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Parallel Tempering Simulation on Generalized Canonical Ensemble

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Abstract. Parallel tempering simulation is widely used in enhanced sampling of systems with complex energy surfaces. We hereby introduce generalized canonical ensemble (GCE) instead of the usual canonical ensemble into the parallel tempering to further improve abilities of the simulation technique. GCE utilizes an adapted weight function to obtain a unimodal energy distribution even in phase-coexisting region and then the parallel tempering on GCE yields the steady swap acceptance rates (SARs) instead of the fluctuated SARs in that on canonical ensemble. With the steady SARs, we can facilitate assign the parameters of the parallel tempering simulation to more efficiently reach equilibrium among different phases. We illustrate the parallel tempering simulation on GCE in the phase-coexisting region of 2-dimensional Potts model, a benchmark system for new simulation method developing. The result indicates that the new parallel tempering method is more efficient to estimate statistical quantities (i.e., to sample the conformational space) than the normal parallel tempering, specially in phase-coexisting regions of larger systems.

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Key words: Parallel tempering, generalized canonical ensemble, enhanced sampling, Potts model.

1 Introduction

To overcome the difficulties in sampling thermodynamical systems with the complex energy landscape, parallel tempering (PT, which is also referred to as replica exchange) [1,2]

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was developed and applied widely in simulations of many different systems. In the standard PT, M identical systems (replicas) with their respective temperature T_i are performed in parallel, two neighboring replicas exchange their microscopic configurations (or temperatures equivalently) with a Metropolis probability. Due to the configuration exchanges among replicas, PT is expected to have stronger abilities than the conventional single-replica simulations in overcoming high free energy barriers which separate different conformational regions. Since the implementation of PT is simple in comparison with some other enhanced sampling methods, PT has been widely applied in simulations of physical and biological systems, by using both Monte Carlo simulation and Molecular Dynamics simulation (see a review [3]).

Efficient PT should have a significant swap acceptance rate (SAR, the average acceptance probability of the configuration exchanges). One of the primary issues of PT is how to pre-set the parameters such as temperatures. For example, in canonical ensemble (fixed number of particle N, volume V and temperature T) parallel tempering (NVT-PT), we need to set the temperature of each replica to make SAR between each two adjacent replicas be significant. Usually one performs a short PT simulation by initially supposing a set of temperatures for the replicas and estimates SARs, then adjusts temperatures of replicas based on the estimated SARs and runs another short PT simulation. Iterating the process to make SARs reach a suitable value, such as $20\sim30\%$ [4]. However, this way does not always work well, specially in phase-coexisting regions [5, 6]. In these regions, conformational trajectories could go back and forth between the different phases, the values of SAR may be large while the adjacent replicas locate in the same phase, but become very small while they locate in different phases. Thus SAR becomes highly time-dependent, it is hard to estimate SAR from short segments of simulations to set temperatures of replicas. In addition, in such cases, it is questionable that the average value of SAR in an entire PT simulation can characterize the efficiency of PT in sampling. For equilibrating different phases, we actually need sufficient inter-phase exchange events rather than total exchange events which measured by the average SAR.

SAR depends on the overlap of conformational energy distributions between adjacent replicas [7]. Considering the fact that the energy fluctuation, σ, is proportional to $N^{1/2}$, where N is the size of system, for completely covering an interesting energy range, ΔE, which is proportional to N, the number of required replicas, $n\sim\Delta E/\sigma\sim N^{1/2}$. The simple estimation implies PT is more efficient in small systems. J. de Pablo and coworkers [8] had quantified this relationship between the overlap of distribution and the value of SAR. They regard the energy distribution of replica as a Gaussian form and SAR of the two adjacent replicas is approximate to

$$P_{acc}\simeq\operatorname{erfc}\Big(\frac{\kappa}{\sqrt{2}}\Big), \tag{1.1}$$

where $\kappa\equiv(\bar{E}_2-\bar{E}_1)/(\sigma_1+\sigma_2)$, $\bar{E}_1$ and $\bar{E}_2$ are the mean energy of two Gaussian distributions and σ_1 and σ_2 are variances, respectively. Other researchers [9–11] have also discussed the relationship between the overlap of distribution and SAR. All of these in-