Static and Optical Properties of Warm Dense Polystyrene
Along the Principal Hugoniot

Warm dense matter (WDM) occupies a critical regime within
the physics branches more traditionally addressed by condensed
matter and plasma physics. WDM has recently received con
siderable attention because of identification with environments
as diverse as the interiors of exoplanets,\(^1\) the atmospheres of
stars,\(^2\) inertial confinement fusion (ICF) capsules,\(^3\) and the
plasma from laser interactions\(^4\) with materials. Broadly, WDM
spans temperatures from a few tens to several hundred electron
volts and densities from \(10^{21}\) to \(10^{25}\) atoms/cm\(^3\), covering
conditions from melt to fully ionized plasmas. Modeling this
regime presents a particularly difficult challenge given that
quantum mechanical effects play a crucial role in accurately
representing this complex medium under extreme conditions.
In addition, many of these environments constitute the dynamic
interplay between mixtures of species in various physical states.
Because of this complexity, few systematic experimental stud
es have examined its nature. One exception is ICF, in which
laser-powered shocks combined with accurate diagnostic tools
have begun to penetrate its intricacies and provide detailed tests
of various WDM theoretical models.

For example, hydrocarbon polymers such as polystyrene
(CH) and glow-discharge–polymer (GDP) plastic are often
used as the ablator material in inertial confinement targets,
for both indirect-drive\(^5\) and direct-drive\(^6\) ICF configurations.
In ICF implosions, the ablator materials are compressed into
the WDM regime by shocks. Typically, the shocked ablators
can have temperatures of \(T = 5\) to \(50\) eV and densities of \(2\times\)
to \(10\times\) solid density. Accurate knowledge of the ablator properties
in the WDM regime is just as crucial for ICF designs as the
properties of the deuterium–tritium (DT) fuel.\(^7\)–\(^14\) The static
equation of state (EOS) determines the material’s compress
ibility,\(^15\) while the dynamic and optical properties affect the
thermal and radiation transports in the material.\(^16\)–\(^18\)

Because of their importance to ICF target designs, the
properties of various polymers in the WDM regime have
recently been extensively studied using laser-driven shock
waves. In contrast to the previous gas-gun experiment\(^19\) in
the low-pressure regime (\(P < 1\) Mbar), an early Nova experi-
ment\(^20\) showed a stiffer behavior of CH at pressures of 10 to
40 Mbar than the Hugoniot derived from the \textit{SESAME}\(^21\)
and “quotidian” equation-of-state (QEoS)\(^22\) models. This
has stimulated more-recent experimental studies\(^23\)–\(^26\) of the
CH Hugoniot in the 1- to 10-Mbar regime. In addition to the
Hugoniot pressure, the temperature and optical reflectivity
of CH shocks have also been measured in some impedance
-matching experiments using the velocity interferometer system
for any reflector (VISAR).\(^27\)–\(^28\) These high-quality experi-
mental data could advance our understanding of the properties of
shocked polymers.

In general, the theoretical exploration of material properties
in the WDM regime remains difficult because of the co-exis
tence of different species including electrons, ions, atoms, and
molecules in strongly coupled and degenerate conditions. To
simulate such complex systems, one must adopt first-principles
methods such as quantum molecular dynamics (QMD),\(^29\)–\(^35\)
path-integral Monte Carlo (PIMC),\(^36\)–\(^39\) and coupled electron–
ion Monte Carlo (CEIMC)\(^40\) methods. For example, using the
QMD method, the principal shock Hugoniot of polyethylene,\(^41\)
CH,\(^42\) and plastic\(^26\) with a composition of CH\(_{136}\) have recently
been investigated up to \(<15\) Mbar. Noticeable differences for
CH\(_{136}\) in the pressure range have been observed when com-
pared to the QEoS-based Livermore EOS prediction.\(^26\) For
CH, the previous QMD simulations (up to only \(<8\) Mbar) by
Wang \textit{et al.}\(^42\) showed good agreement with a recent OMEGA
experiment\(^25\) but failed to predict the measured reflectivity.

In this article, we employed the QMD method to investigate
the principal Hugoniot of CH up to a very high pressure of
62 Mbar. The shock pressure and temperature from our QMD
calculations agree very well with recent impedance-matching
measurements (\(P < 10\) Mbar) on OMEGA. When compared
to the \textit{SESAME} EOS model, a stiffer behavior in CH is pre
dicted by QMD simulations at pressures above 10 Mbar. In
addition, the reflectivity discrepancy seen in previous QMD
simulations\(^42\) has been resolved. The present QMD calcula-
tions recover the measured reflectivity only when the proper
refraction index \(n_0\) of the unshocked CH is taken into account.
The structure change in CH at 1 to 2 Mbar has been found to be consistent with the turn-on of reflectivity in both experiment and QMD calculations.

The Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{43–45} was used for our QMD calculations within the isokinetic ensemble (particle/volume/temperature \textit{NVT} constant). The VASP code is based on the finite-temperature density-functional theory (FTDFT) in which electrons are treated quantum-mechanically by a plane-wave basis within the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation function.\textsuperscript{46} Projector augmented wave (PAW) pseudopotentials were used to account for the core electrons. To converge the energy and pressure calculations, we set the plane-wave cutoff energy to 1000 eV and adopted hard potentials with tight cores (core radii of 1.1 and 0.8 a.u. for C and H, respectively). The system was assumed to be in local thermodynamical equilibrium with equal electron and ion temperatures ($T_e = T_i$). A periodically replicated cubic cell was used with 125 atoms for each species of H and C, with the volume of the cell determined by the CH density. For each molecular dynamics (MD) step, a set of electronic-state functions for each $k$ point was self-consistently determined for a given ionic configuration. Then, the ions were moved classically with a velocity Verlet algorithm, according to the combined ionic and electronic forces. The ion temperature was kept constant by a simple velocity scaling. A set of self-consistent ion trajectories and electronic-wave functions resulted from the MD time propagation. These trajectories provide a consistent set of static, dynamic, and optical properties of warm dense CH.

The QMD calculations employed a $\Gamma$-point ($k = 0$) sampling of the first Brillouin zone in the cubic cell. Testing with a $2 \times 2 \times 2$ Monkhorst–Pack $k$-point grid, we found that the resulting pressure and energy varied by only ~2\%. For the lowest temperature point, we used 650 bands and a time step of $\Delta t = 0.5$ fs, while for the highest temperature points, we employed a larger number (8000) of bands and a smaller time step of $\Delta t = 0.0325$ fs. The correlation times varied slightly at 5.0 to 6.0 fs.

To search for the shock Hugoniot of CH at a given temperature, we performed QMD calculations for two close densities differing by only ~0.05 g/cm\textsuperscript{3}. The obtained energy and pressure were used to evaluate how far the two calculated densities were from the true Hugoniot point, which is defined by the Hugoniot equation

$$Hug = E_f - E_0 + \frac{1}{2} \left( P_f + P_0 \right) \times \left( \frac{1}{\rho_f} - \frac{1}{\rho_0} \right) = 0.$$  

The pressure, internal energy, and density of the initial unshocked CH are characterized by ($P_0$, $E_0$, $\rho_0$), while the shock has the quantities of ($P_f$, $E_f$, $\rho_f$). The initial density used in the experiments was $\rho_0 = 1.05$ g/cm\textsuperscript{3}. By linearly interpolating/extrapolating through the two calculated points to make $Hug = 0$, we can determine the Hugoniot point ($P_h$, $E_h$, $\rho_h$) for the given temperature. The principal Hugoniot of CH is displayed in Table 138.VIII, in which the shock and particle velocities $U_s = \left( \rho_h (P_h - P_0) / (\rho_h \rho_0 - \rho_0^3) \right)$ and $U_p = (P_h - P_0) / (\rho_0 U_s)$, respectively, are also given. The highest calculated pressure point reached an unprecedented level of $P \sim 62$ Mbar.

To explore the change of material structure along the principal Hugoniot, we have plotted the pair-correlation functions $g(r)$ in Fig. 138.43 among ions of (a) carbon–carbon, (b) carbon–hydrogen, and (c) hydrogen–hydrogen. Figure 138.43 displays calculations for two temperatures at $T = 5000$ K (solid red line) and $T = 15,000$ K (dashed blue line), corresponding to pressures of 0.914 Mbar and 2.198 Mbar, respectively. The peaks in $g(r)$ appearing at a low temperature of 5000 K wash out as

Table 138.VIII: The principal Hugoniot of polystyrene (CH) predicted by QMD calculations.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\rho$ (g/cm\textsuperscript{3})</th>
<th>$P$ (Mbar)</th>
<th>$U_s$ (km/s)</th>
<th>$U_p$ (km/s)</th>
<th>$\rho/\rho_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,000</td>
<td>1.941</td>
<td>0.264</td>
<td>6.966</td>
<td>3.198</td>
<td>1.848</td>
</tr>
<tr>
<td>5,000</td>
<td>2.551</td>
<td>0.914</td>
<td>11.961</td>
<td>7.037</td>
<td>2.429</td>
</tr>
<tr>
<td>15,000</td>
<td>2.938</td>
<td>2.198</td>
<td>17.924</td>
<td>11.519</td>
<td>2.798</td>
</tr>
<tr>
<td>30,000</td>
<td>3.139</td>
<td>3.872</td>
<td>23.448</td>
<td>15.605</td>
<td>2.990</td>
</tr>
<tr>
<td>60,000</td>
<td>3.379</td>
<td>7.370</td>
<td>31.848</td>
<td>21.951</td>
<td>3.218</td>
</tr>
<tr>
<td>90,000</td>
<td>3.561</td>
<td>11.392</td>
<td>39.174</td>
<td>27.624</td>
<td>3.392</td>
</tr>
<tr>
<td>120,000</td>
<td>3.681</td>
<td>15.698</td>
<td>45.691</td>
<td>32.659</td>
<td>3.506</td>
</tr>
<tr>
<td>220,000</td>
<td>3.959</td>
<td>31.468</td>
<td>63.835</td>
<td>46.904</td>
<td>3.770</td>
</tr>
<tr>
<td>400,000</td>
<td>4.136</td>
<td>62.406</td>
<td>89.230</td>
<td>66.575</td>
<td>3.939</td>
</tr>
</tbody>
</table>
the pressure increases to ~2 Mbar, indicating a change in the material structure around $P \approx 1$ to 2 Mbar, which is found to be consistent with the turn-on of reflectivity (discussed below).

CH Hugoniot is compared with both experiments and models in Fig. 138.44 by plotting the pressure as a function of the shock density. The QMD results (red circles) are compared with a gas-gun experiment, a Nova experiment, a recent impedance-matching experiment on OMEGA, and SESAME model predictions.

In Fig. 138.45, the measured shock temperatures from the QMD experiment are compared with both the QMD calculations and the SESAME model. It is found that the SESAME model slightly overestimates the shock temperature by ~10\% for this low-pressure regime ($P < 10$ Mbar), while the QMD results reproduce the OMEGA measurement very well except for the highest data point. The highest data point, which has a higher temperature than both the QMD and SESAME predictions by 20\% to 30\%, might have been compromised by the normalization to that of the quartz standard.

A similar discrepancy for the highest data point was also observed in the previous QMD calculation by Wang et al. In the Fig. 138.45 inset, the comparison of shock temperature between QMD and the SESAME model has been extended to a wider range of pressures. The shock temperature predicted by QMD is higher than that of the SESAME model for pressures of $P > 20$ Mbar. This is consistent with the QMD-predicted stiffer behavior of CH for this high-pressure regime (see Fig. 138.44).

Finally, we examine the reflectivity of shocked CH along the principal Hugoniot. In both the OMEGA experiment and a LULI experiment, the reflectivity was determined by the signal level of the probe beam ($\lambda = 532$ nm) reflected by the CH.
The dielectric function, \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \), can be calculated by

\[
\varepsilon_1(\omega) = 1 - \frac{4\pi}{\omega} \sigma_2(\omega),
\]

\[
\varepsilon_2(\omega) = \frac{4\pi}{\omega} \sigma_1(\omega). \tag{3}
\]

Using the dielectric function, one obtains the real \([n(\omega)]\) and imaginary \([k(\omega)]\) parts of the refraction index:

\[
n(\omega) = \sqrt{\frac{\varepsilon(\omega) + \varepsilon_1(\omega)}{2}},
\]

\[
k(\omega) = \sqrt{\frac{\varepsilon(\omega) - \varepsilon_1(\omega)}{2}}. \tag{4}
\]

Finally, the reflectivity is defined in the following general way:

\[
R(\omega) = \frac{\left[ n(\omega) - n_0 \right]^2 + k(\omega)^2}{\left[ n(\omega) + n_0 \right]^2 + k(\omega)^2}, \tag{5}
\]

where \(n_0\) is the refraction index of the ambient. The choice of \(n_0 = 1\) is often seen in textbooks, where the ambient is assumed to be vacuum or air. In the shock experiments, however, the reflectivity was measured as the shock propagated into the unshocked CH foil. The light reflection occurs at the interface between shocked and unshocked CH. Therefore, one must choose \(n_0\) to be the refraction index of the unshocked CH, which was calculated to be \(n_0 = 1.94\) in our QMD simulation of solid CH at room temperature. With this value of \(n_0 = 1.94\), the resulting QMD reflectivity of CH shock is compared with both the OMEGA experiment\(^{25}\) and the LULI measurement\(^{23}\) in Fig. 138.46. The saturation level of the reflectivity predicted by the present QMD calculations agrees well with experiments. The turn-on of reflectivity ~1 to 2 Mbar is in closer agreement with the LULI experiment but seems to appear earlier than for the OMEGA experiment. If we improperly choose \(n_0 = 1\), the results (black triangles) overestimate the reflectivity from ~40% to ~60%. The overestimated reflection level of ~60% was exactly the same as what was seen in the previous QMD calculation by Wang et al.\(^{42}\) The inset in Fig. 138.46 plots the reflectivity for a wider range of pressures, and the reflectivity appears to be slowly increasing beyond 15-Mbar pressures, similar to the behavior seen in shocked deuterium\(^{18,49}\) occurring at \(P \approx 2.8\) Mbar.

In summary, we have performed first-principles calculations for the principal Hugoniot of CH, using the QMD method. The

![Figure 138.45](https://example.com/fig13845)

The shock temperature of CH is plotted as a function of pressure, along the principal Hugoniot. The QMD results (red circles) are compared with the recent impedance-matching experiment on OMEGA.\(^{25}\) The inset shows the temperature comparison between the QMD prediction and the SESAME model to the entire explored pressure range.

In the QMD calculations, we obtained a consistent set of trajectories of the ionic configuration during the molecular dynamics time propagation. We chose about ten uncorrelated snapshots of these configurations to calculate the velocity dipole matrix elements \(D_{mn}\) from the VASP wave functions. The quantity \(D_{mn}\) is used to compute the frequency-dependent Onsager coefficients within the Kubo–Greenwood formalism:\(^{48}\)

\[
L_{ij}(\omega) = \sum_{mn} \frac{2\pi (-\omega)^{i-j}}{3Vm^2_\epsilon \omega} \Gamma_{mn} \left| D_{mn} \right|^2 \times \left( \frac{E_m + E_n}{2} - H \right)^{i-j-2} \delta(E_m - E_n - h\omega), \tag{1}
\]

where \(V = 1/\rho\) is the atomic volume, \(E_m(E_n)\) is the energy of the \(n\)th (\(m\)th) state, and \(H\) is the enthalpy (per atom) of the system. The quantity of \(\Gamma_{mn}\) is the difference between the Fermi–Dirac distributions for the \(m\) and \(n\) states at temperature \(T\). In practical calculations, the \(\delta\) function in the above equation is approximated by a Gaussian function of width \(\Delta E \approx 0.5\) eV. From the real part of the electric conductivity, \(\sigma_1(\omega) = L_{11}(\omega)\), we obtain the imaginary part of the electric conductivity from a principal value integral:

\[
\sigma_2(\omega) = -\frac{2}{\pi} P \int \frac{\omega \sigma_1(\omega')}{\omega^2 - \omega'^2} d\omega'. \tag{2}
\]
Figure 138.46

The reflectivity of shocked CH pressure for VISAR light at \( \lambda = 532 \) nm along the principal Hugoniot. The QMD results, using the proper \( n_0 \) of unshocked CH (red circles) and the improper vacuum \( n_0 \) (black triangles), are compared with the LULI measurement\(^{23}\) and the recent OMEGA experiment.\(^{25}\) The inset shows the reflectivity in the entire pressure range.

QMD results agree very well with the pressure and temperature measurements up to \( P = 10 \) Mbar. In this pressure range, the SESAME model (SESAME 7593) predicted a similar pressure but slightly overestimated the shock temperature. For high-pressure regimes (\( P = 10 \) to 62 Mbar), the QMD-predicted shock temperature is higher than suggested by the SESAME model, thereby resulting in a stiffer CH shock in QMD simulations. Moreover, the QMD-predicted reflectivity of shocked CH agrees with a recent OMEGA experiment once the correct refraction index of the ambient (unshocked CH) is taken into account. It was found that the reflectivity starts to turn on at a somewhat smaller pressure than the recent experiment on OMEGA but appears to be closer to the LULI experiment. These results might stimulate more-accurate experiments at the high-pressure regime. Precise EOS and opacity tables based on these results could benefit fine tuning future ICF designs.

ACKNOWLEDGMENT

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0001944, the University of Rochester, and the New York State Energy Research and Development Authority. The support of DOE does not constitute an endorsement by DOE of the views expressed in this article. This work was also supported by Scientific Campaign 10 at the Los Alamos National Laboratory, operated by Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under Contract No. DE-AC52-06NA25396.

REFERENCES