First Principles Molecular Dynamics of Dense Plasmas

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Ab initio molecular dynamics calculations are performed for the equation of state of aluminum, spanning condensed matter and dense plasma regimes. Electronic exchange and correlation are included with either a zero- or finite-temperature local density approximation potential. Standard methods are extended to above the Fermi temperature by using final state pseudopotentials to describe thermally excited ion cores. The predicted Hugoniot equation of state agrees well with earlier plasma theories and with experiment for temperatures from 0 to 3×10^6 K.

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Molecular dynamics (MD) simulations are widely used to compute equilibrium properties of condensed matter, with *ab initio* methods reaching predictive accuracy. Ions are treated classically while electrons are included in the Born-Oppenheimer approximation and in the local density approximation (LDA) to density functional theory (DFT) [1], including electron temperature with the Mermin formalism [2]. Such methods have already been applied to liquid metals, for moderate temperatures and degenerate electrons [3]. They can be extended to higher temperature using a temperature-dependent exchange and correlation potential [4]. This Letter reports on a further extension to dense matter at temperatures as high as 3×10^6 K, i.e., into the plasma regime. With suitable refinements, MD is ideally suited to theoretical studies of dense plasmas in the strongly interacting limit.

Ab initio MD is typically performed in a plane wave basis using a pseudopotential to eliminate the ion core orbitals. This limits the maximum allowed temperatures to $k_B T < 10$ eV, else thermal depopulation of shallow core levels invalidates the usual rigid core assumption. The restriction could be avoided by pseudopotentials with the shallow core states in the valence manifold, e.g., an Al^{+11} ion rather than the usual Al^{+3}. However, such calculations are prohibitively expensive in a plane wave basis. Recently, pseudopotentials were applied to core-level photoemission, in which a photoexcited hole occurs in an otherwise filled core shell [5–8]. An excited-core atomic calculation is performed in constrained DFT, assuming that the core-hole lifetime is long and neighboring electrons relax under the perturbation. A second pseudopotential is generated for this configuration, giving a new pseudoatom with increased ionic charge. The modified pseudoion is then treated as an impurity species in standard pseudopotential calculations for the solid.

This final state pseudopotential idea is extended here to calculations for a moderate Z plasma, that of shock compressed aluminum. Multiple ion configurations (singly, doubly core ionized, etc.) will occur dynamically at the highest temperatures considered. These can be accounted for by supposing fictitious core-hole dynamics, viz., transitions among the discrete ionization configurations are approximated with a continuously fluctuating, classical state vector. We report results from 0 to 3×10^6 K, at which point K-shell ionization is occurring [9]. The predictions are in good agreement with experiment and with existing theories up to the highest calculated temperature. There are, in principle, no artificial discontinuities in the calculated Hugoniot equation of state between high and low temperatures because a single method encompasses the limits.

The calculations reported here employ a time-independent thermal average of integrally ionized core states [10], which yields a fractionally charged pseudoion. An ensemble average for the atomic core is obtained from the partition function, $\mathcal{Z} = \sum_i D_i \exp[-\beta(E_i - \mu N_i^{\mathrm{val}})]$, using constrained LDA total energies E_i, for isolated neutral atoms of core configuration i, with degeneracy D_i, and including a chemical potential μ for the free valence electrons that is taken from the self-consistent MD calculations. The atomic orbitals and energies are obtained from an existing program [11], modified for ionized core shells. These constrained DFT total energies approximately include a Hubbard repulsion which is missing from the usual average atom approximation [12] (e.g., the doubly ionized core energy exceeds twice the singly ionized energy [13]). The chemical potential imposes an approximate chemical equilibrium between the core and valence subsystems, which are treated separately in the pseudopotential approach [14]. The excited atomic core yields a contribution to the internal energy of the system that must be added to the pseudopotential calculations. In terms of the expected energies of pseudoelectron and all-electron atoms derived from $\mathcal{Z}$, the correction per atom is $\Delta U = \langle E^{\text{all-el}} \rangle - \langle E^{\text{pseudo}} \rangle$. The entropy of the ion cores makes no contribution to the Hellmann-Feynman stress tensor.

The predicted ensemble average does not include the effects of interactions with neighboring ions or the electron gas upon embedding the ion in the plasma environment. Changes in total energy or potential on transferring the atomic cores from vacuum to the plasma environment are, therefore, absent from this model. However, errors on the order of eV, characteristic of chemical differences, make small changes to the predicted concentrations of core species at the temperatures where core ionization is prominent. So-called continuum lowering [15,16] is similarly neglected. Finally, the repulsion of overlapping, filled core shells and the hybridization effect from core-hole delocalization between adjacent ions are not included. Overlap of cores does occur at elevated temperatures and pressures, so a more compressible Hugoniot will result from this last omission.

MD calculations are performed for a neutral, fixed volume cubic cell of either 32 or 4 atoms (the latter only for temperatures of 300 000 K and higher). Brillouin zone sampling of the 4-atom calculations includes eight $\vec{k}$ points for temperatures up to 1.5 MK; all other calculations use only the Γ point. The valence electron chemical potential is self-consistently determined so as to give the correct total number of electrons for a truncated, finite spectrum of eigenvalues. Valence electrons are subsequently kept on the Born-Oppenheimer surface at a fixed temperature $T_{\rm ele}$ by conjugate gradient minimization. An increasing number of conduction bands are required to assess the Fermi-Dirac occupations at higher temperatures [17].

MD time steps ranging from 1.25 to 6 atomic units are used to perform molecular dynamics by Verlet integration. These are smaller than usual, to give average atomic displacements per time step that are comparable to previous MD studies. A Maxwellian distribution of velocities is initially chosen such that $\frac{3}{2}kT_{\rm ion} = E_{\rm ion}^{\rm kin}/N_{\rm ion} = \frac{3}{2}kT_{\rm ele}$. The ions are subsequently allowed to reach thermodynamic equilibrium by MD, before computing thermodynamic expectations. $T_{\rm ion}$ fluctuates during MD, so the atomic velocities are scaled to restore $T_{\rm ion}$ whenever it instantaneously departs from $T_{\rm ele}$ by more than (typically [18]) 10%–15%. Ionic pressure contributions are given by $\langle P_{\rm ion}\rangle V = N_{\rm ion} k_B \langle T_{\rm ion}\rangle$, and electronic pressures are obtained from the Hellmann-Feynman stress tensor [19,20].

The Rankine-Hugoniot relation,

$$[U - U_0] - [P(V_0 - V)/2] = 0, \qquad (1)$$

for internal energy U, pressure P, and volume V, achieved by shock from initial conditions $P_0 = 0, U_0, V_0$, is easily evaluated by this prescription [21]. Statistical fluctuations are minimized by taking the ensemble average of the difference $\langle [U - U_0] - [P(V_0 - V)/2] \rangle$. At the highest temperatures, the predicted Hugoniot equation of state is insensitive to the number of atoms in the MD cell. As evidence, Fig. 1 displays Eq. (1) versus volume as calculated for 4- and 32-atom unit cells at 300 000 K; the Hugoniot point lies at the zero of the ordinate. The predicted density varies by only 0.5% between the 4- and 32-atom cases. Such insensitivity appears to result from ion-ion pair correlations that are dominated by short range repulsion at these temperatures. Figure 2 shows the pair-correlation function plotted to distances of one-half of the unit cell length for the two systems. In principle, a bridge function can be fitted to the results and an improved treatment of the ionic system could be made [22]. However, the 4-atom simulation seems to adequately describe the available configurations.

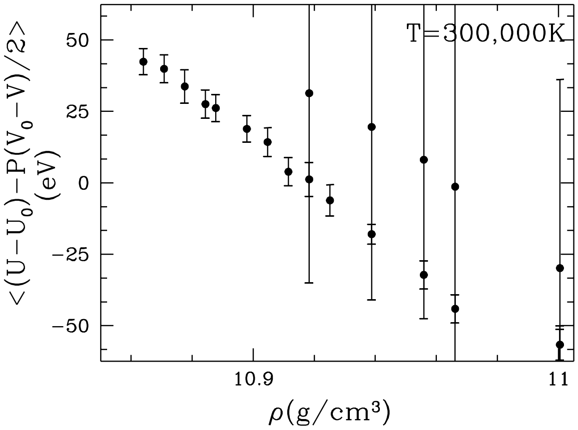

FIG. 1. Comparison of the Hugoniot relation, Eq. (1), versus density as calculated by MD for $T = 300\,000$ K. A linear dependence is evident over this small range in densities. The lower set of points are from 32-atom calculations, the upper are for four atoms. Each data point is derived from between 1500 to 6000 equilibrated time steps. A systematic size dependence is visible; however, the 4-atom calculations are sufficiently accurate for these extreme conditions.

Considerable experimental data exist for shocked Al [23–30]. The MD results are in good agreement, as seen in Fig. 3. Points are displayed for $T = (3, 2.25, 1.75, 1.5, 1.0, 0.75, 0.5, 0.4, 0.3, 0.144) \times 10^6$ K with fractionally ionized cores appropriate to the temperature and with filled cores at 75 000 and 30 000 K. Lower temperature calculations were also performed, but are not shown. A solid line marks a cubic spline interpolation of the MD points calculated using a parametrized exchange and

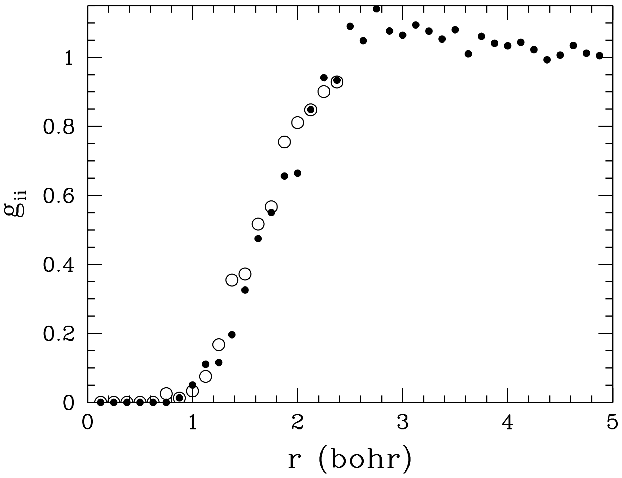

FIG. 2. Ion-ion pair correlation functions as calculated from the 32-atom (small filled circles) and 4-atom ensembles (large open circles). The 4-atom unit cell adequately reproduces the correlation function out to the average neighbor separation, at which point the effective interactions are evidently small and $g_{ii} \simeq 1$.

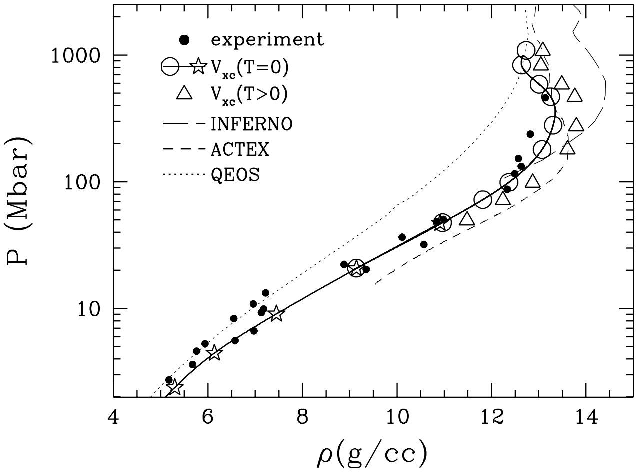

FIG. 3. Comparison of the MD Hugoniot to experimental data from Refs. [23–30] (filled circles) and to other theoretical results: QEOS [40] (dotted line), ACTEX [38] (dashed line), and INFERNO [33] (solid line). The MD calculations with zero-T exchange and correlation are shown with open stars (32 atoms/cell) or circles (4 atoms/cell), and include an interpolating spline curve. Four-atom calculations with the corresponding finite-temperature LDA correction lie at increased density and nearly unchanged pressures, and are shown with open triangles and no interpolating line. Statistical uncertainties in the MD results are comparable to the sizes of the symbols displayed. Additional calculations for 4- and 32-atom systems at temperatures as high as 0.75 MK (not shown) yield essentially identical results.

correlation potential for the ground state electron gas [31]. Additional calculations include a finite-temperature exchange and correlation correction [32]. The corrected results are shown as open triangles at increased compressions, with no interpolating spline curve.

There are numerous theoretical treatments of the dense plasma regime [33–39] available for comparison. Three such equations of state are also shown in Fig. 3. The experimental error bars at the higher pressure points are too large to discriminate between the different theories. QEOS is a Thomas-Fermi theory [34,40] which employs a simplified treatment of atomic shell structure. Therefore, it lacks the reversal (decrease) in density with increasing shock strength that the other theories display, which occurs as a result of increasing ionization in the Al L shell. INFERNO is a cell model treatment of a single-ion core using a zero-T LDA potential [12,33]. The cusps in the MD and INFERNO Hugoniots, due to successive L- and K-shell ionization, are very similar in appearance, although the predicted maximum densities differ appreciably. INFERNO uses an average atom approximation and a simplified atomic pair-correlation function, which might account for this difference. ACTEX is a perturbational, explicitly many-body (non-DFT), plasma theory [38]. It treats electrons quantum mechanically and accounts for the Coulombic ion-ion repulsion, but leaves out contributions from core overlap. The finite-T MD results are in broad agreement with ACTEX, especially regarding the maximum density achieved by single shock. However, the details of the Hugoniot curves are notably different between MD and ACTEX. For example, the cusp in ACTEX at 200–1000 Mbar, which is attributed to ionization of $2s$ and $2p$ subshells, is entirely absent from the MD and INFERNO results. This may arise from the DFT atomic energies used in both MD and ACTEX.

In conclusion, first principles molecular dynamics calculations are applied to the Hugoniot equation of state of shock compressed aluminum. The valence electrons are treated with reliable, fully quantum mechanical methods and the Coulomb repulsion and many-body correlation among classical ions are included explicitly by molecular dynamics. At low temperatures ($T < 10\,000$ K), the method is typical of *ab initio* MD calculations. The Mermin formalism for electronic free energy and a finite-T exchange and correlation extend the method to $T < 100\,000$ K. Finally, the recently developed final state pseudopotential method based on constrained DFT is used for yet higher temperatures, up to 3×10^6 K. This marks the first use of *ab initio* MD methods in the plasma regime. The results are in good agreement with plasma theories and experiment even at the most extreme temperatures considered so far. The core excitation energies and the resulting ionization state are not precisely self-consistent for the ion in plasma. In principle, improved pseudopotentials are easily generated for this situation. It is also straightforward to include the effects of ion-ion core overlap repulsion via an additive short range interaction potential in the MD. These corrections should yield a quantitatively reliable equation of state for the regime of strongly coupled, warm dense plasmas. Work on these topics is ongoing.

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