A calculation of the Deuterium Hugoniot using the classical-map hypernetted-chain (CHNC) approach.

M. W. C. Dharma-wardana
National Research Council of Canada, Ottawa, Canada, K1A 0R6

The Hugoniot for Deuterium is calculated using the classical-map hypernetted-chain (CHNC) approach using several models of the effective temperature that may be assigned to the electron-ion interaction. This effective temperature embodies the exchange-correlation and kinetic energy functional that is assigned to the electron-ion interaction. Deuteron pair distribution functions (calculated using the neutral-pseudo atom method) showing the formation of molecular pre-peaks are displayed to clarify the soft-turning over of the hugoniot in the pressure range of 0.2-0.6 Megabars. This contribution updates a previous CHNC calculation of the deuterium hugoniot given in Phys. Rev. B, 66, 014110 (2002).

I. CALCULATIONS OF THE DEUTERIUM HUGONIOT USING A CLASSICAL REPRESENTATION OF THE ELECTRONS.

The major problem in simulations of warm dense matter is the quantum nature of electrons and the representation of physical variables by operators defined in function space. The higher the temperature, the larger is the number of excited states needed to properly represent this function space. The large basis sets needed make the usual density-functional theory (DFT) and molecular dynamics (MD) method prohibitive for temperatures $T/E_F$ exceeding about 0.5, where $E_F$ is the Fermi energy. At low temperatures, the mean free paths $\lambda_{mfp}$ of electrons become very large, small-$k$ effects become relevant, and large MD simulation cells with the number of ions $N$ exceeding thousands become necessary, making the method impractical or inaccurate for many physical properties.

However, DFT offers the possibility of completely describing at least the static properties, e.g., the equation of state (EOS) of quantum systems using only the one-body electron density $n(r)$, without appeal to wavefunctions. Hence, a classical representation of electrons which interact via an equivalent effective potential can be legitimately anticipated [2] if the effective potentials accurately predict the DFT $n(r)$. Thus the Coulomb interaction $V^{ee}_{\text{cls}}(r)$ inclusive of quantum diffraction corrections, and an additional Pauli-exclusion interaction $P^{ee}(r, \zeta)$ chosen to exactly recover the Fermi hole in the electron-electron pair distribution function (PDF) has to be constructed. That is, the e-e PDF, $g_{ee}(r, \zeta)$ which depends on the spin polarization $\zeta$ needs to be mapped to an effective classical potential $V^{ee}_{\text{cls}}(r) = V^{ee}_{\text{cou}}(r) + P^{ee}(r)$ even at $T = 0$. However, such an equivalent Coulomb system at the physical temperature $T$ will also have an effective classical temperature $T^{ee}_{\text{cls}}$ which takes account of the nonzero kinetic and correlation effects which manifest even at $T = 0$. In effect, $T^{ee}_{\text{cls}}$ is an approximate classical solution to the long standing problem of the representation for the kinetic energy functional of DFT.

Thus the self-consistent construction of $V_{\text{cls}}(r, \zeta, \bar{n})$, and $T^{ee}_{\text{cls}}(\zeta, \bar{n})$ for a given mean electron density $\bar{n}$ and temperature $T$ to accurately recover the one-body density $n(r)$ and the associated PDFs using the classical hyper-netted-chain equation constitutes the classical map of the quantum electrons of spin polarization $\zeta$, denoted by CHNC. If molecular dynamics is used instead of the HNC, for inverting or calculating the PDFs, we refer to it as CMDM.

Pair-distribution functions $g_{ee}(r, \zeta)$ using such a map $V^{ee}_{\text{cls}}, T^{ee}_{\text{cls}}$ can be generated via MD or even more cheaply via the hyper-netted chain (HNC) equation or its modified form known as MHNC containing an appropriate bridge-diagram correction. Dharma-wardana and Perrot have constructed such maps for 2-D and 3-D electrons at zero and finite $T$ [2, 3], and shown accurate agreement of the PDFs with quantum Monte Carlo (QMC) PDFs available at $T = 0$, even for very high coupling, while Dufty et al. [4] have also constructed similar classical maps. Dufty et al. have used additional constraints in constructing potentials rather than using the minimum necessary conditions imposed by DFT and HNC or MD invertible maps. Their methods also link with the older work on effective potentials derived from Slater sums.

In the classical map proposed by Dharma-wardana and Perrot we use an effective temperature $T^{ee}_{\text{cls}}$ which is chosen so that the equivalent classical Coulomb fluid has the correct exchange-correlation (XC) energy at $T = 0$. This is found to be sufficiently accurately given by the form

$$T^{ee} = \left\{ T_q^2 + T^2 \right\}^{1/2}. \quad (1)$$

The “quantum temperature” $T_q$ is of the order of $E_F$; its form proposed in Ref. [2] is a simple function of the electron Wigner-Seitz radius $r_s = \{3/(4\pi \bar{n})\}^{1/3}$. The use of the actual form and the Pauli potential are crucial to the accuracy of the map. This classical map given by Dharma-wardana and Perrot in 2000 was found to be very accurate when results for finite-$T$ QMC exchange-correlation energies [5-8] and finite-$T$ $g_{ee}(r, \zeta)$ became available a decade later.
II. CLASSICAL MAP FOR ELECTRON-ION MIXTURES.

Once the electrons are mapped to an effective classical system, they can now be used with ions (e.g., protons, carbon nuclei etc.) to study the properties of electron-ion systems without the heavy computational burden of purely quantum approaches. However, in including the ions, the electron-ion interaction itself needs to be mapped to a classical form correctly so as to include (i) quantum effects in the effective electron-ion interaction; (ii) quantum effects in the kinetic energy functional applicable to the effective temperature $T_{ei}^c$ of the electron-ion interaction. The ions themselves can usually be taken to be classical and pose no problems, with the ion temperature $T_i = T$. In dealing with $V_{ei}^{cl}$ we need to consider (a) that the quantum electron-ion interactions produce a bound-electron spectrum requiring the use of a pseudopotential with a core radius $r_c$ for $V_{ei}^{cl}$; (b) the fact that transient as well as persistent molecular forms, e.g., H-H, C-H and C-C are formed [8]. Examples of H-H or equivalently D-D PDFs showing pre-peaks in $g_{dd}(r)$ due to the formation of transient D-D bonds, calculated using the neutral-pseudo-atom (NPA) approach [9], are shown in Fig. 1. Unlike many average-atom models, the NPA approach is capable of providing an average description of all transiently bonded forms that may be found in the fluid, as described in Ref. [8]. The CHNC currently does a less satisfactory job of picking up such effects, as this depends on the specification of $T_{ei}^c$.

The CHNC is developed within the DFT conceptual framework where one-body densities and XC-functional rather than wavefunctions determine the physics of the system. We recall [11] that an ion-electron system with one-body densities $n(r)$ for electrons and $\rho(r)$ for ions has a free energy of the form $F(n, \rho)$ and hence the XC-functional and Kohn-Sham potentials need to be calculated via functional derivatives with respect to $n(r)$ and also $\rho(r)$, and not just with respect to $n(r)$. Obtaining XC-potentials needs taking further functional derivatives. Unlike in conventional DFT, the ions are not treated as merely providing a static “external potential” but enter directly into the theory. This leads to two DFT equations (one for the ions, and one for the electrons), and equations connecting these subsystems. They have distinct XC-functional for electrons, ions and for electron-ion interactions. The ion-ion XC functional does not have an exchange part as the ions are treated classically, and the correlation part is expressed as a sum of purely quantum approaches. However, in including ion systems without the heavy computational burden of the calculation of all transiently bonded forms that may be found in the fluid, as described in Ref. [8]. The CHNC currently does a less satisfactory job of picking up such effects, as this depends on the specification of $T_{ei}^c$.

Thus the classical map for electron-ion systems requires, in addition to the map for $e-e$ interactions, a map defining $\beta_{ei} V_{ei}^{cl}$ where $\beta_{ei} = 1/T_{ei}^{cl}$. Bradow et al. [11] used a diffraction corrected Coulomb potential $V_{ei}^{cl}(r) = -|e| Z \{1 - \exp(k_{ei}r)\}/r$, $|e| = 1$ and an effective temperature $T_{ei}^{cl} = (T_{ei}^{cl} T_i)^{1/2}$. This point-ion interaction uses the effective charge $Z$ of the ion; while the model works successfully in some regimes, it was inaccurate, for example for aluminum and other ions where a finite-core radius becomes necessary.

III. CLASSICAL MAP APPLIED TO DEUTERIUM.

However, the classical map applied to hydrogen or deuterium should work successfully in regimes where the system is fully ionized, without having to worry about pseudopotential forms. It should also work successfully even in the regime where there are transient H-H bonds since the attractive potential arises mostly via the exchange interaction which splits the singlet (bonding) and triplet (anti-bonding) interactions. We associate the “softening turnover” (STO) of the deuterium Hugoniot between a density $\rho$ of 0.6 g/cm$^3$ to 0.8 g/cm$^3$ and pressures of 0.2 Mbar to 0.6 Mbar, to the changing influence of transient D-D bonding over this interval of density and pressure (see Fig. 2). In this regime there are no stable (i.e., persistent) H-H or D-D molecules. This regime is extremely sensitive to the choice of XC-functional, finite-$T$ effects etc., used in DFT calculations. The same uncertainty reappears in the determination of the effective classical temperature $T_{ei}^{cl}$; this is abbreviated to $T_{ei}^{c}$ etc. in the
following. In fact, trying out different simple models for \( T^{ei} \) gives insight into the nature of the STO.

Here we consider three models of \( T^{ei} \) and the corresponding CHNC-Deuterium Hugoniots, one of which was published by Dharma-wardana and Perrot in 2002 \cite{perrot1}. There we studied the choice \( T^{ei} = (T^{ei}_{\text{cls}} + T_{i})/2 \) (for details see Ref. \cite{perrot1}). A more extended plot of the Hugoniot is given in Fig. 2. The free energy \( F(r_{ei}, T) \) obtained by coupling-constant integrations over the PDFs obtained from the CHNC method is used to calculate the deuterium Hugoniot. The initial state of internal energy, volume and pressure \((E_{0}, V_{0}, P_{0})\), with \( T = 619.6 \text{ K} \), initial density of 0.171 g/cm\(^3\), \( E_{0} = 15.886 \text{ eV per atom} \), and \( P_{0} = 0 \) were used. The results are shown in Fig. 2.

An alternative CHNC model, with \( T^{ei} = (T^{ee}T_{i})^{1/2} \) is given in Bredow et al. \cite{bredow} but no Hugoniot was calculated. That model, based on ensuring the appropriate behaviour of the structure factors \( S(k) \) as \( k \to 0 \) \cite{perrot2} may need rectification in the limit \( T_{i} \to 0 \).

Since the momentum exchange in an electron-ion collision is determined by the reduced mass \( m^{ei} \) of the colliding pair, one may consider determining \( T^{ei} \) via \( m^{ei}/T^{ei} = m^{ee}/T^{ee} + m^{i}/T_{i} \). This implies that \( T^{ei} = T^{ee} \) since the effective mass is determined predominantly by the light particle, with \( m^{ei} \approx m_{e} \). The corresponding Hugoniot is also presented in Fig. 2. This is clearly incorrect and diverges to high compressibility at the onset of the STO region. In fact, a proper model of \( T^{ei}_{\text{cls}} \) has to be based on considerations of the electron-ion XC and kinetic components and not on collision dynamics which dominate high-energy collisions. A model for which we do not yet have a Hugoniot calculation is where the classical electron-ion interaction \( \beta_{ei}V^{\text{cls}}_{ei} \) is obtained directly by an HNC inversion of the NPA charge-density pileup at the proton. Such a more complete map will be considered in future work for the provision of fast, accurate calculations of Hugoniots.

### IV. CONCLUSION

An accurate classical representation of electrons \cite{perrot2} is not sufficient to deal with electron-ion systems, since the quantum features contained in the electron-ion interaction delicately depend on including additional quantum effects through an electron-ion exchange-correlation functional which contributes to the e-i interaction and the classical temperature associated with it. The soft feature in the hugoniot is shown to be closely related to temperature-dependent exchange correlation effects and the onset of transient deuterium-deuterium molecular bonding that manifests as the temperatures and densities are lowered. The transient bonding is signaled by the appearance of pre-peaks in the deuterium-deuterium pair-distribution functions. Future work will present a more accurate classical mapping of the electron-ion interaction in the context of the models already presented \cite{bredow, perrot1, perrot2}.

Some of the contents of this paper were presented at the DOE/NNSA Equation of State workshop, 31-May, 2017, Rochester, USA).

\[1\] Monica Pozzo et al., Phys. Rev. B, 84, 054203 (2011).
\[2\] M. W. C. Dharma-wardana and F. Perrot, Phys. Rev. Lett. 84, 959 (2000).
\[3\] François Perrot and M. W. C. Dharma-wardana, Phys. Rev. Lett. 87, 206404 (2001).
\[4\] J. Dufty and S. Dutta, Phys. Rev. 87, 032101 (2013).
\[5\] W. E Brown, J. L. DuBuis, M. Holzmann and D. M. Ceperley, Phys. Reb. B 88, 081102 (2013).
\[6\] M. W. C. Dharma-wardana, Proceedings of the Conference in Density Functional Theory, Debrecen, Hungary, 2016. Ed. Karlheinz Schwarz and Agnes Nagy. Computation 4 (2), 16; 2016; \[http://arxiv.org/abs/1602.04734\]
\[7\] Valentin V. Karasiev, Travis Sjostrom, James Dufty, S. B. Trickey, Phys Rev Lett, 112 (7), 076403 (2014).
\[8\] M. W. C. Dharma-wardana, ArXive [cond-mat] 1607.07511 (2017).
\[9\] M. W. C. Dharma-wardana, A review of studies on strongly-coupled Coulomb systems since the rise of DFT and SCCS-1977. Contrib. Plasma Phys. 55, No.2-3, 79-81 (2015).
[10] M. W. C. Dharma-wardana, p 625-650, in E. K. U. Gross, and R. M. Dreizler, Eds. *Density Functional Theory*, NATO ASI series, 337, 625 Plenum Press, New York (1993).

[11] R. Bredow, Th. Bornath, W.-D. Kraeft, M.W.C. Dharma-wardana and R. Redmer, Contrib. Plasma Phys., 55, 222-229 (2015).

[12] G. I. Kerley, *Molecular Based Study of Fluids* (ACS, Washington DC, 1883).

[13] M. W. C. Dharma-wardana and F. Perrot, Phys. Rev. B 66, 014110 (2002).

[14] Th. Bonarth, Private communication (2015)