

T-4
Atomic & Optical Theory**Simulations of Warm Dense Matter**

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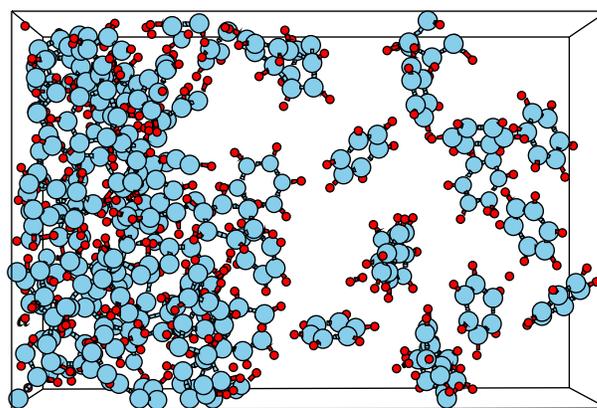
The environments that characterize such diverse systems as the interiors of giant planets, the initial implosion of an inertial confinement fusion capsule, the compression phase in high-energy density devices such as Z-pinches and explosive-magnetic generators, the insulator-metal transition in systems as varied as hydrogen liquid and rare-gas solids, shocked hydrocarbons in detonations, and various stages in primary and secondary nuclear weapons, have many features in

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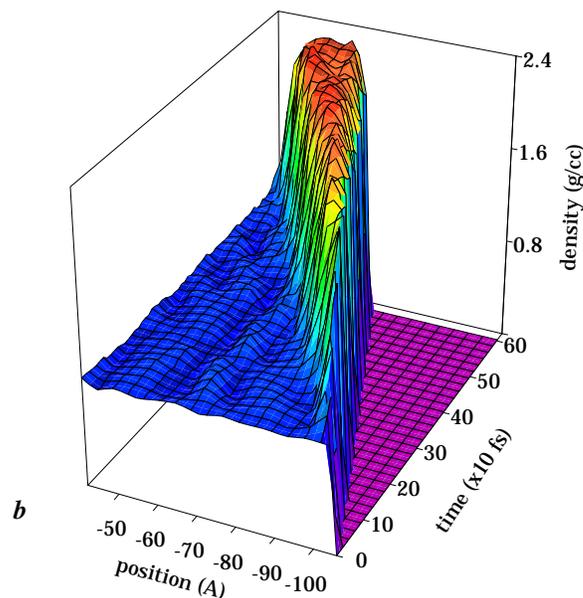
common. These processes span temperatures from 10^2 K to 10^5 K and densities from about one-hundredth to tens of times the solid. The medium resembles a “soup” of various species, including atoms, molecules, ions, and electrons that exhibits distinctly nonclassical behavior in the interaction of all the particles. The strong overlap of the electronic charge clouds of the constituents forces a fully quantum mechanical treatment of at least the electrons since models must include such mechanisms as breaking and forming of molecular bonds, ionizing various species, and the recombining of free electrons.

To model such systems, we have developed very sophisticated molecular dynamics (MD) simulation methods that employ highly-accurate density functional approaches. The system evolves temporally according to a two-step prescription. First, we consider a representative cell of particles, replicated throughout space, to resemble a fluid. For this configuration, we perform a density functional calculation using either a local-density or generalized gradient approach. The latter introduces corrections due to the nonlocality of the electron density. From the resulting electronic wavefunctions, we determine a force. The nuclei are then usually advanced by the classical equations of motion according to this quantal force. Through this prescription, we can represent very complex structural and dynamical quantum processes that dominate these media. These methods currently allow the treatment of a few hundred particles; however, scaling tests for massively-parallel computers indicate that simulations with thousands of atoms will shortly become routine.

Even on the new parallel computers, the above techniques have limitations. Certain nonequilibrium situations may require much larger samples of particles. To this end, we have also used and developed accurate semiempirical



a



b

Figure 1: (a) Snapshot of shock-compressed benzene. The carbon and hydrogen atoms are colored blue and red, respectively. (b) Time evolution of the density profile for one-half the simulation cell for shock-compressed benzene.

approaches that include the basic quantal interactions but utilize more approximate forms for the hamiltonian. Both Hydrogen and hydrocarbons have received such a treatment. For hydrocarbons, an order (N) algorithm, where the computational effort for solving the electronic structure problem scales linearly with the number of particles N , has been implemented on the ASCI Blue Mountain computer for samples reaching 10^4 particles on 126 processors.

We have applied these methods to a large variety of systems and environments, including isotopic mixtures of dense hydrogen; highly-compressed rare-gas solids; alkali metals near melt and along the vapor-liquid coexistence boundary; impurity atoms in dense hydrogen plasmas; shock-compressed atoms and hydrocarbons; and CuCl solid structures. For purposes of demonstration, we concentrate on three representative cases.

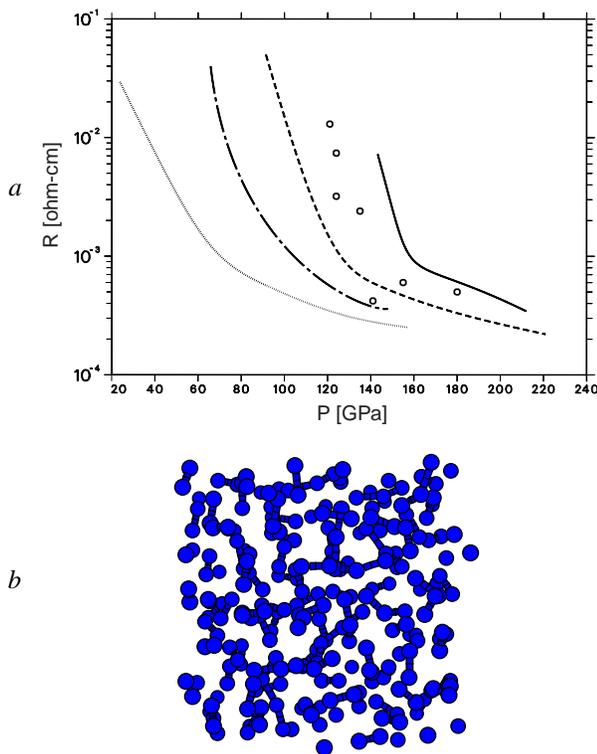


Figure 2: (a) *Electrical Resistivity versus pressure(density) for fluid H from 3000 K to 1000 K. Circles represent the experimental results;* (b) *Snapshot of dense Hydrogen showing molecular-atomic “soup.”*

Our first demonstration centers on order (N) tight-binding molecular dynamics simulations of shock-compressed hydrocarbons. First, a thermal sample of methane or benzene is prepared in a simulation cell elongated along the shock direction. Then, in a nonequilibrium MD simulation, the ends of the simulation cell perpendicular to the shock direction move inward, with appropriate periodic velocity boundary

conditions, thus mimicking a driving “piston” in a shock experiment. In Figure 1a, the piston is pushing in from the left, and the position of the shock front is visible as a density gradient between gaseous and condensed phases. We now consider shock compression of a liquid by starting a piston moving inward at a speed of 6 km/s. A shock front forms and begins to propagate through the medium as depicted by the abrupt rise in density along the diagonal in Figure 1b. The shock moves with a velocity of 10 km/s and produces an almost three-fold compression.

Second, we have made an extensive study of Hydrogen over a wide range of temperatures and densities. A recurring question revolves around under what conditions compressed solid or liquid Hydrogen becomes a metal. This still remains unanswered for the atomic metal; however, recent gas-gun experiments have uncovered a very interesting state that shows low conductivities [$\sim 2000/\Omega\text{-cm}$] while remaining in basically a molecular form as the density increases but the temperature remains low [~ 2000 K]. In Figure 2a, we show the results of simulations that indicate very good agreement with the experiments. The nature of the conducting media arises from the small amount of dissociation induced by the rising pressure. Due to the overlapping wavefunctions under these conditions, the monomers in conjunction with a few of the molecules permit electrons to move across the medium. Figure 2b gives an illustration of this state.

As a third example, we move in the opposite direction in relative density space and study, with density-function molecular dynamics, expanded fluid sodium along the boundary that separates the liquid and vapor phases. When sodium is expanded along this boundary, the dc-electrical conductivity drops as the density decreases. In Figure 3, snapshots from the molecular dynamics simulations for a density of $1/8$ solid are shown. At $T = 2500$ K, a gaseous phase is observed (Figure 3a), where the atoms are fairly well distributed in the whole simulation volume. As the temperature is lowered to 1000 K, the gas actually condenses (Figure 3b), with the atoms now occupying only 25% of original volume.

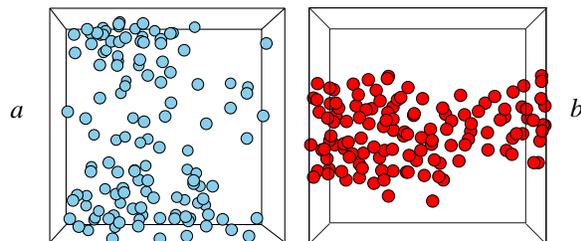


Figure 3: (a) *Gaseous Sodium at start of simulation;* (b) *Condensed, liquid Sodium at the end.*