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Computation, the Gibbs Free Energy, and Inelastic Scattering

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J.W. Gibbs founded the field of materials science, basing it on the concept of free energy, G = E - TS + PV. For the past century, free energies of materials have been tabulated from measurements of heat capacities, which do not identify the physical sources of enthalpy and entropy. For the past 30 years, it has often been possible to calculate E and PV, but the entropy S has remained more difficult.

Most of the entropy S(T) comes from atomic vibrations, i.e., phonons. The phonon entropy is big, small fractional differences are important, and the harmonic approximation is not sufficiently accurate to be useful for materials thermodynamics at elevated temperatures. Ab initio molecular dynamics (AIMD) has proved a versatile approach for calculating the phonon entropy at elevated temperatures, including the parts from phonon-phonon and electron-phonon interactions. The results have enough accuracy so that a calculated S(T) can compete with S(T) from calorimetry. Almost in parallel, inelastic scattering methods have become capable of determining the phonon entropy to similar accuracy. AIMD simulations can also provide Van Hove space-time correlation functions, allowing comparisons to results from inelastic scattering experiments by at the level of individual phonon modes (rather than comparing an integral quantity like S).

The entropy of fcc Al metal has been determined by calorimetry, AIMD, many-body perturbation theory, and inelastic neutron scattering. Although fcc Al is modestly anharmonic, these four different results for entropy agree well. Other cases of cubic Ag2O and rutile TiO2 show enormous phonon-phonon anharmonicity, but the AIMD results are still consistent with experimental phonon measurements. With thermal expansion, several modes in rutile TiO2 are known to become unstable in the quasiharmonic approximation. From AIMD simulations it was found that the bottom of the Ti-O interatomic potential flattens with temperature, giving a quartic character that stabilizes the rutile structure.

Understanding S(T) is essential for the practical design and use of materials at finite temperatures. Inelastic scattering is a natural partner to ab initio simulations, offering important validations. Likewise, the simulations give deeper insights into the experimental results. The time is ripe for better connections between computational materials science and inelastic scattering research.

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