First-principles entropy calculations for liquid metals and warm dense matter

Michael Desjarlais, Sandia National Laboratories*, Albuquerque, New Mexico.

An important thermodynamic quantity for developing equations of state, particularly with respect to phase boundaries and melt curves, is the total entropy, an essential component of the free energy. In high-pressure shock physics the entropy of the shock state determines the release adiabat, and important consideration, for example, in the study of planetary impacts. Unfortunately, the total entropy is not an explicit or easily accessible quantity in molecular dynamics simulations. A powerful and rigorously justifiable method for computing the entropy is thermodynamic integration from a well-characterized reference state.   For solids one can employ thermodynamic integration from a quasi-harmonic reference state to obtain accurate entropies and free energies. The entropy is somewhat harder to obtain for liquids through thermodynamic integration. This can, for materials at extreme conditions or complex interactions, be a tedious process requiring careful force matching and numerous integration steps from the reference state, perhaps a Lennard-Jones liquid.   An alternative method, proposed by Lin *et al.*, [J. Chem. Phys. 2003] computes the translational and vibrational contributions to the entropy directly from the velocity autocorrelation through decomposition into solid-like and gas-like components, extraction of their corresponding frequency spectra, and applying appropriate thermodynamic weighting functions for the entropy. This method, referred to as 2PT, was originally validated at the few percent level with the Lennard-Jones system, and has since seen wide application. Tests of the method on liquid metals, for which good data is available, reveal a systematic overestimate of the entropy. In this work, a generalization of the 2PT method, using memory function methods to characterize the frequency spectrum of the gas-like component, significantly improves the accuracy. The results are compared to data for liquid sodium, aluminum, tin, gallium, and iron. An example application to the determination of a melt boundary is presented for the high-pressure bcc phase of sodium.