First-principles computational methods beyond the quasi-harmonic approximation and the improved high temperature EOS models of mantle minerals

Paul Sanders and Jianjun Dong
Department of Physics, Auburn University, Auburn, Alabama 36849-5311

First-principles electronic structure theory based computational methods, such as VASP, Quantum ESPRESSO, or ABINIT, have been widely adopted to study energetic, structural, elastic, and vibrational properties of complex Earth materials. When modeling the finite temperature equation of state (EOS) of crystalline minerals, the method of choice is the so-called quasi-harmonic approximation (QHA) method. QHA describes the lattice vibrational free energy at a given volume with the harmonic phonon gas model along with the corrections of volume-dependent phonon density of states resulting from the anharmonicity induced phonon-phonon interactions. Despite its success in predicting thermal properties of crystals are moderate temperatures, the QHA method fails to accurately predict thermodynamic properties of solids at very high temperatures (such as those temperatures right below the melting temperatures). In this report, we first discuss our recent implementation of a new computational method to calculate high temperature EOS of complex mantle minerals beyond the QHA. Our method combines the first-principles calculations of lattice anharmonicity up to the fourth-order and a statistical perturbation theory for vibrational free energy. Then, we will discuss the convergence of the numerical accuracy, the corresponding computational loads, and the limits of our method. Finally, we will present our preliminary data on the improved theoretical models of finite temperature EOS for MgO, $MgSiO_3$ perovskite and post-perovskite in comparison to the QHA. We will analyze the p-T conditions, where the QHA fails in these three mantle minerals.