Equations of State—Theoretical Formalism

by Bard I. Bennett

Theoretical and experimental research in equations of state and material modeling is essential to ensuring a firm scientific footing for these disciplines. This type of research is necessary not only for assessing the nuclear weapons stockpile but also for developing a predictive computational capability. Here, I will outline the general theoretical formalism for calculating equations of state and then expand on the contribution from the vibrational (or thermal) excitations of solids to the equation of state (EOS). The temperature dependence of the Debye temperature reported in the main article has a direct bearing on our models for the vibrational contribution.

The EOS for any material is typically expressed as an equation for the pressure as a function of temperature and density. Generally speaking, at densities less than 100 grams per cubic centimeter (g/cm^3) and temperatures less than 100 kilo-electron-volt (keV), there are three distinct contributions to the pressure:

$$P(\rho,T) = P_c(\rho) + P_N(\rho,T) + P_e(\rho,T) \quad . \tag{1}$$

The pressure at $T = 0$, $P_c(\rho)$, is commonly called the "cold curve" and is due to the electronic forces that bind the individual atoms into a solid; $P_N(\rho,T)$ is the pressure due to the vibrational excitation of the nuclei in the solid, liquid, or gas states; and $P_e(\rho,T)$ is the pressure due to the electrons' thermal excitation.

The cold curve is traditionally modeled by empirical formulae (Lennard-Jones and Morse potentials combined with Thomas-Fermi-Dirac theory). Modern calculations of electronic band structure include relativistic effects. Experimental measurements conducted in a diamond-anvil or tungsten carbide cell can provide data for pressures up to approximately 2 megabars.

The vibrational contribution for the solid state, $P_N(\rho,T)$, is traditionally modeled with the Debye theory. Models of the liquid state use an interpolation scheme between a Debye solid and an ideal gas. Modern theory for all these states uses molecular dynamics or Monte Carlo methods to obtain pressures as a function of density and temperature. No direct experimental data are available, but to infer a melting temperature, we use shock wave methods and laser-heated diamond-anvil cells.

The pressure for electron excitations, $P_e(\rho,T)$, is traditionally modeled by Saha or Thomas-Fermi-Dirac theories. Modern theory for this contribution to the pressure uses relativistic, quantum mechanical, self-consistent field theory. No direct experimental data are available, but $P_e(\rho,T)$ can be inferred from data obtained from pressure waves generated by nuclear explosions.

We now add more detail to the vibrational contribution to pressure from the motion of the nuclei. The Mie-Grüneisen form is given by

$$P_N(\rho,T) = \rho\Gamma(\rho,T)E_N(\rho,T) \quad , \tag{2}$$

where the energy in the Debye model is given by

$$E_N(\rho,T) = \frac{3N_0k_BT}{A}\left\{D_3\left(\frac{\Theta_D}{T}\right) + \frac{3}{8}\frac{\Theta_D}{T}\right\}\left\{1 + \frac{\partial \ln \Theta_D(\rho,T)}{\partial \ln T}\right\} \quad , \tag{3}$$

and the Grüneisen parameter Γ is defined by the following equation:

$$\Gamma(\rho,T) = \frac{\int \ln \Theta_D(\rho,T)}{\int \ln \rho} \quad . \tag{4}$$

The Debye temperature $\Theta_D(\rho,T)$ is the effective atomic vibrational temperature, and it determines when a material melts or loses its strength. In Equation (3), $D_3(x)$ is the Debye integral of the third kind. In traditional EOS modeling, Θ_D is assumed to be independent of temperature—that is, $\Theta_D(\rho)$. Consequently, Γ would also be a simple function only of density. Modern theories suggest that Θ_D and Γ depend on a material's density, temperature, and electronic structure.

The neutron diffraction measurements reported in the main article confirm these theoretical ideas. The data show that the Debye temperature and the Grüneisen parameter are, indeed, a function of temperature and electronic structure.

To verify the predictions from quantum mechanical theory, we need to further validate our current models. Measuring the Debye-Waller factor with a new, heated high-pressure cell shows great promise. By using the apparatus containing this cell, we have obtained interesting data for molybdenum. After validation, the theory will be used in modeling material melting and strength for applications in weapons physics (conventional and nuclear), metal casting, or explosively driven shape-forming.