Thermal Excitations and the Equation of State of Tantalum

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An important part of the mission of the Equation of State and Mechanics of Materials Group (T-1) is the development of highly accurate equations of state (EOS) that cover wide ranges of densities and temperatures. Typically, empirical EOS have been based on experimental data on the shock Hugoniot and extrapolated to other states through the use of models for the temperature dependence of the pressure and internal energy [1]. This kind of extrapolation has formed the basis for the pressure standards used in static compression experiments, and is needed to predict the results of dynamic compression experiments when the loading is more complex than a single shock. The thermal dependence of the EOS is determined by the excitations of the condensed matter system. We aim to exploit the capability of modern electronic structure theory to predict the spectrum of phonon and electron excitations in solids to create EOS of the highest possible accuracy. This work describes application of these ideas to the EOS of tantalum, which is used as a standard in both dynamic and static high-pressure experiments.

Recently, a new experimental technique has been developed [2] that allows for dynamic compression of samples to high pressures with smooth, magnetically driven waves. In principle, this smooth loading maintains nearly constant entropy, in contrast to dissipative shock loading. It is expected that it will soon be possible to carry out isentropic compression experiments (ICE) to pressures of 400 GPa (higher than the earth's center) in Ta. In this range, the ICE loading should result in much lower temperatures than single shock loading, allowing the investigation of the EOS on a very different path. The design and interpretation of these experiments is significantly more involved than that of standard shock Hugoniot measurements. Supporting the design of ICE and predicting their results is an important motivation for this work.

We formulate the EOS by writing the total Helmholtz free energy as a sum of terms $F(V,T) = \Phi_0(V) + F_{vib}(V,T) + F_{ei}(V,T)$, where Φ_0 is the energy of a perfect lattice, and F_{vib} and F_{ei} are lattice vibration and electronic excitation free energies, respectively. To evaluate F_{vib} and F_{ei}, we require the densities of states for the phonons and electrons as functions of density. These have been obtained from electronic structure theory. The capability to predict the phonon excitations this way is illustrated in Fig. 1, where the calculated phonon dispersions curves are compared with experiments done at ambient pressure. The calculations use no adjustable parameters, and so the accuracy of the results gives us confidence in our ability to predict the excitation spectrum at high pressure, where it is not directly measured. The static lattice energy Φ_0 is determined partially empirically, using the accurately measured lattice spacing and bulk modulus, while requiring that Φ_0 be consistent with theory at high compression.

Having constructed the EOS, we have an accurate basis for predicting properties that are not measured. This is illustrated in Fig. 2, which shows the temperatures along two thermodynamic paths, the

Hugoniot and the principal isentrope. Hugoniot states are those reached in single shock compression, while the isentrope is approached in smooth compression. We see from the figure that at 400 GPa, the pressure of the proposed ICE, the Hugoniot is in the liquid, at a temperature of over 1 eV, while the isentrope is at a modest 750 K. At this low temperature, the isentrope pressure is completely dominated by Φ_0, while the Hugoniot pressure has a 100 GPa contribution from thermal excitations.

An important aspect of the design of ICE is to control the shape of the drive pulse, so that a shock is not formed as the wave propagates through the sample. With our EOS, we can predict the required pulse shape for a given peak pressure and sample thickness. Results of such a calculation are shown in Fig. 3. Calculations like these are necessary to design a successful experiment, especially an ambitious one like 400 GPa ICE. We are also using our models and codes to investigate the importance of non-ideal effects, like dissipation of plastic work, on ICE. These calculations on Ta illustrate how we are using modern theory and computational techniques to improve the accuracy of our EOS, and support important new experimental capabilities.

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[1] R.G. McQueen, et al., in *High Velocity Impact Phenomena*, R. Kinslow, Ed. (Academic Press, New York, 1970).
[2] C.A. Hall, *Phys. Plasmas* **7**, 2069 (2000).

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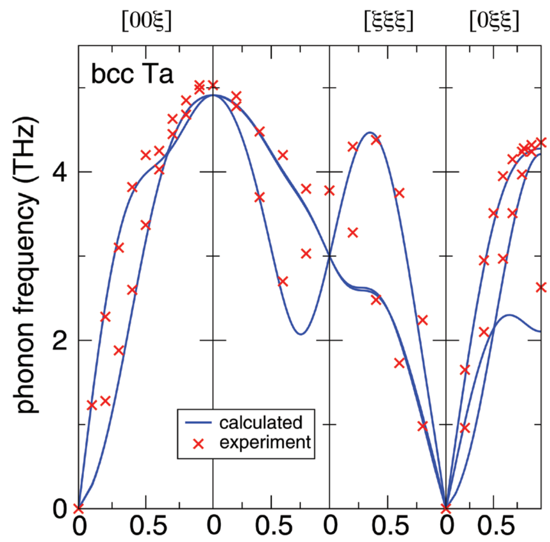

Fig. 1.
Phonon dispersion curves for Ta at ambient density. Solid blue curves are calculated with density functional theory, and red symbols are experimental data.

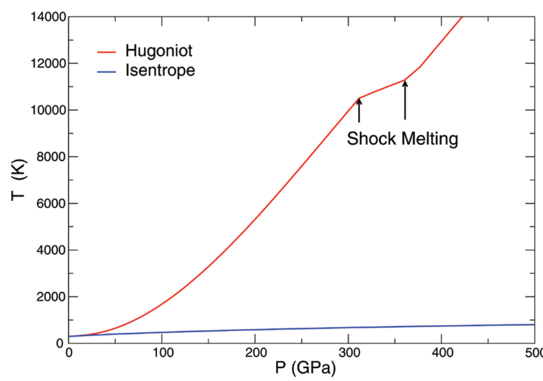

Fig. 2.
Hugoniot and principal isentrope of Ta. The kink in the Hugoniot at 310 GPa is due to the melting transition.

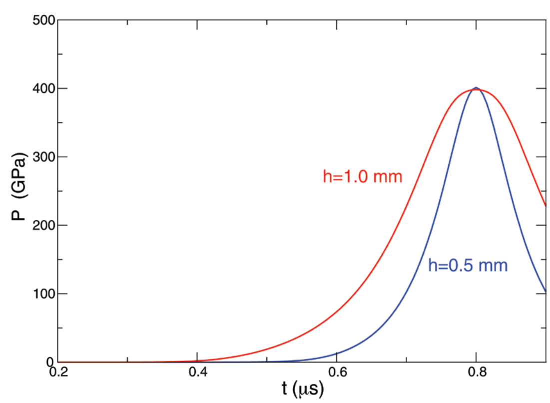

Fig. 3.
Calculated drive pressures needed to achieve shockless compression of Ta to 400 GPa. Red curve is for sample thickness of 1 mm, and blue curve is for thickness of 0.5 mm.