Direct coupling of replica exchange Monte Carlo method with first-principles calculations for thermodynamic sampling of configurational disorder in solids

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Metal and oxide alloy systems have varying degrees of disorder which determine the physical properties of those systems. To simulate such disorder, a natural approach may be to combine first-principles calculations based on density functional theory (DFT) with Metropolis Monte Carlo sampling. However, due to the high computational cost of DFT calculations, many previous works have relied on lightweight models fitted to density functional calculations. Due to the difficulty in obtaining reliable *and* lightweight models, this approach has seen limited use in many-component systems. Thus, in this project, we decided to reexamine the feasibility of bypassing the use of fitted models through efficient use of cluster supercomputers.

To we decided to rely on the replica exchange Monte Carlo (RXMC) method [1]. The Figure shows our computational scheme. There are N_{repl} Metropolis samplers running in parallel. Each of the samplers spawns parallel DFT processes (we used VASP [2]) to perform local structural relaxation and energy calculation at every Metropolis step. We benchmarked the scheme on the calculation of the degree of cation disorder in $MgAl_2O_4$ and found that it is efficient enough to perform sampling without resorting to fitting models [3]. In other words, we showed that it is now possible to sample configurational disorder in solid state systems directly from first principles through a combination of parallel sampling algorithms and state-of-the-art supercomputers,

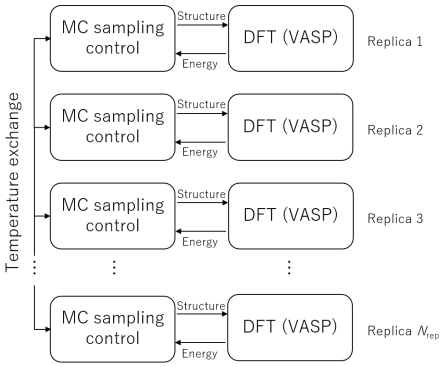

Fig. :. Our RXMC-DFT sampling scheme.

References

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[3] S. Kasamatsu and O. Sugino: J. Phys.: Condens. Matter **31** (2019) 085901.