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Equation of state and the Hugoniot of laser shock-compressed deuterium: Demonstration of a basis-function-free method for quantum calculations

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In most density functionals the energy is a functional of the electron density $n(\vec{r})$ and a *function* of the nuclear positions $\vec{R}_i$. We consider, a functional of *both* $n(\vec{r})$ and the nuclear density $\rho(\vec{r})=\Sigma\delta(\vec{r}-\vec{R}_i)$. In reducing the two Kohn–Sham equations, a classical mapping valid for interacting electrons is invoked. The exchange-correlation is nonlocal and free of self-interaction errors. As a challenging application, we calculate the equation of state and the shock Hugoniot of deuterium relevant to topical shock experiments. The calculated Hugoniot is quite close to the SESAME and path-integral Monte Carlo Hugoniots. We also treat the *nonequilibrium* case, which is extremely difficult for standard methods. Here the D$^+$ are assumed to be hotter than the electrons, and lead to the soft Hugoniots similar to those seen in the laser-shock data. The softening arises from hot D$^+$–e pairs occurring close to the zero of the electron chemical potential.

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Hydrogen isotopes have been extensively studied; yet laser-shock experiments of Da Silva *et al.*,[1] Collins *et al.*,[2] and Mostovych *et al.*[3] produced unexpected disagreement with the equation of state (EOS) of the SESAME database.[4] The disagreement occurs for temperatures T with $\sim$0.8 eV $<T<\sim$10 eV, and for densities $1.8<r_s<\sim 2$, where the electron-sphere radius (in a.u.), $r_s=(3/4\pi\bar{n})^{1/3}$. Here $\bar{n}$ is the electron-number density. The coupling constant Γ=(potential energy)/(kinetic energy) ranges from 1 to $\sim$30.

The degenerate electrons begin to change to a classical system in the anomaly regime (AR), while the e–D$^+$ interaction is close to bound-state formation. Thus the AR poses a difficult, strongly correlated many-body problem of wide interest—from astrophysics and fusion to materials science. Hence a flurry of activity has focused on the deuterium EOS and its Hugoniot.[5] These involve intuitive approaches (called "chemical models"),[6] assuming the existence of molecules, D,D$^+$, etc., and first-principles approaches like the path-integral Monte Carlo (PIMC), a finite-T quantum Monte Carlo approach.[7] Unlike PIMC, density-functional theory (DFT) as embodied in standard codes (e.g., VASP),[8] and standard quantum Monte Carlo (QMC) methods become inapplicable at finite-T and partial degeneracies. Configuration-interaction (CI) type calculations with a basis of N functions grows exponentially with N, while even the $T=0$ ground-state problem increases as N.[4] Even simplified tight-binding approaches (using one or two functions per nucleus) which may be useful in some regimes, can become numerically prohibitive.[9] One of the objectives of this paper is to demonstrate an "order-zero" (basis-set independent) approach to equilibrium and nonequilibrium quantum calculations.

PIMC at higher T, and DFT at low T (full degeneracy), can be joined to yield a deuterium EOS close to SESAME, and disagreeing with the laser-shock data in showing no strong softening.[7,11] Recent magnetic-shock experiments from Sandia are also close to the SESAME Hugoniot.[10] However a high degree of agreement exists in the independent laser-shock results.[11]

We present first-principles results for the EOS and the Hugoniot of deuterium, using novel theoretical methods. Our method is computationally simple and uses simple integral equations and a basis-set free classical mapping of quantum systems using DFT ideas. We calculate all the pair-distribution functions (PDFs), g_{ij}, with $i=1,2,3$; (or $e_\uparrow$, $e_\downarrow$, and D$^+$ nuclei) of a three-component system. Being based on the PDFs, it is manifestly nonlocal (i.e., gradient corrections are not needed), and it has no self-interaction errors. The method can be used for the quasiequilibrium two-temperature case with $T_\mathrm{D}\neq T_e$ as well. Consider the fluid with a D$^+$ at the origin, and let the one-body densities of the electrons and D$^+$ be $n(r)$ and $\rho(r)$. Then $n(r)$ is really $n_{\mathrm{De}}(r)=\bar{n}g_{\mathrm{De}}(r)$. Similarly, the $\rho(r)$ is really the mean nuclear desnity multiplied by the deuteron-deuteron PDF. The free energy F is a functional of the form $F[n(r),\rho(r)]$. Taking functional derivatives, we have *two* coupled Kohn–Sham–Mermin equations:

$$\delta F[n(r),\rho(r)]/\delta n(r)=0, \tag{1}$$

$$\delta F[n(r),\rho(r)]/\delta\rho(r)=0. \tag{2}$$

As shown in Refs. 12 and 13, Eq. (1) leads to a (quantum) Kohn–Sham (KS) equation for the electrons, while Eq. (2), a classical KS equation, becomes the hyper-netted-chain (HNC)[14] equation for a specific choice of the correlation potential (there being no exchange potential in the classical system). Thus the KS eigenfunctions, as well as the $n(r)$, $\rho(r)$, in the hydrogen fluid were calculated by solving Eqs. (1) and (2).[12] In Car-Parrinello approaches the N ions at sites $\vec{R}_i$ are explicitly treated. By treating *both* electrons and ions via their distributions, we achieved a major simplification. Our hydrogen calculations were later confirmed by lengthy QMC.[15] However, while Eqs. (1) and (2) provide the $g_{ie}(r)$, $g_{ii}(r)$, i=ion, the $g_{ee}(r)$ was available only in LDA.

Recently, we showed how the electrons at the physical temperature T_e could be replaced by an equivalent classical system at $T_{ee}=(T_e^2+T_q^2)^{1/2}$, such that the quantum effects are correctly incorporated.[16] A simple expression for the electron "quantum temperature" T_q as a function of r_s was

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given. Application of the method, denoted the "Classical Mapping of Quantum Systems using the hyper-netted-chain equation (CHNC)," to three- and two-dimensional uniform electron liquids at $T=0$ and finite-T, showed excellent agreement of the g_{ij}, energies, etc., with QMC results, for even very strongly coupled situations.[16–18] *Here we present an application going beyond pure uniform electron fluids.* Electrons in a uniform neutralizing background are mathematically identical to a D$^+$ system, except for changes of scale [e.g, for D$^+$, $r_{s\mathrm{D}}=r_s(M_\mathrm{D}/m_e)$, etc., M_D is the deuteron mass and $m_e=1$]. Hence the D$^+$-quantum temperature $T_{\mathrm{D}q}$ is also available, and is negligible in the regime of interest; thus D$^+$ are treated as classical particles.

The densities $\overline{\rho}$ and $\overline{n}$ are equal since the nuclear charge $Z=1$. Consider a fluid of total density n_{tot}, with three species. Let $x_i=n_i/n_{tot}, n_{tot}=\overline{\rho}+\overline{n}$. The physical temperature is *T*, while the inverse temperature of the electrons is $1/\beta_{ee}$, with $1/\beta_{ee}=\sqrt{(T^2+T_q^2)}$. For D$^+$, no quantum correction is needed and $T_\mathrm{DD}=1/\beta_\mathrm{DD}$ is *T*. The β_{ij} between electrons and D$^+$ is actually not needed since the *product*, $\beta_{e\mathrm{D}}\phi_{e\mathrm{D}}(r)$ is completely determined by quantum mechanics (see the following). However, here it is just the mean kinetic energy of the D$^+$–*e* pair, i.e., $T_{e\mathrm{D}}=(T_{ee}+T_\mathrm{DD})/2$.

The classical equations for the PDFs and the Ornstein–Zernike (OZ) relations are

$$g_{ij}(r)=\exp[-\beta_{ij}\phi_{ij}(r)+h_{ij}(r)-c_{ij}(r)+B_{ij}(r)], \quad (3)$$

$$h_{ij}(r)=c_{ij}(r)+\Sigma_s n_s\int d\mathbf{r}'\,h_{i,s}(|\mathbf{r}-\mathbf{r}'|)c_{s,j}(\mathbf{r}'). \quad (4)$$

Here $\phi_{ij}(r)$ is the pair potential between species i,j. For e–e (or D$^+$–D$^+$) this is just the Coulomb potential $V_{cou}(r)$. For parallel-spin electrons, the Pauli principle prevents occupation of the same orbital. As before,[16] we introduce a "Pauli exclusion potential," $\mathcal{P}(r)$. Thus $\phi_{ij}(r)$ becomes $\mathcal{P}(r)\delta_{ij}+V_{cou}(r)$, when i,j denote electrons. The function $h(r)=g(r)-1$. The $c(r)$ is the "direct correlation function (DCF)" of the OZ equations. The $B_{ij}(r)$ is the "bridge" term due to certain cluster interactions. If this is neglected, Eqs. (3) and (4) form a closed set defining the HNC approximation. (In effect, the KS equations become HNC equations if the correlation potentials are evaluated as a sum of hyper-netted-chain diagrams.) The HNC is sufficient for the uniform 3D electron (3DEG) for a range of r_s, up to $r_s=50$, as shown previously.[17] Hence we neglect the bridge corrections in this study of deuterium.

The $\mathcal{P}(r)$ is defined as in Ref. 16 from the zeroth-order PDFs of the parallel-spin electrons. Thus:

$$\beta\mathcal{P}(r)=h_{11}^0(r)-c_{11}^0(r)-\ln[g_{11}^0(r)], \quad (5)$$

where, e.g., $c_{11}^0(r)$ is the spin-$\|$ DCF of the OZ equation. Only the product $\beta\mathcal{P}(r)$ is needed.

The Coulomb potential $V_{cou}(r)$ for two point-charge electrons is $1/r$. However, an electron at the temperature *T* is localized to within a thermal de Broglie length (dBL). Thus, for the 3DEG we used a "diffraction corrected" form,[19] $V_{cou}^{ee}(r)=(1/r)[1-e^{-rk_{ee}}]$; here $k_{ee}=(2\pi m^*T_{ee})^{1/2}$ as shown by Minoo *et al.*, and $m^*=1/2$ is the reduced mass of the electron *pair*. Minoo *et al.* used $T_{ee}=T$, and holds only at high *T*. The use of $T_{ee}=(T^2+T_{eq}^2)^{1/2}$ instead of *T* validates it down to $T=0$ as well.[16]

Since the D$^+$ are classical particles, the D$^+$–D$^+$ interaction is the Coulomb interaction $\phi_{33}(r)=1/r$. The *e*–D$^+$ interaction is more tricky. The V_{cou}^{ee} with the dBL correction is based on the quantum mechanics of two electrons. Similarly we determine the *e*–D$^+$ interaction, $\phi_{e\mathrm{D}}(r)$, from the density profile $n_{\mathrm{D}e}(r)$ given by the KS equation for electrons interacting with *a single* D$^+$ at the origin. We have discussed this in the context of the "neutral pseudo-atom" DFT model (NPA-DFT) for solving the KS equations.[13,20] This gives the deuteron-electron PDF, i.e., $g_{\mathrm{D}e}(r)=n_{\mathrm{D}e}(r)/\overline{n}$. This $n_{\mathrm{D}e}(r)$ includes *both bound-state and continuum-state* densities. Applying the CHNC and the OZ equation to this system containing a *single* D$^+$, we have

$$-\beta_{\mathrm{D}e}\phi_{\mathrm{D}e}(r)=\log[g_{\mathrm{D}e}(r)]-h_{\mathrm{D}e}(r)+c_{\mathrm{D}e}(r), \quad (6)$$

$$h_{\mathrm{D}e}(r)=c_{\mathrm{D}e}(r)+\overline{n}\int d\vec{r}'\,c_{\mathrm{D}e}(\vec{r}-\vec{r}')h_{ee}(r'). \quad (7)$$

The D$^+$–D$^+$ DCF does not appear as there is only a single D$^+$. Hence, knowing the $g_{\mathrm{D}e}(r)$ from the solution of the KS equation for the single deuteron problem, we can obtain $c_{\mathrm{D}e}(r)$ in terms of $h_{\mathrm{D}e}(r)$. Hence the *e*–*D* potential can be extracted. This determines the product, $\beta_{\mathrm{D}e}\phi_{\mathrm{D}e}(r)$, while $\beta_{\mathrm{D}e}$ and $\phi_{\mathrm{D}e}$ are not needed individually. However, on solving the KS equation for the regime of interest, *no atomic bound states* are found; the effective ionic charge $Z-n_b=1$, i.e, n_b, the number of bound electrons per nucleus, is zero. This does not contradict *transient* bound states found in PIMC.[21] Hence, at least in this regime of $\overline{n}$ and *T*, Kohn–Sham NPA-DFT is not needed; we set:

$$\phi_{\mathrm{D}e}(r)=-(1/r)[1-e^{-rk_{\mathrm{D}e}}], \quad (8)$$

$$k_{\mathrm{D}e}=(2\pi m_e T_{ee})^{1/2}, \quad (9)$$

$$1/\beta_{\mathrm{D}e}=(T_\mathrm{DD}+T_{ee})/2. \quad (10)$$

The first equation is just the V_{cou} with the $r=0$ value set to an inverse dBL for the D$^+$–*e* pair, $k_{\mathrm{D}e}$, as in the *e*–*e* interaction. The dBL $1/k_{\mathrm{D}e}$ contains only the electron contribution since the D$^+$ is a classical particle. Thus only the T_{ee} appears in $k_{\mathrm{D}e}$ (the effective mass of the D$^+$–*e* pair is m_e, since the deuteron mass $M_\mathrm{D}\gg m_e$).

Finally, we solve the coupled set of CHNC equations to determine the six PDFs of the e,D$^+$ system. The excess free-energy $F_{exc}(r_s,T)$ is determined via a coupling-constant integration, as in Ref. 17, for a range of r_s and *T*. The total free energy $F(r_s,T)$ is obtained by adding on the ideal electron and D$^+$ contributions F_0^e, F_0^D. The total pressure *P* and the total internal energy *E* are obtained as usual by $P=\partial F(r_s,T)/\partial V$, where *V* is the volume, and $E=\partial\beta F(r_s,T)/\partial\beta$, where $\beta=1/T$. In the regime of interest, i.e., $1.8<r_s<2.1$, and $0.8\ \mathrm{eV}<T<15$, we find that $F_{exc}(r_s,T)$ is approximately linear, i.e., $F_{exc}(r_s,T)$

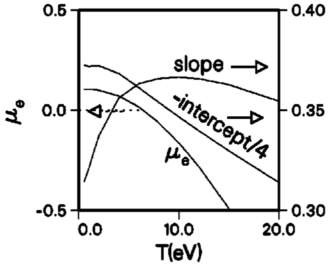

FIG. 1. The excess free energy in the regime of interest fits the linear form $F_{exc}(r_s,T)=M(T)r_s+C(T)$; the slope $M(T)$ and the intercept $C(T)$ are shown as a function of T. Note the change of character in $M(T)$ when μ_e passes through zero.

$=M(T)r_s+C(T)$. The T dependence of $M(T),C(T)$ is quite nonlinear. Figure 1 shows that $M(T)$ changes character near $T=6$ eV, close to the zero of μ_e.

Our P,E are compared with the PIMC data (MC) in Table I, showing good agreement for $T>2.75$ eV. For lower T, our pressures are somewhat smaller.

The free energy $F(r_s,T)$ is used to calculate the deuterium Hugoniot for the initial state, (E_0,V_0,P_0), with $T=19.6$ K and an initial density $\rho_0=0.171$ g/cm^3. The initial state $E_0=-15.886$ eV per atom, and $P_0=0$. The results are shown in Fig. 2. The CHNC Hugoniot, similar to PIMC, approaches SESAME at high T. A softening of the Hugoniot around 2 Mbar, not seen in the PIMC, is also noted. This appears near $\overline{n}$ and T where the interacting chemical potential $\mu_e(r_s,T)$ passes through zero.

We can use the CHNC equations even when electrons and D^+ are at two different temperatures, T_e and T_D. The shock is launched from an aluminum pusher; the shock acts on molecules initially around ~ 20 K. Consider a scenario where the shock energy transfers preferentially to the ions which become much hotter than the electrons. The velocity measurements begin after about 3 ns in the laser work, and after a longer time delay in the Sandia work. Landau–Spitzer theory would indicate that the D^+-e equilibriation occurs well within the experimental time scales. Simple estimates might give $\sim 10^4$ collisions within the time window of the experiments. However, the formation of coupled modes in plasmas with $\Gamma>1$ strongly reduces the ion–electron equilibriation rate.[22] Experimental evidence exists for this point of view.[23] A compactly held screening charge at each ion would act like a neutral object which, while having a very hot deuteron at the center, would screen it from the cooler outer electrons. The effect could lower the electron–ion relaxation by an order of magnitude.[22,23] If laser shock data were gathered at several time delays, the details of the relaxation would be available. In lieu of such relaxation results, here we assume that the D^+ nuclei are about 5 eV hotter than the nominal electron temperature (i.e., $T_D=T_e+5$ eV), except at the lowest temperatures. Using T_e,T_D in the HNC equations as before, we have calculated a quasiequilibrium $F_{exc}(r_s,T_e,T_D)$ and a shock Hugoniot (quasiequilibrium concepts are discussed in Ref. 22). The resulting nonequilibrium Hugoniot is given in Fig. 2.

TABLE I. The total pressure P (Mbar) and total energy E (eV), from the classical-map HNC (CHNC) approach, and the path-integral Monte Carlo (PIMC) approach of Militzer and Ceperley (MC) at $r_s=2.0$, i.e., at a deuterium density of 0.6691 g/cm^3.

T(K)	F_{exc}	P(CHNC)	P(MC)	E(CHNC)	E(MC)
500000	−5.35310	26.278	25.980	113.30	113.20
250000	−2.14960	12.244	12.120	47.57	45.70
125000	−0.99712	5.374	5.290	13.60	11.50
65000	−0.64405	2.143	2.280	−3.21	−3.80
31250	−0.57058	0.754	1.110	−10.74	−9.90
15625	−0.57119	0.213	0.540	−13.97	−12.90
10000	−0.57890	0.058	0.470	−14.91	−13.60

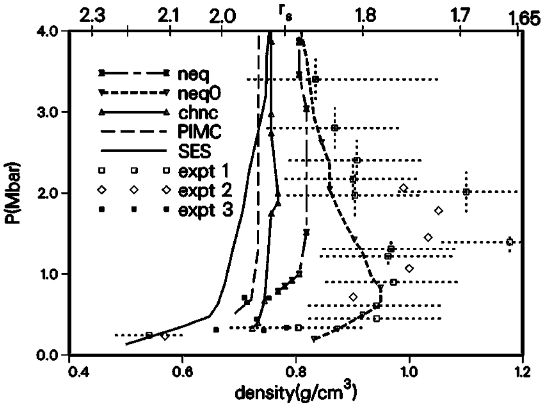

FIG. 2. Comparison of the CHNC Hugoniot with experiment and other theories. Two nonequilibrium Hugoniots are also shown (see the text). Experiments 1, 2, and 3 refer to Da Silva *et al.*, Collins *et al.*, and Knudson *et al.*, respectively.

The higher T_D makes the D^+-e fluid more compressible. This appears counterintuitive if one considers only the D^+ contribution. The quasifree energy $F(r_s,T_e,T_D)$ consists of F_e, F_D, and F_{De}. On setting $T_D>T_e$, the F_D term taken alone *reduces* the compressibility, but the total compressibility is increased by the major role of the pair-term F_{De}. As seen in Fig. 1, the fluid is in a regime close to the $\mu_e=0$ transition. Thus a higher T_D increases T_{De} and reduces the electron degeneracy even more, making it more compressible. When this effect is strong enough to offset the reduction of the compressibility from the ideal gas term of the hotter deuterons, a softening of the Hugoniot could result. In Fig. 2 we show a Hugoniot labeled NEQ0 where the ideal term P_0 was computed just as in the equilibrium Hugoniot, while in NEQ the full effect was included. Thus we see that except for the lowest temperatures, the contribution of the deuteron–electron pairs dominate.

Our explanation of the observed laser-shock Hugoniot emphasizes the equilibriation issue. Other factors like the planarity, constancy, and duration of the shock wave are also relevant. However, the present discussion strongly calls for experimental and theoretical equilibriation studies. The CHNC approach is numerically and computationally very simple and should be a handy tool in such studies in a variety of disciplines. This simplicity enabled us to tackle the calculation of a quasiequilibrium Hugoniot—a problem so far not addressed by other quantum calculations. All the calculations presented here used only very modest computational facilities.[24] Our computer codes may be remotely accessed by interested researchers by visiting our website.[25]

In conclusion, we present a parameter-free calculation of the EOS of deuterium in the regime of densities and temperatures addressed by recent laser and magnetic shock experiments. Kohn–Sham calculations show the absence of atomic bound states in this regime. The analysis of the energy as a functional of the electron density *and* the nuclear density, together with the classical mapping of the electrons produced a very powerful but computationally simple method, applicable to equilibrium and quasiequilibrium systems. The equilibrium Hugoniot is in good agreement with other first-principles calculations. Calculations with the D^+ ions hotter than the electrons by ~ 5 eV suggest that the anomalous Hugoniots of the laser experiments may result from hitherto unsuspected nonequilibrium effects which can be addressed via new time-delay experiments.

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

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

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

[4] G. I. Kerley, *Molecular Based Study of Fluids* (ACS, Washington, DC, 1983), p 107.

[5] Hugoniot is the locus of states (P,ρ,T) generated by shock compression from a given initial state.

[6] M. Ross, Phys. Rev. B **58**, 669 (1998); D. Beule *et al.*, Phys. Rev. E **63**, 060202 (2001); D. Saumon *et al.*, High Press. Res. **16**, 331 (2000).

[7] B. Militzer *et al.*, Phys. Rev. Lett. **85**, 1890 (2000).

[8] G. Kresse *et al.*, http://cms.mpi.univie.ac.at/vasp

[9] T. J. Lenosky *et al.*, Phys. Rev. B **61**, 1 (2000); G. Galli *et al.*, *ibid.* **61**, 909 (2000).

[10] M. D. Knudson *et al.*, Phys. Rev. Lett. **87**, 225501 (2001).

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

[12] M. W. C. Dharma-wardana and F. Perrot, Phys. Rev. A **26**, 2096 (1982).

[13] M. W. C. Dharma-wardana and François Perrot, in *Density Functional Theory*, edited E. K. U. Gross and R. M. Dreizler (Plenum, New York, 1995), p. 625.

[14] J. M. J. van Leeuwen, J. Gröneveld, and J. de Boer, Physica (Amsterdam) **25**, 792 (1959).

[15] I. Kwon *et al.*, Phys. Rev. E **54**, 2844 (1996).

[16] M. W. C. Dharma-wardana and F. Perrot, Phys. Rev. Lett. **84**, 959 (2000).

[17] François Perrot and M. W. C. Dharma-wardana, Phys. Rev. B **62**, 16 536 (2000).

[18] Franćois Perrot and M. W. C. Dharma-wardana, Phys. Rev. Lett. **87**, 206404 (2001).

[19] H. Minoo *et al.*, Phys. Rev. A **23**, 924 (1981).

[20] François Perrot, Phys. Rev. E **47**, 570 (1993).

[21] Similar transient bonding effects are seen in, e.g., liquid-Si,Ge simulations using Car-Parrinello methods, while parallel calculations by us produce static PDFs in excellent agreement with experiment. See: M.W.C. Dharma-wardana and F. Perrot, Phys. Rev. Lett. **65**, 76 (1990).

[22] M. W. C. Dharma-wardana and François Perrot, Phys. Rev. E **58**, 3705 (1998); **63,** 069901(E) (2001); M. W. C. Dharma-wardana, *ibid.* **64**, 035401(R) (2001).

[23] D. Riley *et al.*, Phys. Rev. Lett. **84**, 1704 (2000).

[24] A Silicon Graphics SGI02/MIPS R5000/180 MHz workstation running IRIX 6.5 was used.

[25] http://nrcphy1.phy.nrc.ca/ims/qp/chandre/chnc/