Plasma Waves and the Compressibility of Warm Dense Hydrogen

Fernandez-Pañella (2019)
deuterium re-shock

~1 eV/atom energy difference

Experimental data
- Single shock data
- Re-shock data

Theoretical models:
- Kerley
- SESAME 5267
- Caillabet et al.
- FPEOS

Internal energy of plasma waves

\[ U / N \text{ [eV/atom]} \]

\[ C_v / Nk \]

\[ kT \text{ [eV]} \]

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The heat capacity of plasma waves can explain the high experimental D$_2$ compressibility near 500 GPa

- Recent shock, re-shock, and sound speed experiments$^{1,2}$ report higher compression of deuterium ($^2$H) near 500 GPa than predicted by models.

- Using a Debye-type model, a specific heat contribution up to k$_B$/2 per atom is calculated for plasmons in warm dense hydrogen.

- Warm dense matter: the thermal energy, Fermi energy, electron plasmon energy, Coulomb coupling energy, and ionization energy are all approximately and simultaneously equal to 1 Ry (1 Ry = 13.6 eV).

- This specific heat contribution is not explicitly considered in current hydrogen equation of state models, including those of both the “chemical free energy” and “quantum ab initio” varieties.

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In warm dense matter (WDM), all energies are ~1 Ry

Atomic Energy (Rydberg):
\[ E_R = 13.6 \text{ eV} \]

Thermal Energy:
\[ E_T = k_B T \]

Fermi Energy:
\[ E_F = \left(3\pi^2\right)^{2/3} \frac{\hbar^2}{2m_e} n_e^{2/3} \]

Coulomb Potential Energy:
\[ E_C = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{4}{3}\pi n_e\right)^{1/3} \]

Plasmon Energy:
\[ \hbar \omega_{pe} = \hbar \left(\frac{n_e e^2}{\varepsilon_0 m_e}\right)^{1/2} \]

* Contours assume full ionization
Recent experimental data suggest model discrepancies in the high-pressure, high-density D\textsubscript{2} EOS

This is not a single datum with a 1-sigma discrepancy. This is a systematic discrepancy consistent across 3 different experimental techniques: (1) shock, (2) reshock, (3) sound speed. Each technique has different systematic uncertainties.

The compression difference can be explained by an additional internal energy of about 1 eV/atom

D$_2$ shock [1]

~5% (or 8%*) difference in the shock compression.

From Rankine-Hugoniot energy relation:

\[ E_1 - E_0 = \frac{1}{2} (P_1 + P_0) \left( \frac{1}{\rho_0} - \frac{1}{\rho_1} \right) \]

Rearrange terms (and define $E_0=0$):

\[ E_1 = \frac{P_1 + P_0}{2\rho_0} \left( 1 - \frac{\rho_0}{\rho_1} \right) \]

The different final densities between theory and experiment gives a difference of order 1 eV/atom in the final internal energy.

Let’s see if collective plasma oscillations can plausibly account for this energy missing from the models.

* 8% based on re-analysis using new measurements\(^1\) of shock standard

Review: heat capacity and the Debye\textsuperscript{1} phonon model

- In classical solids at high temperature, heat capacity is $3Nk_B$ for N particles (Dulong-Petit limit).

- At low temperatures, the heat capacity drops as oscillations are “frozen out”.

- The Debye model\textsuperscript{1} considers long-range correlations in the lattice and is a good representation for most solids.

- For hot plasmas, long-range correlations are usually neglected, since the plasma screening length suppresses its importance.

- However, for warm dense plasmas (moderate coupling) these long-range correlations may again play a role.

\begin{center}
\textbf{Phonon heat capacity in silver}
\end{center}

\begin{itemize}
\item Dulong-Petit limit $= 3Nk_B$
\item Debye model (long-range correlations)
\item Einstein model (independent oscillators)
\end{itemize}


J. R. Rygg, APS-DPP-2021
Debye model\(^1\) for phonon internal energy and \(C_V\)

The Debye model for phonon internal energy is:

\[
E = \int_0^{q_c} \epsilon(q) g(q) n_{BE}(q) \, dq
\]

Dispersion relation

\[
\epsilon(q) = \hbar \omega(q) = \hbar c_s q
\]

Density of states

\[
g(q) = \frac{V q^2}{2\pi^2}
\]

Bose-Einstein distribution function (zero chemical potential for phonons)

\[
n_{BE}(q) = \frac{1}{e^{\hbar c_s q / k_B T} - 1}
\]

Cutoff wavenumber is related to the Debye temperature (to reproduce Dulong-Petit limit)

\[
q_c = (6\pi^2 n)^{1/3} = \frac{k_B T_D}{\hbar c_s}
\]

Putting it all together, we have expressions for energy and heat capacity

\[
E = \frac{V}{2\pi^2} \int_0^{q_c} \frac{\hbar c_s q^3 \, dq}{e^{\hbar c_s q / k_B T} - 1}
\]

\[
C_V = \left( \frac{\partial E}{\partial T} \right)_V
\]

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We can use the Debye model for plasma oscillations

The Debye model for phonon internal energy is:

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Dispersion relation

\[ \epsilon(q) = \hbar \omega(q) \]

Density of states

\[ g(q) = \frac{V q^2}{2\pi^2} \]

Bose-Einstein distribution function (zero chemical potential for phonons)

\[ n_{BE}(q) = \frac{1}{e^{\hbar c_s q / k_B T} - 1} \]

Cutoff wavenumber

\[ q_c \propto \frac{1}{\lambda_{screen}} \]

Putting it all together, we have expressions for energy and heat capacity

\[ E = \frac{V}{2\pi^2} \int_0^{q_c} \frac{\hbar c_s q^3 \, dq}{e^{\hbar c_s q / k_B T} - 1} \]

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_V \]

Need to modify the dispersion relation for plasma oscillations\(^1,2\)

Need to modify the cutoff wavenumber for screening\(^1,2\)

Plasma dispersion and screening for arbitrary degeneracy, eg:

Ion plasma excitations contain sufficient energy to explain the shock compression difference

Energy and heat capacity of plasma oscillations

- Ion acoustic waves may have the ~1eV/atom internal energy required to explain the shock compression discrepancy
- Electron plasma waves have less energy content due to higher frequency and lower Bose-Einstein occupancy factor
- The energy content peaks at a temperature near the Fermi energy, above which plasma screening limits the available oscillation modes
The heat capacity of plasma waves can explain the high experimental $D_2$ compressibility near 500 GPa

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