# Monte Carlo simulation for first principles free energy calculation

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Free energy change of the system is essential for the design of materials. Since the first principles calculations are ground state ones, phonon calculation packages are developed and supplied for the finite temperature predictions [1]. The phonon calculation is based on the quasi-harmonic approximation. Because the behaviors of the semiconductors and near phase transition points are basically anharmonic, such packages are necessary but not supplied.

For investigating such anharmonic calculations, the first principle molecular dynamic simulations are the first choice. Unfortunately, the absolute value of free energy is hardly obtained from the molecular dynamic simulations. On the other hand, in Monte Carlo world, we have Frenkel method for the free energy calculations [2]. In that method, free energy is obtained from the direct integration of the transition states from a standard state, such as Einstein crystal, to the state described by the realistic interatomic potential.

For applying Frenkel method on the first principles calculations, there are some difficulties. One is the exact method connecting the Einstein crystals and the first principles lattice, and the other is the drifts or rotations of the whole system during the transition. For the latter, we are trying a multiple atoms movement with cancelling the drift and rotation of the whole system. By this restriction, some of the degrees of freedom are frozen, but the ensemble would be described correctly. For the former, in spite of simultaneous calculations of each atoms and the interatomic potential, we are trying to deal two whole system energies of Einstein crystal and the first principles lattice independently and produce the transition state later.

## References

[1] K. Parlinski, Z. Q. Li and Y. Kawazoe, Phys. Rev. Let., **78**, 4063-4066 (1997).

[2] D. Frenkel and A. J. C. Ladd, J. Chem. Phys., **81**, 3188–3193(1984).