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Local-spin-density-approximation molecular-dynamics simulations of dense deuterium

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Local-spin-density-approximation molecular-dynamics simulations of deuterium in the dissociating regime are presented, with a particular emphasis on the molecular phase of two isochores corresponding for deuterium to $V=6$ cm^3/mole, $\rho=0.670$ g/cm^3 and $V=4$ cm^3/mole, $\rho=1$ g/cm^3. It is shown that the transition from the molecular regime, well described by the local-spin-density-approximation functional, to the dissociated regime where previous local-density-approximation results are recovered, comes with a negative curvature $\delta P/\delta T<0$ in the isochore. We show that this effect is not enough to explain the large compressibility measured in the laser experiments [L. B. DaSilva *et al.*, Phys. Rev. Lett. **78**, 483 (1997); G. W. Collins *et al.*, Science **281**, 1178 (1998); P. Celliers *et al.*, Phys. Rev. Lett. **84**, 5564 (2000)].

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Despite numerous attempts, the experimental hugoniot of hydrogen, recently obtained by laser induced shock compression [1–3], remains not properly reproduced by *ab initio* numerical simulations such as tight binding (TB) [4], density functional theory simulations (DFT) including gradient generalized approximation (GGA) [5,6], variational density matrix method (VDM) [7] or wave packet molecular dynamics (WPMD) [8]. It is worthwhile to note that, now, those very different *ab initio* approaches are converging to the same side of the hugoniot diagram shown in Fig. 1, predicting a maximum compression ρ/ρ_0 between 4 and 4.6, far from the experimental data and close to the SESAME [9] prediction. On the contrary, so-called ''chemical models'' such as Ross's linear mixing (LM) model [10], Saumon Chabrier [11], or Arnault's nonlinear mixing model [12] are going across most of the experimental data. Moreover, very recently, Rogers extended the Actex model to account for bound states [13], reproducing by this way the high compressibility of deuterium. But the physical reasons for this observed high compressibility are still not understood, as well as the detailed behavior of the electrical conductivity in this regime [14] (5000 K$<T<$30 000 K, 0.3 g/cm$^3<\rho<1$ g/cm^3). Density functional theory (DFT), which has been very successful when applied to condensed matter, fails to describe properly the high compressibility of hydrogen ($\rho/\rho_0\simeq6$), questioning the validity of the local-density approximation (LDA) and its improvements such as generalized gradient approximation (GGA) in this region. If we believe in the experimental data, we must dig in the approximations and the physics left in the LDA-GGA scheme. An important ingredient which has not been explicitly treated, up to now, is the spin of the electrons, which clearly plays a major role in the binding of molecules and thus in the mechanism of dissociation. Moreover, spin fluctuations are believed to play an important role for metal insulator transitions. In the fully dissociated regime the influence of the spin must vanish and we should recover LDA-GGA results. In the DFT framework, an explicit description of the spin is introduced through the local-spin-density approximation (LSDA) for *up* and *down* spin populations.

In this Rapid Communication we present extensive calculations performed with the VASP code, which is a plane-wave pseudopotential code developed at the Technical University of Vienna [15]. Vanderbilt ultrasoft pseudopotentials [16] are used with a LSDA functional given by the Perdew-Wang 91 parametrization of GGA (including explicitly the spin) [17]. After discussing the dissociation properties within the LSDA formulation, we will assess the different approximations made. Isochores (pressure versus temperature) curves for two densities corresponding to $V=6$ cc/mole and $V=4$ cc/mole will be shown, with a particular emphasis on the molecular phase. For those later densities, the existence of solutions of the Hugoniot equation will be discussed and a more general curve will be eventually deduced from a series of simulations on different volumes.

The hugoniot calculations presented in the following sections, rely on a precise estimation of the internal energy of

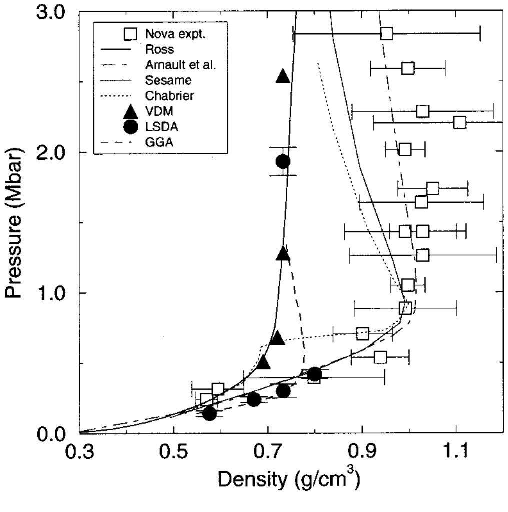

FIG. 1. Comparison between experimental laser hugoniot data for deuterium [1–3], with SESAME prediction (thick line) and *chemical models*: Ross (solid line) [10], Arnault *et al.* (dotted-dashed line) [12], and Chabrier and co-workers (dotted line) [11]. *Ab initio* models are variational density matrix (closed triangles) [7], DFT-GGA simulations (thick dashed line) [5,6], and our DFT-LSDA results (closed circles).

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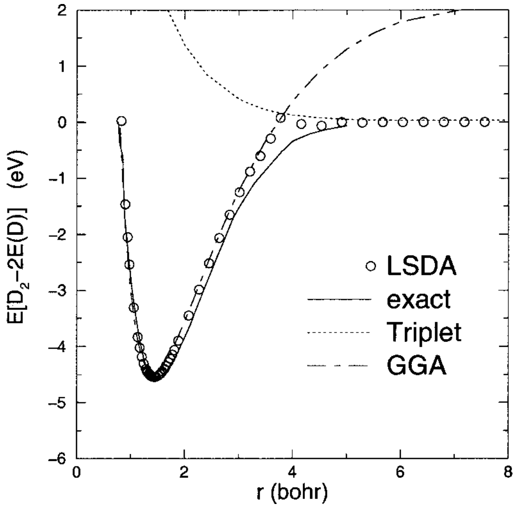

FIG. 2. Dissociation curve $E[D_2]-2E[D]$ in eV, for deuterium molecule vs internuclei distance. Circles are the LSDA result, dashed-dotted line the GGA result, and dotted line the LSDA in triplet state. Solid line is the Gunnarson and Lundqvist result [18].

the reference state, which is the liquid deuterium at 20 K and $V=23.5$ cm^3/mole. Such a volume is not accessible to a plane wave method, due to the excessive computational cost associated with the very large amount of plane waves required. In the dilute regime, the total energy can be approximated by the isolated molecule energy because, as we checked, interactions are negligible. Both GGA and LSDA theories are giving almost the same energy for the molecule $E[D_2]=-1.169$ ryd/at., but the binding energy defined by $E[D_2]-2E[D]$ is different due to the difference in the isolated atom energy which is -0.920 ryd/at. in GGA theory and -1.0012 ryd/at. in the LSDA theory. Thus, the binding energy (-4.5 eV) is correctly reproduced by LSDA theory and is coherent with isolated atom energy evaluation. Moreover, as it is well known, LDA (or GGA) are by nature unable to reproduce a correct molecular dissociation. Actually, when the distance between nuclei becomes larger than 3.2 a.u., LSDA energy becomes lower than GGA energy due to the flip of the electrons changing from a singlet to a triplet state [18]. This flip is reproduced by LSDA functional, as shown in Fig. 2, but the electronic symmetry change appears more discontinuous than theory would predict. We have also checked that the vibrational frequencies computed either by the energy curve or by molecular dynamics are in agreement with the theoretical values.

Most of the simulations have been carried out with 64 or 108 deuterons. Temperature, pressure, and total energies were averaged, and mean square fluctuation computed, over 600 time steps of 0.2 fs of purely microcanonical simulations after 300 time steps of thermalization by velocities rescaling. The electronic temperature was set equal to the required ionic temperature. The number of electronic states was taken in order to have an occupancy for the highest state, given by the Fermi-Dirac statistics, smaller than 10^{-5}. We have identified three sources of inaccuracies: the number of particles, the pseudopotential cutoff and Brillouin zone sampling. An estimation of size effects can be done by comparing the pressures obtained with 64 and 108 particles. In most cases this difference is of order of 15%, particularly in the dissociation region. Convergence in the ultrasoft pseudopotential cutoff needs a value of 450 eV. Tests have shown that the pressure is very sensitive to the cutoff and that the use of a 150 eV cutoff would lower the pressure by 30%. Concerning Brillouin zone sampling, for $N=108$ atoms, using the gamma point or a mesh of 3^3 points, gives a 5% variation in pressure. We thus have chosen to stay at gamma point in order to perform longer simulations (600 time steps of 0.2 fs). This reduces the statistical noise, and further permit computation of dynamical properties, which will the subjet of a subsequent paper.

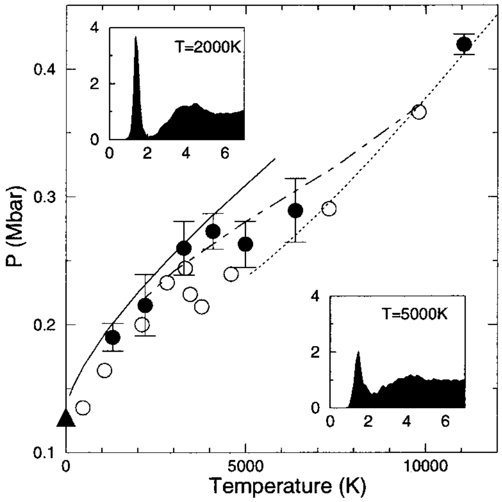

FIG. 3. Isochore (P vs T) for $V=6$ cm^3/mole, $\rho=0.670$ g/cm^3. Open circles (○) are $N=64$ simulations and closed circles (●) are $N=108$ simulations. The errors bars have been omitted for $N=64$ for the clarity of the figure but are of the same order of magnitude. Solid line is the FVT result, dashed line is the fit given by Lenosky *et al.* [5], and dotted-dashed line the DM result [21]. The triangle indicates the zero temperature experimental pressure given by the Vinet equation [20]. The upper left inset is the pair distribution function $g(r)$ computed for $T=2000$ K, and the lower right inset is $g(r)$ computed for $T=5000$ K.

In Fig. 3 we have plotted P (Mbar) versus T (K) (isochores) for $V=6$ cc/mole corresponding to a density $\rho=0.670$ g/cm^3 for deuterium. Open circles correspond to $N=64$ deuterons simulations and closed circles to $N=108$ deuterons simulations (error bars are not represented for $N=64$ for the sake of clarity). The dashed line is the fit proposed by Lenosky *et al.* [5]. A first inspection of Fig. 3, clearly reveals the existence of two well defined branches. In the low temperature branch ($T<4000$ K at $V=6$), pressures are in good agreement with models based on classical interacting molecules (solid line) and computed by fluid variational theory (FVT) using the Ross Ree Young interaction potential [19]. Further, they are coherent with the zero temperature limit given by the experimental Vinet equation [20] (solid triangle). The molecular character is also attested by the pair distribution function $g(r)$ (see upper left inset of Fig. 3) which exhibits a marked peak at 1.4 a.u., followed by a minimum close to zero. In this region, changing the num-

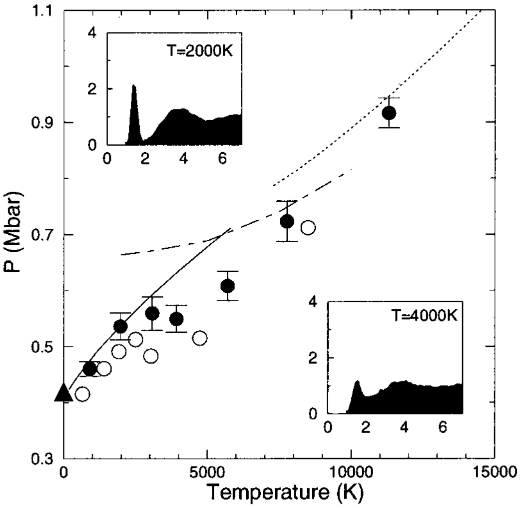

FIG. 4. Same as Fig. 3 for $V=4$ cm^3/mole, $\rho=1$ g/cm^3. Pair distribution functions are computed for $T=2000$ K (upper left) and $T=4000$ K (lower right).

ber of particles from 64 to 108 increases the pressure towards the FVT prediction. In the high temperature branch, ($T>7000$ K), our results are compatible, as expected, with GGA calculations of Galli *et al.* [6] and of Lenosky *et al.* [5], and well represented by the fit given by those authors.

Between those two regions we observe large fluctuations in the pressure corresponding to the breaking of a few molecules as can be inferred from the pair distribution function $g(r)$ (see lower right inset of Fig. 3) which shows now a much lower molecular peak as well as a nonzero first minimum. Those first dissociations are accompanied by a negative slope $\partial P/\partial T<0$ in the pressure, which persists for a larger system with a slight shift in the temperature. Clearly, simulations with more particles (216 or more) are needed to minimize the fluctuations in this regime, but those simulations are now beyond the possibilities of the computers we can use. The curve computed by Redmer's dissociation model (DM) [21], has been also added to Fig. 3, which shows a smooth transition between molecular and dissociated state.

The same features are observed in Fig. 4 at $V=4$ cc/mole corresponding to $\rho=1$ g/cm^3, but the extension of the molecular phase narrows and the transition region starts now at 3000 K. The $g(r)$ plotted for the same temperature ($T=2000$ K) as the previous case shows a lower molecular peak. In this regime, it must be quoted that classical models with pair interactions are overestimating the pressure by 50 Kbar. Consequently, FVT must be corrected to be coherent with the zero temperature limit given by Vinet. DM also strongly overestimates the pressure at $T=2000$ K, but is in better agreement at $T>10\,000$ K. We again observe a transition region characterized by negative slope in the pressure, but with a much lower amplitude than suggested by the model of Ross [10].

From the pressures and energies computed for the volumes $V=6$ cc/mole and $V=4$ cc/mole we have plotted the curves P in Mbar and $2(E-E_0)/(V_0-V)$ in Mbar in Fig. 5. This representation of the Hugoniot equation,

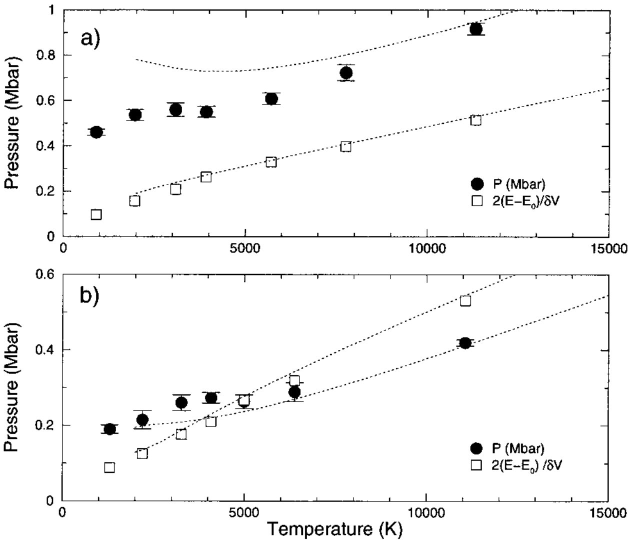

FIG. 5. Comparisons between P and $2(E-E_0)/(V_0-V)$ in Mbar for: (a) $V=4$ cm^3/mole, $\rho=1$ g/cm^3 and (b) $V=6$ cm^3/mole, $\rho=0.670$ g/cm^3. Dashed lines are the fits given by Lenosky for the pressure and the energy.

$$\tfrac{1}{2}(P+P_0)(V_0-V)=(E-E_0),$$

where $P_0=0$, $V_0=23.5$ cc/mole and E_0 is the reference state of liquid deuterium, allows for a direct graphic estimation of the hugoniot pressure (and temperature). It is clear from Fig. 5(a), which corresponds to the bend of the experimental hugoniot at $\rho=1$ g/cm^3, that no solution of the Hugoniot equation can be found with our data, even including large size effects. On the contrary, pressures and energies curves are crossing in Fig. 5(b) at a value close to 5000 K and 270 Kbar. Except in the low temperature range, corresponding to the pure molecular regime, ($T<4000$ K), which is beyond the range of validity of Lenosky's fit formulas, we observe a very good overall agreement with LDA-GGA simulations. A more systematic comparison, from a series of simulations performed for $V=7$, 6, 5.5, 5, and 4 cc/mole, allows us to affirm that our hugoniot curve is close to the former GGA results [5,6] shown in Fig. 1. In order to make connection with Holmes *et al.* gas-gun experiments [22], we have also investigated the $V=7$ cc/mole isochore for which we found a hugoniot pressure of 140 Kbar instead of 226 Kbar in the experiment, without any adjustments in the energies of the reference state. This discrepancy can be traced back to the increasing difficulty of producing well thermalized simulations in the low density regime due to the cost (number of plane waves) of the simulations and the weakness of the interactions between molecules. Our molecular pressures are consequently lower than FVT pressures. If we replace the pressures obtained by simulations by those computed by FVT we get an excellent agreement with gas-gun experiments.

In this paper, we have investigated the dense fluid deuterium using a well established functional including explicitly the spin density for *up* and *down* electrons, providing a coherent estimation of the reference molecular state for the hugoniot curve. We have checked the influence of most of relevant parameters such as the number of particles, the cutoff of the pseudopotential, and the Brillouin zone sampling. A series of *ab initio* molecular dynamics runs for several volumes $V=7$, 6, 5.5, 5, and 4 cc/mole and temperatures ranging from 1000 to 20 000 K, has been performed with a particular emphasis on the molecular phase of two isochores corresponding for deuterium to $V=6$ cm^3/mole, $\rho=0.670$ g/cm^3 and $V=4$ cm^3/mole, $\rho=1$ g/cm^3. The effect of LSDA is to reproduce a well behaved molecular phase and to give rise to a negative slope $(\partial P/\partial T<0)$ in the pressure versus temperature diagram (isochore), when first dissociations occurs, with a lower amplitude than predicted by chemical models. The effect of spin statistics seems to disappear after dissociation since no spin fluctuations or magnetic moment are observed, and also because our thermodynamic data are in agreement with previous LDA calculations [5,6] in this regime. The fact that, even with the most complete functional available, the experimental compressibility of deuterium remains not well reproduced, might suggest that the treatment of exchange correlation terms is not satisfactory in the general LDA framework. This conclusion is supported by preliminary results obtained by Knaup *et al.* [23] with the WPMD model, which includes a more precise treatment of exchange, showing a larger compressibility. It is clear also that dissociation, as well as the hypothetical formation of clusters, are very sensitive to the number of simulated particles, and hence, a more conclusive study of the dissociation regime would require a larger cell and more particles (216 or 512). Such dynamical simulations are now beyond the possibilities of present computers. This limitation is a drawback of plane wave codes, which are scaling as the cube of the number of particles. New methods, such as the recursion method, scaling linearly with the number of particles, which have been introduced and developed by Bagnier *et al.* [24], are a promising way to solve this problem.

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$$P=3K_0\left(\frac{V}{V_0}\right)\left[1-\left(\frac{V}{V_0}\right)^{1/3}\right]\exp\left\{\frac{3}{2}(K_0'-1)\left[1-\left(\frac{V}{V_0}\right)^{1/3}\right]\right\},$$

with $V_0=25.433$ cm^3 mol^{-1}, $K_0=1.62$ Kbar, and $K_0'=6.813$.

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