Order-disorder transition and free energy of the crystal of Lennard-Jones diatomics

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In statistical mechanics and molecular simulation, a proper usage of symmetry number is important to obtain free energy. In this work, we perform free energy calculations of the Lennard-Jones (LJ) dimer crystal by using expanded ensemble Monte Carlo (EEMC) method combined with the Einstein molecule approach. Anisotropic isothermal isobaric Monte Carlo (NPT MC) simulations are performed to obtain a hysteresis loop of phase transition between orientationally ordered and disordered crystal phases. In the ordered phase, orientational free energy is estimated in only one part of orientational configurational space. The corresponding symmetry number for the ordered phase should be unity. In contrast, in the disordered phase, orientational configurational space is fully accessed similarly as in the liquid phase. The symmetry number of the disordered phase should be the same as that of the ideal gas. It is found that the phase transition determined from the equality of chemical potential (molar Gibbs energy) is in accord with the phase transition predicted by the NPT MC simulations.