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Harmonic and Anharmonic Free Energies in Superlattices of Soft Particle Systems[1] ALEX TRAVESSET, Iowa State Univ and Ames lab, CARLES CALERO, Center for Polymer Studies and Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, USA, CHRIS KNOROWSKI, Iowa State Univ and Ames lab — Many problems in self and directed assembly rely on the rigorous calculation of free energies. In systems of nanoparticles with capping ligands, for example, superlattices are found in closely competing structures, such as hcp/fcc, cubic/hexagonal diamond or those isomorphic between $MgCu_2$ and $MgZn_2$. With this motivation, we investigate a general method to calculate free energy of crystalline solids by considering the harmonic approximation and quasistatically switching the anharmonic contribution. The advantage of the method is that the harmonic approximation provides an already very accurate estimate of the free energy, and therefore the anharmonic term is numerically very small and can be determined to very high accuracy. We further show that the anharmonic contribution to the free energy satisfies a number of exact inequalities that place con- strains on its magnitude and allows approximate but fast and accurate estimates. We apply it to Lennard Jones sytems where we demonstrate that hcp is the equilibrium phase at low temperature and pressure and obtain the coexistence curve with the fcc phase, which exhibits reentrant behavior and binary systems that model nanoparticle superlattices with hydrocarbon capping ligand.

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