PHYSICAL REVIEW B, VOLUME 65, 220102(R)

Electronic excitations and the compressibility of deuterium

François Gygi and Giulia Galli
Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550
(Received 18 April 2002; published 7 June 2002)

We propose an explanation of the large compressibility of deuterium observed in recent laser shock experiments, as inferred from large-scale first-principles simulations. Contrary to usual assumptions about dynamical compression of matter, we found that electronic excitations can occur during shock propagation in fluid deuterium. Their origin is traceable to nonadiabatic processes caused by transitions through avoided crossings near the Fermi level as the liquid is impacted by the shock front. Our results indicate that the observed large compressibility is determined by shock-induced electronic excitations and does not arise from new equilibrium properties of hydrogen in the liquid state.

DOI: 10.1103/PhysRevB.65.220102 PACS number(s): 71.15.Pd, 47.40.Nm, 61.20.−p, 62.50.+p

The phase diagram of hydrogen has been the subject of active theoretical and experimental investigation for almost a century.[1] Yet the properties of hydrogen at high pressure are poorly understood, in particular the compressibility of the fluid and the insulator-to-metal transition remain controversial issues. Recently laser shock experiments[2–6] produced unexpected results on liquid deuterium under pressure, indicating that the fluid is much more compressible than previously thought.[6] They also showed that a transition to a metallic state occurs at pressures significantly lower than previously reported,[7] although at higher temperature. Furthermore, the temperature at which metalization seems to occur in laser shocked deuterium is lower than predicted by any existing model. These results have very important implications for models of Jovian and extra-solar giant planets,[8] brown dwarfs and low-mass stars, as well as for the design of deuterium-tritium targets for inertial confinement fusion (ICF).[9] They also cast doubts on our general understanding of the phase diagram of hydrogen, one of the simplest and most studied elements.

After laser shock data appeared in the literature, several first-principles calculations[10–13] were carried out, in order to rationalize the experimental results. However none of those calculations appear to support the enhanced compressibility found experimentally. *Ab initio* molecular dynamics (MD) (Refs. 12 and 13) and path-integral Monte Carlo simulations[10] are consistent with old, well established models of the hydrogen equation of state (EOS),[6] and with classical spin Hamiltonian models,[14] but they do not agree with single[3] and double shock laser experiments.[5,11] Contrary to *ab initio* approaches, several semiempirical thermodynamic models[15,16] reasonably reproduce the recent data of Collins *et al.*,[3] similar to theories developed for strongly coupled plasmas.[17]

All simulations of liquid deuterium performed so far have been carried out at fixed thermodynamic conditions. Results were then used to extract the pressure-density curve satisfying the Hugoniot relations, thus ignoring the dynamical processes occurring during shock propagation. Direct simulations of shock propagation in deuterium are very challenging, since they require an accurate modeling of complex dynamical processes such as dissociation and ionization over a wide range of thermodynamic conditions.

In this paper, we report the results of dynamical simulations of shocked deuterium carried out entirely from first-principles. Using highly optimized *ab initio* MD algorithms and codes, we have succeeded in performing *ab initio* simulations of the early stages of shock propagation in fluid deuterium, and in observing the formation of a shock front on the atomic scale. Our simulations were designed to reproduce as closely as possible the experimental conditions in which an impactor is driven at supersonic speed into a sample of liquid deuterium. Our results show that electronic excitations occurring during shock propagation play an important role in determining the density of the compressed fluid.

We carried out calculations[18] within density functional theory in the local density approximation,[19] using the Car-Parrinello (CP) method.[20] Shocks were created in liquid deuterium by hitting a liquid sample consisting of D_2 molecules with a group of atoms arranged in the geometry of an ''impactor''[21] (see Fig. 1). We performed constant energy MD simulations explicitly designed to simulate shocks in the presence of periodic boundary conditions (PBC), which were imposed in order to properly evolve the electronic states expanded in plane waves. Performing constant energy simulations in the absence of external forces had the advantage of allowing us to check the internal consistency of the theory by verifying the Hugoniot relation for mass and momentum conservation in two different, independent manners.

Shock simulations consisted of three phases. First a short MD run was performed to equilibrate the liquid, while the impactor and the wall were kept fixed (see Fig. 1). Second, the impactor was accelerated by applying a force F on all impactor atoms of mass M_I in the x direction for a duration $\Delta t = M_I u_p / F$, which brings the impactor to the desired velocity u_p. We used $F = 555.0$ a.u. and values of Δt appropriate to reach velocities of 10, 15, 20, and 30 km/s, which correspond to impactor speeds used experimentally in laser driven shocks. At the end of the acceleration phase, the forces on the impactor were removed. In the third phase, the impactor was allowed to continue its trajectory, its large mass ensuring that it traveled across the entire unit cell without reducing its velocity or changing its shape. No external forces were applied on any atom during the compression so that the total energy was conserved. During compression, the

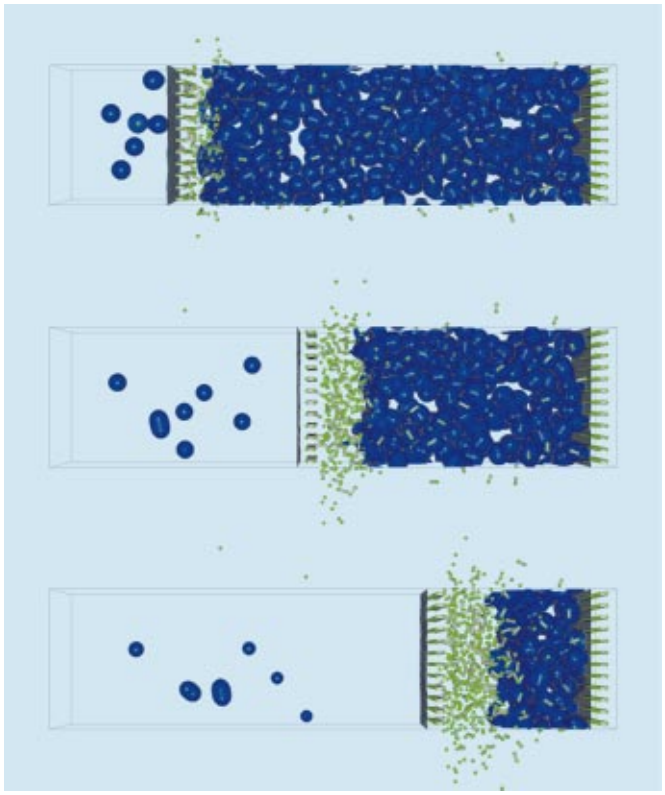

FIG. 1. (Color) Snapshots of a shock simulation, showing deuterium atoms (green spheres) and electronic charge densities (blue isosurfaces) at three subsequent times during the shock propagation. Small green spheres represent the instantaneous position of deuterium atoms; bonds between atoms were drawn using a cutoff of 0.8 Å for distances. Electronic charge density isosurfaces are represented in blue for a chosen value of the charge ($\overline{\rho}$). The region of space where electronic isosurfaces are not drawn corresponds to electronic densities higher than the value $\overline{\rho}$ and coincides with the shock front region. Interactions with deuterium atoms represented outside the simulation box in the snapshots were appropriately taken into account by using PBC (see text). We note that the impactor (moving in the x direction) as designed in this simulation permitted some leaks, i.e., some deuterium atoms belonging to the fluid could go through the impactor as the liquid was compressed. The effect of these leaks on the computed density of the compressed fluid was negligible.

sample was characterized by density profiles along the x direction, which were then used to compute the shock front velocity, similar to what is done experimentally.[22]

The total force acting on the impactor was measured during compression, and provided a direct determination of the x component of the stress in the compressed liquid through the relation $\sigma_x=(\Sigma_{i=1}^{N}F_x^i)/(b\,c)$ where b and c are the dimensions of the unit cell in the y and z directions, and the index i runs over all the atoms of the impactor. The values of σ_x are in close agreement with those of $\rho_0 u_s u_p$, which confirms that the Hugoniot relation expressing momentum conservation is satisfied. The compression ratio $\eta=\rho/\rho_0$ was computed both from a direct determination of the number density of the compressed liquid and from the relationship $\eta=u_s/(u_s-u_p)$, where $\rho_0=0.171$ g/cc is the equilibrium density of deuterium at 20 K. The good agreement between the values obtained in these two different ways offers another internal consistency check (conservation of mass). Assuming isotropy of the stress tensor in the compressed liquid, we represent in Fig. 2 the curves $p(\rho)$ corresponding to the values obtained for four different particle speeds. At low impactor velocity (10 km/s), the results of our direct simulation agree with previous theoretical results, and are consistent

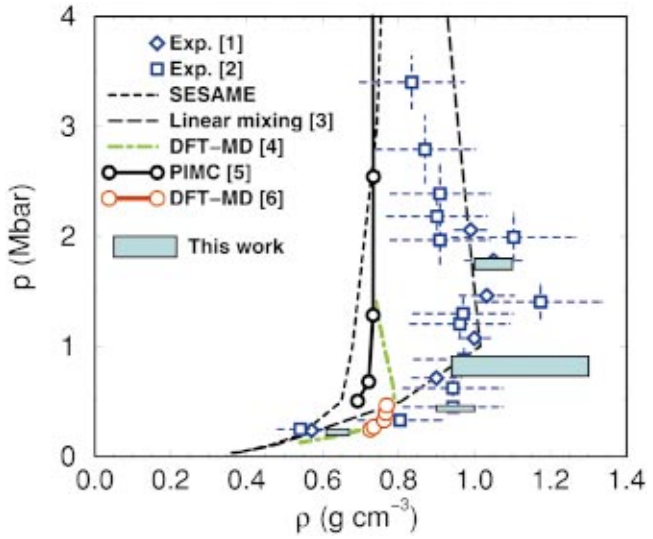

FIG. 2. (Color) Pressure p vs density $[p(\rho)]$ for shocked deuterium. Together with the data obtained with the present shock simulations for four impact velocities (see text), we also show the results of laser-driven shock experiments (squares), as well as the results from previous first-principles calculations based on equilibrium simulations of the final shocked state. In the present work the $p(\rho)$ curve was obtained directly from computed shock speeds and pressure values and did not involve the calculation of energy differences between the final and initial state.

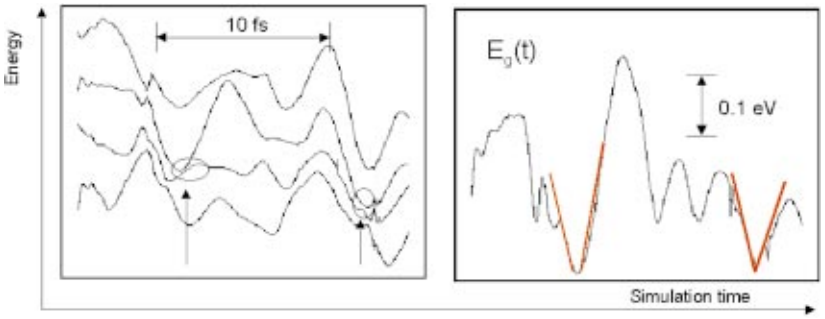

FIG. 3. (Color) Eigenvalues (left panel) and value of the HOMO-LUMO gap $[E_g(t)$, right panel] as a function of time as computed in the 288 atom shock simulation (see text). The circles (left panel) show avoided crossing between HOMO and LUMO states. The straight line (right panel) point out the rapid variation of the $E_g(t)$ at the avoided crossings.

with the the so-called SESAME EOS (Ref. 6) and with low pressure experimental data. However, at higher impactor velocities (15–30 km/s), we observed a higher compressibility in agreement with laser shock experiments, and in contrast with previous theoretical results.

These findings were surprising since we used the same level of *ab initio* theory as in previous calculations,[12] and led us to investigate in detail all possible sources of discrepancies between equilibrium and shock propagation simulations. In particular, both types of simulations were tested for their sensitivity to the value of the fictitious electronic mass μ entering the CP Lagrangian.[20] The parameter μ is associated with the classical degrees of freedom describing Kohn-Sham (KS) orbitals, and determines how far the system can deviate from the Born-Oppenheimer (BO) surface during the simulation. Smaller values of μ result in smaller deviations from the BO surface, and in a better approximation of BO ionic trajectories.[23]

Equilibrium simulations were shown to be insensitive to the choice of μ (Ref. 12) within a reasonable range and to give the same results as *ab initio* simulations where the total energy is minimized at each ionic step. In contrast, shock propagation simulations were found to be very sensitive to the choice of the parameter μ for particle speeds higher than 10 Km/sec. We repeated shock simulations, decreasing the value of μ from 396 to 44 a.u. Correspondingly, the simulation time step was reduced from 3 a.u. to 1 a.u. to ensure stability of the integration of the electronic equations of motion. This set of simulations resulted in a smaller compression ratio, bringing it close to the results of equilibrium simulations. This shows that allowing smaller deviations away from the BO surface results in a lower compression ratio.

Although the CP Lagrangian does not include the quantum dynamics of excitation processes, CP simulations often mimic them by allowing a transfer of energy between the ionic and the electronic degrees of freedom.[23] Our results therefore suggest that electronic excitations occurring during shock propagation play an important role in determining the maximum compressibility of deuterium. In the absence of external perturbations, electronic excitations can be caused by nonadiabatic processes if the coupling constant $(m_e/M_i)^{1/4}$ is large, where m_e denotes the electronic mass and M_i is the mass of the deuterium nucleus. In deuterium, $(m_e/M_i)^{1/4}=0.128$. Quantitative investigations of nonadiabatic effects require solving the time-dependent Schrödinger equation for both ions and electrons, and are currently not feasible for more than a few particles.

We therefore looked for signatures of nonadiabatic effects in our simulations of shock propagation, without resorting to full Schrödinger dynamics. The conventional perturbative approach to nonadiabatic excitations is based on the Landau-Zener (LZ) theory,[24] which applies to pairs of eigenstates well separated in energy from the rest of the Hamiltonian spectrum.[24] Considering the case of the ground state and the first excited state, the probability that the system will remain in the ground state depends sensitively on the occurrence of avoided crossings (ACS) between the two energy levels during dynamical evolution. We assumed that ACS of the highest occupied (HOMO) and lowest unoccupied (LUMO) one-particle KS eigenvalues are indicative of ACS between the ground and first excited state of the system. Therefore we computed the time evolution of both occupied and empty KS eigenvalues during shock propagation and investigated the occurrence of ACS.

In order to compute occupied and excited electronic states at each step of our simulations we used the algorithm proposed in Ref. 25. Since this procedure is computationally much more expensive than a CP simulation, we had to resort to a smaller MD cell (288 atoms) when including excited states. The time evolution of the single particle energy gap (E_g) revealed the occurrence of avoided crossings between the HOMO and the LUMO of the fluid and a sharp increase of $dE_g(t)/dt$ during avoided crossings (see Fig. 3). These avoided crossings are likely to cause nonadiabatic transitions at high shock velocities in a fluid of light particles such as deuterons. The transition probability between HOMO and LUMO states depends exponentially on the variation of $dE_g(t)/dt$ and could in principle be estimated. However, we regard the trajectories generated by a CP dynamics as a qualitative estimate of the actual ones and no attempt has been made to quantitatively estimate transition probabilities from the LZ formula.

Our direct shock simulations have highlighted an important physical phenomenon, which may be responsible for the high compressibility of deuterium shocked at high velocity: high shock speeds and the light deuterium mass are responsible for nonadiabatic effects occurring during shock propagation. Ground state trajectories and trajectories recorded during shock propagation differ in a substantial way and, correspondingly, the way the single particle energies vary as a function of time differ substantially in the two cases. Because of these differences and because of the light mass of deuterium, nonadiabatic effects at the shock front play an important role, contrary to the ground state case. These effects allow the system to depart from its BO trajectory and cause energy to be spent in driving electronic excitations. Consequently the ions remain colder and the fluid is more compressible than in the absence of electronic excitations.

These results are consistent with both pyrometric[26] and optical reflectance[4] measurements of laser shocked deuterium. Optical reflectance data show that the transformation of deuterium from a semiconducting to a metallic fluid occurs at a significantly lower pressure and density than the metallic state produced by Weir *et al.*,[7] although at higher temperature. This is consistent with electronic excitations being present in the liquid, during the shock and yielding a high density of carriers, as extracted from reflectance measurements. In addition pyrometric measurements have found that the temperature is lower than that predicted by any existing model, when deuterium becomes metallic, consistent with ions remaining colder in the presence of electronic excitations.

Our first-principle calculations could simulate only the early stages of shock propagation and several issues need further investigation. In particular there remain open questions about the lifetime of the electronic excitations induced by nonadiabatic transitions during the shock. The large num-

ber of deexcitation mechanisms (radiative and nonradiative) makes it very difficult to estimate how long the compressed liquid will take to go back to its ground state after the shock.

In conclusion, the use of CP *ab initio* MD simulations of direct shock propagation in liquid deuterium has allowed us to identify a physical mechanism which may be responsible for the high compressibility of deuterium when shocked at high velocity. Our results show that the enhanced compressibility of deuterium found experimentally is determined by shock-induced electronic excitations and not by unexpected ground state properties of hydrogen in the liquid state. This implies that the understanding of hydrogen's EOS as derived from *ab initio* theories and old models[6] is correct and does not contradict recent laser-shock data.

We are indebted to R. Cauble for numerous illuminating discussions on the experimental data and for a critical reading of the manuscript. We would also like to thank R. Car, G. Collins, P. Celliers, B. Militzer, D. Boercker, Y. Gupta, J. Asay, and M. Knudson for many useful discussions. This work was performed by University of California Lawrence Livermore National Laboratory, under Contract No. W-7405-ENG-48.

[1] E. Wigner and H.B. Huntington, J. Chem. Phys. **3**, 764 (1935); K.A. Johnson and N.W. Ashcroft, Nature (London) **403**, 632 (2000).

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

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

[4] P.M. Celliers *et al.*, Phys. Rev. Lett. **84**, 5564 (2000).

[5] A.N. Mostovych *et al.*, Phys. Rev. Lett. **85**, 3870 (2000).

[6] 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.

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

[8] W.B. Hubbard, Science **214**, 145 (1981); T. Guillot, *ibid.* **286**, 72 (1999).

[9] J. Lindl, Phys. Plasmas **2**, 3933 (1995).

[10] B. Militzer and D. Ceperley, Phys. Rev. Lett. **85**, 1890 (2000).

[11] B. Militzer *et al.*, Phys. Rev. Lett. **87**, 275502 (2001).

[12] G. Galli, R.Q. Hood, A.U. Hazi, and F. Gygi, Phys. Rev. B **61**, 909 (2000).

[13] T.J. Lenosky, S.R. Bickham, J.D. Kress, and L.A. Collins, Phys. Rev. B **61**, 1 (2000).

[14] T. Rescigno, Phys. Rev. Lett. **84**, 4377 (2000).

[15] M. Ross, Phys. Rev. B **58**, 669 (1998); Z. Zinamon and Y. Rosenfeld, Phys. Rev. Lett. **81**, 4668 (1998).

[16] D. Saumon and G. Chabrier, Phys. Rev. A **44**, 5122 (1991); **46**, 2084 (1992); D. Saumon *et al.*, Astrophys. J. **460**, 993 (1996).

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

[18] We used norm-conserving pseudopotentials [D. Hamann, Phys. Rev. B **40**, 2980 (1989)] and a plane wave representation of electronic wave functions with an energy cutoff of 44 Ry. Simulations were performed using the first-principles MD code JEEP 1.6.6 (F. Gygi, Lawrence Livermore National Laboratory, 1999–2001).

[19] W. Kohn and L.J. Sham, Phys. Rev. A **140**, 1133 (1965).

[20] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985). The fictitious electronic mass μ in the CP Lagrangian was set to 396 a.u. and a time step Δt of 3 a.u. was used.

[21] A total of 1320 deuterium atoms were placed in an orthorhombic, periodic unit cell of dimensions $120\times30\times30$ a.u. A first group of 288 atoms (the ''impactor'') was arranged to form a slab of 144 D_2 molecules oriented along the x axis and packed in a square lattice placed at one end ($x=-57$ a.u.) of the unit cell. The atoms constituting the impactor were artificially assigned a mass of 10 000 times the mass of a deuterium atom, in order to preserve the geometry of the impactor during the simulation. A similar slab (the ''wall'') was placed at the other end of the unit cell ($x=+57$ a.u.) and was kept fixed during the simulation. Finally, 744 deuterium atoms were included in the center of the unit cell in the form of randomly distributed and oriented D_2 molecules. This last set of molecules constitutes the sample of liquid D_2 to be compressed during the simulation. The initial liquid density corresponds to the experimental density at 20 K and ambient pressure (0.171 g/cc).

[22] Histograms of particle density were computed by counting deuterium atoms in bins of thickness $\Delta x=1$ a.u. along the x direction. Density profiles computed at different times were then assembled into two-dimensional density maps. The density profiles and maps were used to determine the position of the shock front $x_s(t)$, and its velocity u_s. The velocity of the shock front u_s was obtained from a least-square fit of $x_s^\rho(t)$ to a linear function of time (t), $x(t)=u_s t+c$. $x_s^\rho(t)$ denotes the location at which the leading edge of the density distribution reaches the threshold ρ. We verified that the values of u_s obtained in this way are insensitive to the choice of ρ in the range $\rho\in[0.4,0.8]$ g/cc.

[23] F.A. Bornemann and C. Schuette, Numer. Math. **78**, 359 (1998); G. Pastore, E. Smargiassi, and F. Buda, Phys. Rev. A **44**, 6334 (1991).

[24] G.A. Hagedorn, Rev. Math. Phys. **11**, 41 (1999); I. Dobrovsky and R.D. Levine, Chem. Phys. Lett. **286**, 155 (1997).

[25] N. Marzari, D. Vanderbilt, and M.C. Payne, Phys. Rev. Lett. **79**, 1337 (1997).

[26] G. W. Collins *et al.*, Phys. Rev. Lett. **87**, 165504 (2001).