Free energy of monatomic crystals: The comparison of expanded ensemble method and acceptance ratio method

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In statistical mechanics, free energy difference is given as a ratio of partition functions. The Free energy difference can be calculated by various method including thermodynamic integration method, expanded ensemble (EE) method, and Bennett's acceptance ratio (BAR) method. In this work, by using EE method and BAR method, we calculate free energy difference between hard sphere crystal and the classical Einstein crystal with fixed one-molecule-method at ρ^*=1.04086. Results from both methods agree well with each other for the free energies of hard sphere crystals and Lennard Jones crystals. As it is yet clarified whether which method is more efficient and reliable in calculating free energy difference, we compare the advantage and drawback of EE method and BAR method through the detailed free energy simulation. For the most cases we studied, BAR method is robust; however, due to a large number of sampling intervals, BAR method needs long simulation time. With accurate weight factors determined from preliminary simulations or having an efficient way to calculate weight factors on the fly, EE method could be more efficient than BAR method.