spin, as well as quantum Monte Carlo treatments of the many body interactions, are under way.

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[1] S. T. Weir, A. C. Mitchell, and W. J. Nellis, Phys. Rev. Lett. **76**, 1860 (1996).

[2] W. J. Nellis, S. T. Weir, and A. C. Mitchell, Phys. Rev. B **59**, 3434 (1999); W. J. Nellis, A. A. Louis, and N. W. Ashcroft, Philos. Trans. R. Soc. London, Ser. A **356**, 119 (1998).

[3] L. B. Da Silva *et al.*, Phys. Rev. Lett. **78**, 483 (1997).

[4] G. W. Collins *et al.*, Science **281**, 1178 (1998).

[5] M. Ross, Phys. Rev. B **58**, 669 (1998).

[6] Z. Zinamon and Y. Rosenfeld, Phys. Rev. Lett. **81**, 4668 (1998).

[7] D. Saumon and G. Chabrier, Phys. Rev. A **44**, 5122 (1991); *ibid.* **46**, 2084 (1992); D. Saumon, G. Chabrier, and H. M. V. Horn, Astrophys. J., Suppl. Ser. **99** (1995).

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

[9] F. J. Rogers and D. A. Young, Phys. Rev. E **56**, 5876 (1997).

[10] T. J. Lenosky, J. D. Kress, and L. A. Collins, Phys. Rev. B **56**, 5164 (1997).

[11] G. I. Kerley, in *Molecular Based Study of Fluids*, edited by J. M. Haile and G. A. Mansoori (ACS, Washington, DC, 1983), pp. 107–138.

[12] T. Rescigno (unpublished).

[13] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[14] At 20 K the densities of hydrogen and deuterium are 0.071 and 0.171 g/cm^3, respectively.

[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[16] We used the first-principles molecular dynamics code JEEP 1.4.6, F. Gygi, Lawrence Livermore National Laboratory, 1999.

[17] D. Hamann, Phys. Rev. B **40**, 2980 (1989).

[18] P. Focher *et al.*, Europhys. Lett. **36**, 345 (1994).

[19] T. Lenosky *et al.*, Phys. Rev. B **55**, 11 907 (1997).

[20] L.A. Collins *et al.*, Phys. Rev. E **52**, 6202 (1995).

[21] B. Militzer (private communication).

[22] See, e.g., D. J. Thouless, Phys. Rep. **13**, 93 (1974).

[23] I. Kwon, L. Collins, J. Kress, N. Troullier, Phys. Rev. E **54**, 2844 (1996); T. Lenosky, J. Kress, L. Collins, and I. Kwon, J. Quant. Spectrosc. Radiat. Transf. **58**, 743 (1997).

[24] N. F. Mott, *Metal Insulator Transitions* (Taylor and Francis, London, 1990).

[25] P. Celliers *et al.* (unpublished).

[26] L. A. Collins and T. J. Lenosky (private communication); T. J. Lenosky *et al.*, Phys. Rev. B **61**, 1 (2000).