FIRST-PRINCIPLES COMPUTER SIMULATIONS OF HYDROCARBONS UNDER FUSION CONDITIONS

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EXECUTIVE SUMMARY

Matter in the interiors of giant planets and stars is exposed to conditions of extreme temperature and pressure. In addition to the astrophysical relevance, a rigorous and consistent theoretical description of materials properties in the warm dense matter and dense plasma regimes has been identified as a central goal in the development of key energy technologies such as advanced nuclear reactors and inertial confined fusion, shock physics, plasma science, and stockpile stewardship. The optimal design of new plasma experiments relies on computational models of the equation of state, transport, and optical properties in order to achieve desired pressures and temperatures and to make the first, key measurements. Here we use first-principles computer simulations to study the properties of hydrocarbons at extreme conditions.

RESEARCH CHALLENGE

The development of a first-principles methodology for warm dense matter (WDM) applications that treat temperature effects consistently is a key component of the stewardship of plasma science [1]. Indeed, technological progress in high-energy-density physics (HEDP) applications, such as fusion energy [2], shock-wave physics [3], astrophysical processes [4], and planetary [5] and stellar interiors, relies on simulations for input and guidance. WDM is broadly described as the HEDP regime between condensed matter and ideal plasmas, where strong electron correlation, and quantum and ionization effects, are all important.

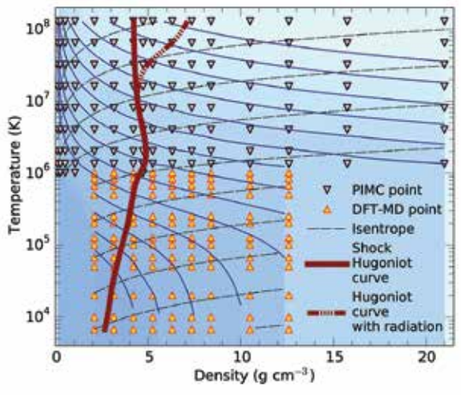

Figure 1: Temperature–density conditions of our path integral Monte Carlo and density functional molecular dynamics simulations of CH plastic materials. The red curves show the predicted path of fusion experiments. The solid blue and dashed black lines, respectively, show isobars and isentropes that we derived from our equation of state.

Hydrocarbons are the primary materials used for the ablator in inertial confinement fusion target capsules. It follows that the determination of the correct equation of state (EOS) of hydrocarbon ablators is important in order to optimize experimental designs to achieve desired density and temperature conditions. In this work, we perform state-of-the-art, benchmark-quality EOS calculations by combining high-temperature path integral Monte Carlo (PIMC) data and low-temperature density functional theory molecular dynamics (DFT-MD) data to construct coherent EOSs for several hydrocarbon materials over a wide range of densities and temperatures. At a commonly accessible temperature of 10^6°K, we find PIMC and DFT-MD predict consistent internal energies and pressures, validating their accuracy. While there have been several previous simulations of CH reaching into the WDM regime based on DFT-MD methods alone, our calculations provide the first set of first-principles data across the entire WDM regime that properly treats the many-body and shell-structure ionization effects. These processes affect the structure of the Hugoniot curve, which represents the density that can be achieved with various shock wave experiments. Our simulation results provide a benchmark for widely used EOS tables such as SESAME and QEOS as well as orbital-free DFT and average-atom methods. Our calculations are also timely for interpretation of ongoing spherically converging shock experiments on the Gbar platform at NIF and OMEGA.

METHODS & CODES

Since we need to cover a large temperature interval that spans five orders of magnitude (10^4–10^9°K), we rely on two different first-principles simulation methods (see Fig. 1). To study the high-temperature regime, we focus on the development of the PIMC method [6], which naturally incorporates finite temperature quantum effects by working within the many-body thermal density matrix formalism. The combination of Feynman's imaginary time path integrals and efficient Monte Carlo sampling techniques makes this approach one of the most appropriate first-principles simulation techniques for quantum systems at high temperature, T. Since the length of the path scales like 1/T, the method becomes increasingly efficient for high temperatures. Electrons and nuclei are often treated equally as paths, but here we treat the nuclei classically because their zero-point motion is negligible for the temperatures under consideration. All PIMC simulations were performed with our own code, CUPID [7].

For the low-temperature part of the WDM regime, DFT-MD is an accurate and efficient first-principles simulation method for these conditions. The thermal occupation of electronic states is treated as a perturbation of the ground state by Fermi–Dirac smearing. The main drawback of this method is that it becomes computationally infeasible as electrons occupy a large number of bands at high temperature, which is why we switch to PIMC simulation at high temperature (see Fig. 1). All DFT-MD simulations were performed with the VASP code [8].

RESULTS & IMPACT

We performed an entirely first-principles determination of hydrocarbon mixtures in the WDM regime by including all nonideal effects. Based on PIMC and DFT-MD, we obtained coherent sets of EOS over a wide range of density and temperature conditions and derived the shock Hugoniot curves of a series of hydrocarbon materials [9]. For polystyrene, we predict a maximum shock compression ratio of 4.7, whereas earlier estimates range from 4.3–4.7. Our calculated shock Hugoniot curve (Fig. 1) agrees very well with experimental measurements and provides guidance for the interpretation of experiments on the Gbar platform at NIF. We observe a single compression maximum for hydrocarbon materials while there are two compression maxima in the Hugoniot curve of nitrogen, oxygen, and neon. We have shown that this difference is related to the properties of the L-shell ionization, which is much more gradual for carbon. We found that the linear isobaric–isothermal mixing approximation works very well, resulting in a discrepancy in the density of CH of 1% or less under stellar core conditions. This implies that it is sufficient to derive only accurate EOS tables for the end members in order to provide a thermodynamic description of deep stellar interiors. In the past, models for stellar and giant planetary interiors relied on semianalytical models and experimental results for a few key conditions. Through high-performance computation, it has become possible to provide a more rigorous theoretical description of matter at extreme conditions. While, in the past, the characterization of one material has taken a Ph.D. thesis [5], on HPC systems like Blue Waters many materials can now be characterized in parallel within a single year.

WHY BLUE WATERS

Our Blue Waters allocation is one order of magnitude larger than any other allocation that we have obtained elsewhere. This enabled us to perform simulations with more accurate fermion nodes that are more realistic but also much more expensive. Besides the hydrocarbons discussed in this report, we performed simulations for a variety of other materials, including sodium, lithium fluoride, and silicon. In each case, we studied many temperature–density conditions as illustrated in Fig. 1. Hydrocarbons, however, posed a special challenge because they are produced for a variety of chemical compositions. Because we had access to the Blue Waters system, we could meet the composition challenge rigorously. In addition to a typical 2D parameter scan in density–temperature space, we performed 3D parameter scans in density–temperature–composition space by performing simulations of C, C_2H, CH, CH_2, CH_3, CH_4 as well H.

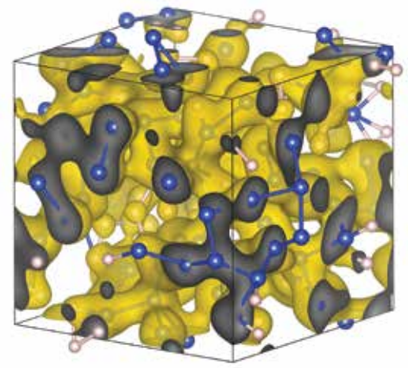

Figure 2: CH plastic at extreme pressure–temperature conditions studied with atomistic simulations. The C and H atoms are denoted as blue and pink spheres. Their interactions are governed by myriad short-lived chemical bonds that are mitigated by hot electrons. Their density is illustrated by the yellow isosurface.

PUBLICATIONS AND DATA SETS

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