

Shock-Induced Metallization of Polystyrene Along the Principal Hugoniot Investigated by Advanced Thermal Density Functionals

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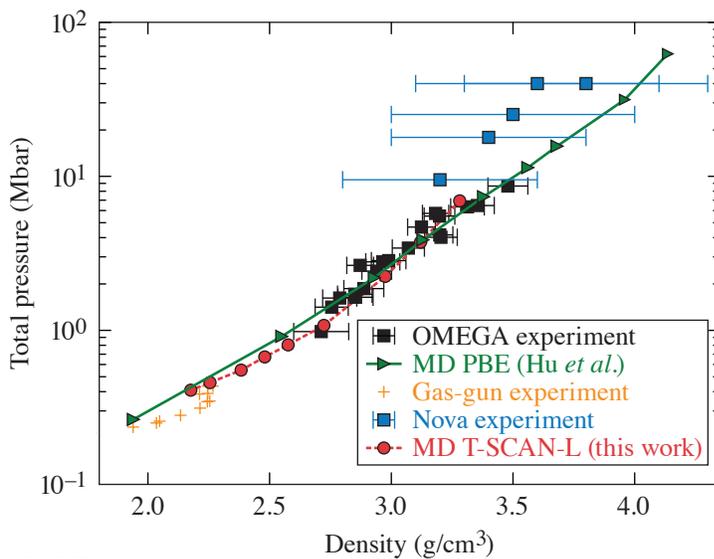
Use of a recently developed thermal strongly constrained and appropriately normed Laplacian (T-SCAN-L)-dependent meta-generalized gradient approximation exchange correlation (XC) density functional¹ and thermal hybrid XC density functional (KDT0)² within the framework of density functional theory as implemented in Vienna *ab-initio* simulation package (VASP) to show that the inclusion of thermal and inhomogeneity effects is crucial for accurate prediction of structural evolution and corresponding insulator–metal transition (IMT) during shock compression. Optical reflectivity calculated as an indicator of IMT is in perfect accord with experimental data.³ The discrepancy between experiment and *ab-initio* simulation results was reported several times during last decade.^{4–6}

The equation of state (EOS) of shocked material just behind the shock front satisfies the Rankine–Hugoniot equation

$$E_1 - E_0 + \frac{1}{2}(P_1 + P_0) \left(\frac{1}{\rho_1} - \frac{1}{\rho_0} \right) = 0,$$

where the subscripts “0” and “1” stand for unshocked and shocked sides, respectively. The unshocked side of the ablator (CH) is in ambient conditions. At ambient conditions ($T = 300$ K and $\rho = 1.055$ g/cm³), the pressure P_0 can be approximated by zero since it is orders of magnitude lower than the pressure at $\sim 10^3$ K. Based on the results from the *ab-initio* molecular dynamics (AIMD) calculations, E_0 is set to be -93 kJ/g.

Figure 1 shows the comparison between various experimental and theoretical studies of principal Hugoniot on the pressure–density plane. Both Perdew–Burke–Ernzerhof (PBE)⁵ and T-SCAN-L AIMD calculations overestimate shock pressure compared



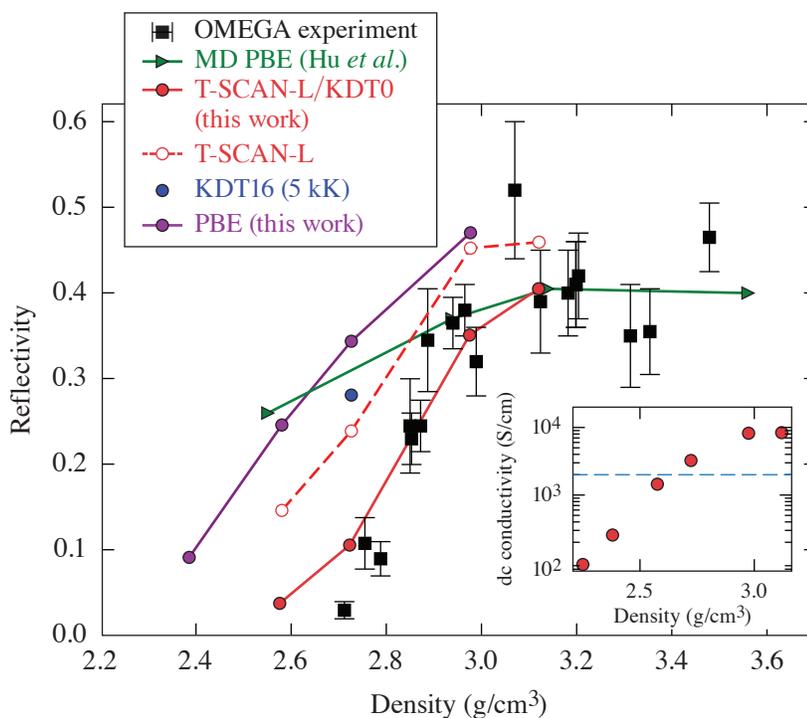
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Figure 1

CH pressure as a function of density along the principal Hugoniot. The T-SCAN-L results are compared with PBE calculations by Hu *et al.*,⁵ the Nova experiment,⁷ gas-gun experiment,⁸ and the OMEGA experiment³ based on latest quartz EOS (black rectangles).

to a gas-gun⁸ experiment below 1 Mbar. In the mid-pressure range (1 to 10 Mbar), T-SCAN-L shows concave behavior opposing more-linear PBE results. Apart from using a higher-rung XC functional with explicit temperature dependence, this change might also be associated with the proper treatment of structural characteristics of shocked CH. We carefully run structural relaxation until no structure remains, observing melting/dissociation exactly at these mid-range pressures.

Optical calculations are performed within the Kubo–Greenwood formalism, obtaining CH reflectivity by averaging the uncorrelated snapshots of ionic configurations from the AIMD simulations. The details of the process can be found in Ref. 5. A comparison of the results from the calculations with the OMEGA experiment and PBE-based AIMD study⁵ is shown in Fig. 2. Note that the reflectivity turn-on point is shifted to higher pressures and the jump is much sharper, making it in perfect agreement with the OMEGA experiment. By separately plotting the results obtained by T-SCAN-L and KDT0 on top of the T-SCAN-L-generated ionic configurations in Fig. 2, we demonstrate that the improved results are the consequence of not only accurate ionic configurations, but also accurate electronic structure calculations. There are several factors that contribute to this enhancement. Foremost, our PBE calculations show that it underestimates the drop in density of states (DOS) as compared to T-SCAN-L at exactly the same conditions as shown in Fig. 3, which shows a comparison of DOS in the temperature range from 3500 to 5000 K along the principal Hugoniot. The second aspect is the shift in Hugoniot data. At lower densities, T-SCAN-L gives lower Hugoniot pressures compared to PBE calculations. As a result, the Hugoniot points at a fixed density predicted by T-SCAN-L have much less molecular dissociation and consequently exhibit a deeper drop in DOS, leading to smaller reflectivity.



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Figure 2

Reflectivity of shocked CH along the principal Hugoniot at 532-nm VISAR (velocity interferometer system for any reflection) light.

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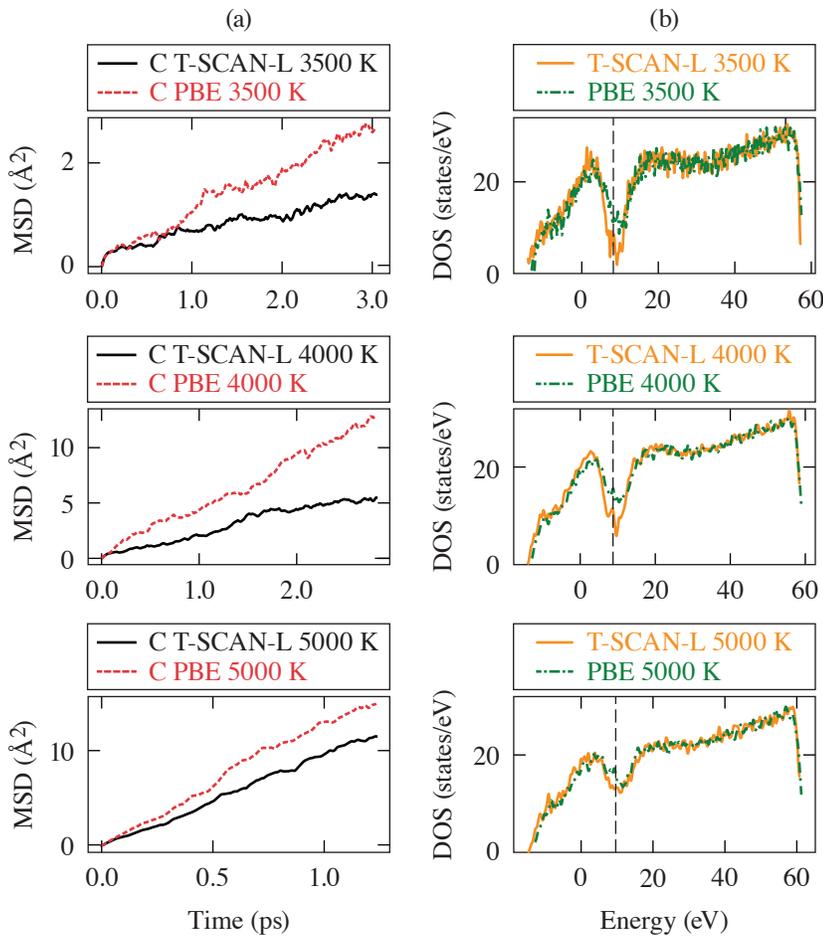


Figure 3

(a) Comparison of mean square displacement predicted by PBE versus TSCAN-L XC functionals and (b) comparison of corresponding DOS in the temperature range of 3500 to 5000 K. MSD: mean squared displacement.

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