MATERIALS SIMULATIONS IN GEOPHYSICS

Allocation: Innovation and Exploration/200 Knh
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EXECUTIVE SUMMARY

Thermodynamics of materials is a fundamental subject for understanding planetary processes and states. The research team has contributed to the development and application of *ab initio* methods for computing thermal properties of minerals and their aggregates (rocks). Thermodynamic and thermoelastic properties and thermal conductivity are among the main properties needed for modeling thermal convection in and interpreting the seismic tomographic structure of Earth's interior. Discovery of novel silicate and oxide phases at pressures (P) of tens of Mbar and temperatures (T) of approximately 10^4 K are also advancing understanding of the internal structure of recently discovered terrestrial-type exoplanets. Blue Waters has been used by the research group to perform high-throughput calculations of thermal properties of mineral phases required to model heat transport and interpret the 3D pattern of seismic wave propagation throughout the Earth's mantle and the inner cores of Earth and terrestrial exoplanets.

RESEARCH CHALLENGE

Ab initio materials simulations for geophysics applications are intrinsically high-throughput calculations since materials properties need to be computed vs. P, T, composition (x_i), strains (ε_j), atomic configuration, and the like. Such simulations are essentially a "phase space" sampling problem. Mineral phases are structurally and chemically complex, consisting of solid solutions with multiple components, including strongly correlated ones such as FeO, Fe_2O_3, etc., with primitive cells containing tens of atoms. In addition to properties of single phases, properties of polycrystalline aggregates—rocks—in thermodynamic equilibrium must also be addressed. The thermodynamic equilibrium problem in a multiphase system with multiple components, a challenge of its own, can only be addressed after thermodynamic properties of single phases are accurately obtained. To facilitate these HPC (high-performance computing) calculations, novel methods and workflows have been developed and implemented on Blue Waters for the calculations of single-phase thermal properties.

METHODS & CODES

Two novel methods based on the phonon quasiparticle concept [1] have been implemented and used on Blue Waters. The first is for computation of lattice thermal conductivity, κ_{lat}, and the second for thermodynamic properties of anharmonic systems, both in the thermodynamic limit (N → ∞, with N = number of atoms). Molecular dynamics (MD) is first used to obtain phonon quasiparticle properties, *i.e.*, phonon lifetimes (τ_i) and temperature-dependent phonon frequencies [$\omega_i(T,V)$] at few-phonon wave vectors. Novel interpolation schemes are then used to obtain quasiparticle properties throughout the Brillouin zone (a uniquely defined primitive cell in reciprocal space), which are then used in conjunction with the Boltzmann transport equation (BTE) to compute κ_{lat}. T-dependent phonon dispersions are also used to

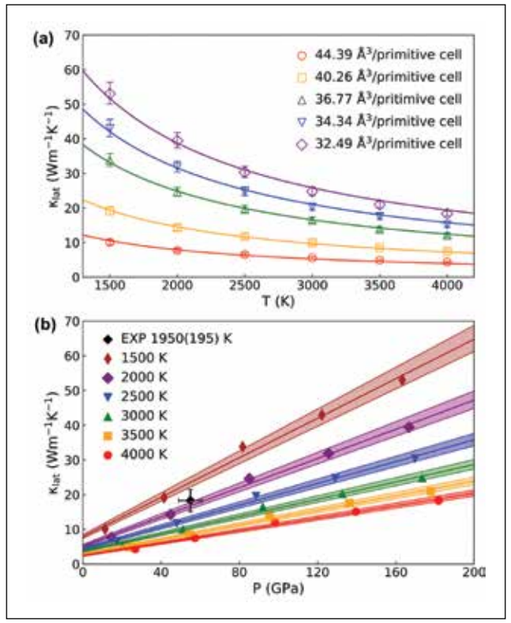

Figure 1: (a) κ_{lat} vs. T of Ca-Pv at five volumes. Solid curves show the 1/T dependence. (b) κ_{lat} vs. P of Ca-Pv at six temperatures. Solid curves show the linear fit. The error bars and the shaded areas indicate the uncertainties caused by fitting errors. κ_{lat} in both (a) and (b) are calculated from phonon quasiparticles properties sampled in a 20×20×20 q-point grid obtained using an interpolation of *ri(ω)* vs. ω obtained by direct MD calculations sampling 2×2×2 (40 atoms), 3×3×3 (135 atoms), and 4×4×4 (320 atoms) q-point grids. The experimental datapoint was measured using laser-heated diamond anvil cell by K. Hirose and K. Ohta [Zhang *et al.*, 2019].

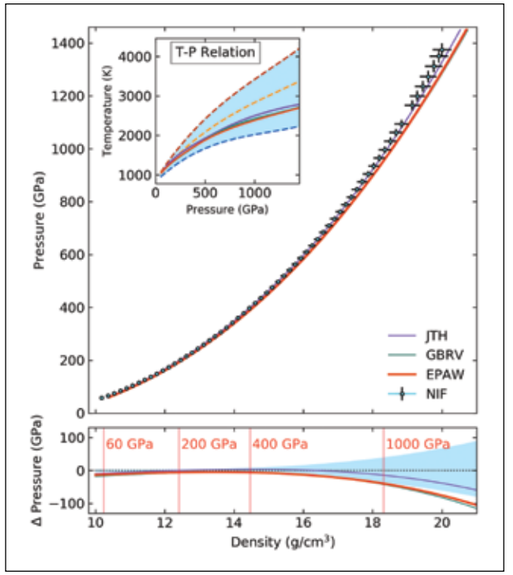

Figure 2: Isentropic P-ρ EoS of ε-Fe. The NIF data are shown as circles with uncertainty. The pink curve stands for this work, using a novel evolutionary PAW for iron validated up to 8 Mbar [2]. Other colored lines were obtained using a JTH PAW and a GBRV ultrasoft potential. The T-P plot in the inset indicates adiabatic temperature. In the NIF experiment, the temperature is uncertain (blue shaded area), and several profiles are possible depending on assumptions made, such as an intermediate-strength model (red dashed line) and low-strength model (yellow dashed line) for iron. Pink, purple, and green lines show the adiabatic T-P relation obtained with EPAW, JTH, and GBRV potentials, respectively. The bottom figure shows the predicted pressure difference, ΔP=0, between that along the predicted adiabats and those predicted along NIF estimated temperature profiles [Zhuang *et al.*, 2019].

compute thermodynamic properties for weakly or strongly anharmonic systems in the thermodynamic limit. The alternative approach is thermodynamic integration, which carries uncertainties related to limited simulation cell sizes.

RESULTS & IMPACT

Applications of these methods on Blue Waters are illustrated here for two problems. The first is the calculation of κ_{lat} in $CaSiO_3$-perovskite (Ca-Pv), an important phase (up to 10 vol%) of the Earth's lower mantle and a major phase in basaltic crust (approximately 25 vol%). Ca-Pv exists in the cubic structure in Earth's lower mantle. At low temperatures (T < approximately 700 K) it is mechanically unstable and becomes tetragonal. Calculations and measurements of its properties at relevant conditions (T > 2,000 K and P > 23 GPa) have been highly controversial because of its strongly anharmonic nature, preventing calculations of lifetimes using perturbation theory and of κ using BTE. Fig. 1 shows calculated (LDA) values compared to a single experimental datapoint obtained by collaborators (see Fig. 1 caption). Experimental verification of these results, still underway, is important because of the novelty of the approach and because Ca-Pv's κ_{lat} is three times larger than that of Mg-Pv, the major mantle phase. This result will change the estimated values of κ_{lat} in the lower mantle by up to 20% to 30%, with profound implications for convection style in the Earth, heat extraction from the core, and the age of Earth's inner core.

The second problem is the calculation of thermodynamic properties and high-T and adiabatic equations of state of ε-iron, the solid phase of iron expected to exist in planetary cores. These calculations provided T-dependent phonon dispersion, which were subsequently employed to compute thermodynamic properties using a novel method [1] based on the phonon gas model. In metallic ε-iron, electron thermal excitations and not anharmonicity are the main source of T-dependent phonon frequencies. These calculations were carried out up to 14 Mbar, a condition achieved only at the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory. Temperature in the NIF data (Fig. 2) is expected to follow an adiabat. The research team's adiabatic equation of state agrees well with the NIF data up to 4 Mbar, deviating at higher pressures. This result suggests the unknown temperature in the NIF data might not quite follow an adiabat, with a cumulative effect causing deviations from adiabaticity in wide pressure ranges.

WHY BLUE WATERS

Such calculations require the execution of large numbers (approximately 10^2 to 10^3) of HPC tasks (approximately 10 nodes each). The large number of Blue Waters' nodes allows the execution of independent tasks simultaneously. This is important for efficient execution of workflows with subsequent stages, each requiring the execution of large numbers of tasks that have dependencies across but are independent within different stages.

PUBLICATIONS & DATA SETS

G. Shukla, K. Sarkar, and R. M. Wentzcovitch, "Thermoelasticity of iron- and aluminum-bearing $MgSiO_3$ postperovskite," *J. Geophys. Res.–Solid Earth*, vol. 124, pp. 2417–2427, 2019, doi: 10.1029/2018jb016379.

Z. Zhang, D. B. Zhang, T. Sun, and R. M. Wentzcovitch, "phq: A Fortran code to compute phonon quasiparticle properties and dispersions," *Comput. Phys. Commun.*, vol. 243, pp. 110–120, 2019, doi: 10.1016/j.cpc.2019.05.003.

Z. Zhang *et al.*, "Thermal conductivity of $CaSiO_3$ perovskite at lower mantle conditions," in preparation for *Science*, 2019.

J. Zhuang, H. Wang, Q. Zhang, and R. Wentzcovitch, "Thermodynamics properties of ε-iron to 14 Mbar," in preparation for *Phys. Rev. Materials*, 2019.