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Selection of temperature intervals for parallel-tempering simulations

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In this work we consider a criterion for selecting temperature intervals in parallel-tempering molecular simulations. Parallel tempering (or replica exchange) is a technique used to enhance the sampling of configurations.[1] The primary aim is to enable systems being simulated at low temperatures to overcome energetic barriers that hinder their sampling and sometimes lead to nonergodicities. The essence of the method is to couple the sampling of systems at different temperatures, such that a system simulated at a high temperature trades configurations with the one at a lower temperature. The effect is to give the low-temperature simulation a fresh configuration for sampling, presumably at a point in phase space that is distant from the one it traded away. At the same time, the low-temperature configuration is traded up to a higher temperature, at which it has a better opportunity to overcome energy barriers and move into a new region of phase space before being traded back down to the low-temperature simulation.

In a replica-exchange simulation, configurations are exchanged via a Monte Carlo process that typically follows the Metropolis algorithm.[2] Thus occasionally an attempt is made to swap the configurations for systems simulated at two different temperatures, and the attempt is accepted with the probability

$$\min\{1,\exp[-(\beta_0-\beta_1)(E_1-E_0)]\}. \tag{1}$$

Here β_0 and β_1 are the reciprocal temperatures in energy units $(1/kT)$ of the two systems, labeled 0 and 1, and E_0 and E_1 are their respective energies at the time the swap is attempted; we use the convention $\beta_0 > \beta_1$. The probability to accept an attempted swap is smaller to the extent that the systems are more different in temperature, and as the systems are larger. If the (extensive) heat capacity C (in units of the Boltzmann constant) can be assumed constant over the range of the swap temperatures, the average acceptance probability is well represented by the formula[3]

$$\overline{p}_{\mathrm{acc}} = \mathrm{erfc}\left(\frac{1-B}{1+B}C^{1/2}\right), \tag{2}$$

where $B \equiv \beta_1/\beta_0 < 1$. This result shows that the acceptance rate depends on the temperatures primarily through their *ratio* (B).

Normally replica-exchange simulations are conducted using multiple phases spread across a range of temperatures. One can approach from several points of view of the question of how to choose an optimal schedule of temperatures to use here. We avoid a view that requires optimizing on the number of simulated systems to use across a given interval, as this brings in difficult-to-generalize specifications regarding the cost of adding another simulation (which among other things can depend on the computing architecture and method of scheduling of resources[4]). Instead, we consider that one has a low-temperature system for which improved sampling is desired, and that a fixed computational budget specifies the number of parallel-tempering stages that will be used. There is no specified upper limit to the temperature range. The question then is how far apart to spread the temperatures: if they are too separated, most attempts to exchange will be rejected; but if they are not spread far enough, the highest temperature in the range might not be very different from the lowest. In either case the low-temperature simulation does not gain much variety from the attempted exchanges.

Let us treat this question by following a particular "phase" as it moves from one temperature to another via replica-exchange swaps. A one-dimensional random walk model can be used to describe this process.[5] Let us further stipulate that the heat capacity is constant across the entire temperature range, and that adjacent temperatures in the range will all have the same ratio B. We will optimize based on a criterion of maximizing the mean-square displacement σ^2 of a phase undergoing this random walk over the temperatures. Ignoring end effects at high and low temperatures, σ^2 is proportional to the number of *accepted* swaps (and thus the swap-acceptance probability) and the square of the size of each constant "step" $\ln B$:

$$\sigma^2 \propto (\ln B)^2 \overline{p}_{\mathrm{acc}}(B). \tag{3}$$

Maximization of σ^2 with respect to B using Eqs. (2) and (3) gives a specification that varies significantly with the heat capacity C. Instead we maximize with respect to $\overline{p}_{\mathrm{acc}}$ with $B(\overline{p}_{\mathrm{acc}})$ given by inverting Eq. (2). A plot of $\sigma^2(\overline{p}_{\mathrm{acc}})$ is given in Fig. 1, where a maximum can be observed at about $\overline{p}_{\mathrm{acc}} = 0.23$, almost independent of C.

We performed replica-exchange Monte Carlo simulations of a Lennard-Jones (LJ) fluid to test the conclusions developed by the model. Simulations were conducted of $N = 108$ particles, and we examined tempering schemes using five and ten phases, respectively (each phase comprising N particles), with the lowest temperature always equal to 0.7 (in LJ units). Additional simulations were performed using 256 particles and five phases. We followed the movement of each phase from one temperature to another during the process, and evaluated the mean-square displacement as a func-

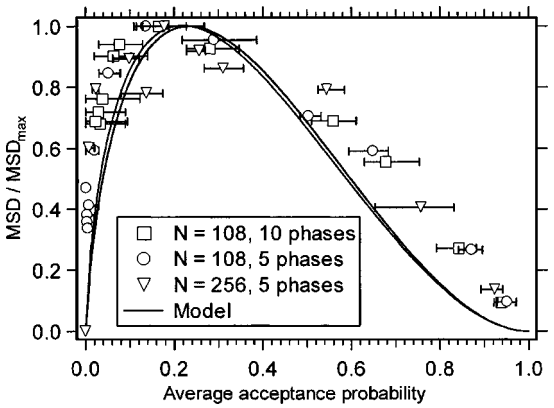

FIG. 1. The initial slope of the curve mean-square displacement (MSD) vs swap attempts, where MSD is in terms of the log temperature of a phase as it moves from one temperature to another via parallel-tempering Monte Carlo. The slope is presented here as a function of the average swap-acceptance probability; each set of MSD-slope values are scaled to unity by dividing by their maximum values. The lines are according to Eqs. (2) and (3) for dimensionless heat capacity values $C=10$, 10^2, and 10^3, respectively. The points are data from the Monte Carlo simulations of N Lennard-Jones atoms in a parallel-tempering series using five or ten phases, as indicated.

tion of the number of swap attempts from a given sampling origin $\sigma^2(n)$, averaging over all phases and sampling origins. We consider the initial slope of this function as the measure of the rate of movement of a phase across temperatures. Data are included in Fig. 1 and agree well with the model. Observed differences might be ascribed to end effects associated with using a small number of phases.

Rathore *et al.*[6] have recently provided an empirical demonstration of the 20% acceptance rule. They performed calculations of the heat capacity using histogram reweighting of the data taken with the parallel-tempering simulations. They optimized the calculation as applied to two systems, the Lennard-Jones model and a model protein, and find that the most accurate data for a fixed amount of computation are obtained when using replicas spaced to give a 20% rate of acceptance of the exchange trials.

In summary, this analysis indicates that temperatures in a parallel-tempering scheme should be set such that about 20% of all the swap attempts are accepted. Although the development here is based on an assumption of a constant heat capacity in the simulated system, the 20% rule is found to be virtually independent of the value of the heat capacity. Thus if the system can be assumed to have an at least piecewise-constant heat capacity (between adjacent stages) this suggests that the 20% rule can be taken to apply over a broad range of temperatures, even if the heat capacity varies considerably across the range. A 20% acceptance rate can be achieved by tuning the temperature interval for each pair during an "equilibration phase," much as one tunes particle displacement step sizes to achieve a given acceptance rate. This process can be guided by Eq. (2) (with a different C for each swap pair, and thus not strictly requiring a geometric progression of temperatures), which provides an effective relation between the temperatures and the acceptance rate for a pair of systems.

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