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ARTICLES

On the acceptance probability of replica-exchange Monte Carlo trials

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An analysis is presented of the average probability of accepting an exchange trial in the parallel-tempering Monte Carlo molecular simulation method. Arguments are given that this quantity should be related to the entropy difference between the phases, and results from simulations of a simple Lennard-Jones system are presented to support this argument qualitatively. Another analysis based on the energy distributions of a replica pair is presented, and an exact expression for the trial-move acceptance probability in terms of the overlap of these distributions is derived. A more detailed expression is presented using an approximation of constant heat capacity, and an asymptotic form for this result, good for large system sizes, is reported. The detailed analyses are in quantitative agreement with the simulation data. It is further shown that treatment of the energy distributions as Gaussians is an inappropriate way to analyze the acceptance probability. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1507776]

I. INTRODUCTION

In recent years the replica-exchange Monte Carlo method[1,2] (also known as *parallel tempering*) has grown in popularity as a means to enhance the sampling of configurations in systems that exhibit many disconnected low-energy regions of configuration space. The method and its extensions have been applied to many problems and systems, including protein folding,[2–8] spin glasses,[1,9] clusters,[5,10,11] QCD,[12] zeolite structure solution,[13] polymers,[14–17] free-energy calculations,[18] and vapor–liquid phase coexistence in electrolytes and other systems.[19–21] The technique calls for the simultaneous sampling of several independent realizations of the system of interest, each differing in the temperature that governs sampling. As the simulation proceeds, configurations from a pair of systems (subscript 0 and 1) are exchanged occasionally, and acceptance of the new state is made with probability,

$$\min[1,\exp(-(\beta_0-\beta_1)(U_1-U_0))], \tag{1}$$

where the argument of the exponential is simply the difference in the sum of βU for the two systems, evaluated before and after the trial. Here β_i is the reciprocal temperature $1/kT$ of system i, with k the Boltzmann's constant, and U_i is the potential energy of the system i (before the exchange is performed).

The replica-exchange method has been found to be very effective in enhancing sampling of low-energy states. The higher-temperature systems are better able to surmount barriers between low-energy states, and thereby provide the low-temperature systems with a source of trial configurations that cover a broader range of configuration space. Simulated annealing provides similar benefits, but the replica-exchange method is superior because the high-temperature system is not forced to quench and then climb out of the well before beginning to explore new regions of configuration space. With parallel tempering, quenching occurs (i.e., the exchange trial is accepted) only when the high-temperature system already happens to have found one of the low-energy regions. All replicas remain equilibrated at all times, and computation is not wasted on repeated equilibrations (or worse, partial equilibrations) of the systems.

Application of the replica-exchange method requires a bit of calibration. If the temperatures of the replica systems differ by too much, the high-temperature system will sample configurations that are largely unacceptable to the low-temperature one; consequently the rate of acceptance of the trials becomes small, and the method ceases to function well. To remedy this problem, additional stages can be introduced between the lowest and highest temperatures, each set to simulate the system at an intermediate temperature. Then perhaps five or six realizations are simulated simultaneously, and replica-exchange trials are attempted occasionally between systems adjacent in temperature. Determining the required number of intermediates, and their placement along the temperature interval, sometimes requires preliminary study using short simulation runs to examine the energy distributions sampled at each temperature.

A related problem arises when the system size (number of simulated molecules N) is increased. The energy, and thus the average energy difference, increases proportionally with the system size, while the width of the distribution of energies sampled increases only as the square root of the system size. Thus the energy distributions becomes relatively narrower and farther apart, and they may lose their region of overlap. Again the remedy is to introduce stages at intermediate temperatures to bridge the gap.

It would be helpful to the design and implementation of a replica-exchange temperature schedule to have detailed un-

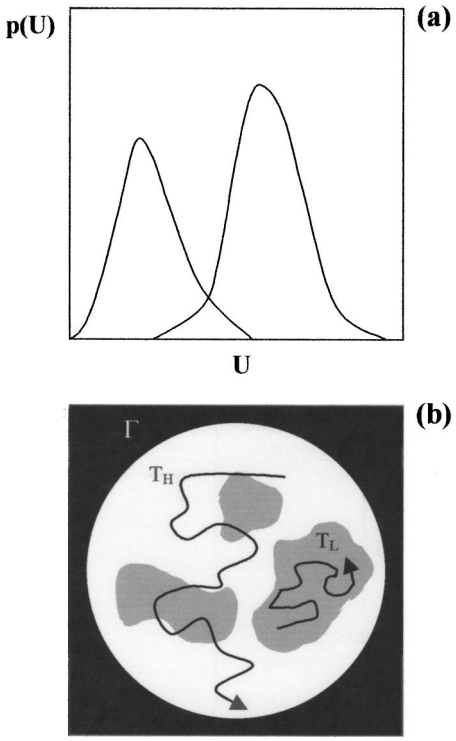

FIG. 1. Schematic representation of (a) energy distributions and (b) phase space as they pertain to the replica exchange method. In (a), the high-temperature distribution is on the right, and the low-temperature one is on the left. In (b), the large black square represents all of phase or configuration space. The large white region inside it depicts the set of configurations important to the high-temperature system, while the disconnected gray regions are those important to the low-temperature system. Lines portray trajectories followed (or configurations sampled) by a high- or low-temperature simulation.

derstanding of the factors involved in the acceptance probability of an exchange trial. This topic is discussed in many studies applying the method, but the considerations given, while reasonable, are superficial. The simplicity of the method invites a more detailed analysis. In the next section we first argue physically, claiming that the acceptance probability is strongly tied to the entropy difference between the exchanging replicas, and support the contention with simulation data for a simple system. In Sec. III we provide more detailed results based on the energy distributions of the systems, and in Sec. IV we conclude.

II. ENTROPY MODEL

The energy-distribution picture is commonly used as just described to explain the limitations and failures of the replica-exchange method. An illustration is presented in Fig. 1(a). The view is correct, but somewhat misleading in that it implies an inappropriate symmetry between the systems. A schematic consideration in configuration space is more telling [consider Fig. 1(b)]. We can identify a set of configurations that are important to the high-temperature system, defined for example as those configurations that contribute some large fraction to the partition function for the system. Likewise, there are a set of configurations important to the low-temperature system. These configurations will necessarily form a subset of the high-temperature configurations, and in the illustration we show them schematically as a set of disconnected subregions. In this view, these configurations are the only ones that are acceptable to the low-temperature system. The sampling trajectory of the high-temperature system moves about the high-temperature region, and occasionally, by chance, happens into one of the low-temperature subset regions. If the exchange trial is performed at this time, it will be accepted, otherwise, if the exchange is attempted when the high-temperature system is not in one of the subregions, it is rejected.

Thus we postulate that the acceptance rate for the trials is exactly the likelihood that the system sampling the high temperature happens to reside in one of the low-temperature important regions. This likelihood can be approximated as the fraction that these regions occupy in the high-temperature important region. The size of the important regions correlates with the entropy of the respective system at the given temperature, and in particular it is proportional to $\exp(S/k)$. Thus the average acceptance probability $\overline{p}_{\mathrm{acc}}$ (i.e., the fraction of all trials that are accepted) will go in relation to the entropy difference,

$$\overline{p}_{\mathrm{acc}} \sim \exp(-\Delta S/k), \tag{2}$$

where $\Delta S > 0$ is the entropy of the high-temperature system minus that of the low-temperature one.

We can quickly make two conclusions: First, because ΔS is extensive, the acceptance rate decreases exponentially with system size N. Second, the heat capacity modulates the decrease in acceptance probability as the temperature interval is increased. Assuming a constant heat capacity over the interval, and using $T\Delta S = Nc_V\Delta T$, we have

$$\overline{p}_{\mathrm{acc}} \sim \left(\frac{T_0}{T_1}\right)^{Nc_V/k}, \tag{3}$$

where $T_0 < T_1$ and c_V is the molar heat capacity at constant volume. Of course, the connection to the heat capacity is consistent with the distribution-overlap view, inasmuch as the distance between the distributions, their widths, and thus their degree of overlap are related to the heat capacity. The relevance of the heat capacity to $\overline{p}_{\mathrm{acc}}$ is well known.[9]

As a test of the foregoing results, we performed replica-exchange Monte Carlo simulations of a Lennard-Jones (LJ) liquid, considering three system sizes (consisting of 32, 64, and 108 particles, respectively) and several temperature differences, and recorded the acceptance rate for the replica-exchange trials. All simulations were performed for a system of number density $\rho = 0.80$, and temperatures ranging from $T = 1.0$ to 2.0 were considered, in increments of 0.2 (all state conditions and simulation results are reported in LJ units, for which the LJ diameter σ and well-depth ϵ are unity). Only one pair of systems was studied in any single simulation, with temperatures as follows: $1.0 \leftrightarrow 1.2$; $1.0 \leftrightarrow 1.4$; $1.0 \leftrightarrow 1.6$; $1.0 \leftrightarrow 1.8$; $1.0 \leftrightarrow 2.0$; $1.2 \leftrightarrow 1.6$; $1.4 \leftrightarrow 1.6$; $1.6 \leftrightarrow 1.8$; $1.6 \leftrightarrow 2.0$; $1.2 \leftrightarrow 2.0$; $1.4 \leftrightarrow 2.0$; $1.8 \leftrightarrow 2.0$. Each simulation performed sampling sufficient to ensure satisfactory statistics for the exchange acceptance rate, and thus ranged between 5×10^5 and 2×10^7 elementary Monte Carlo trials. In each MC trial, either an atom displacement or a replica exchange was attempted, selected at random with probability that had

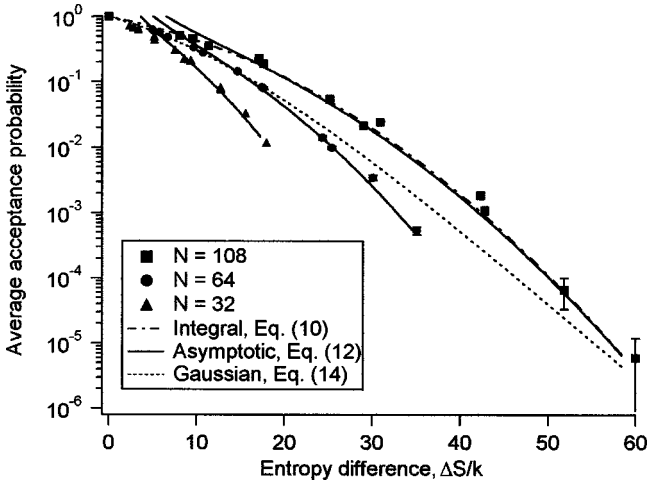

FIG. 2. Average acceptance probability $\overline{p}_{\mathrm{acc}}$ of replica-exchange trials as a function of the difference in entropy between the systems undergoing exchange. Points are data from Monte Carlo simulations of a Lennard-Jones system having numbers of molecules as indicated in the legend. Solid lines are the asymptotic formula, Eq. (12), shown for all three system sizes; dotted–dashed line is the integral formula, Eq. (10), shown only for $N=108$ (and is almost completely obscured by the solid line for the same system size); dotted line is the Gaussian-based formula, Eq. (13), for $N=108$. The asymptotic formula breaks down only as the entropy difference approaches zero (temperature ratio approaches unity).

displacements attempted 100 times more often than exchanges. Entropy differences were computed for each system size by thermodynamic integration of the internal energy as measured in the simulations. The value of the molar heat capacity at $T=1.5$ is used in some of the analyses described below where a constant heat capacity is assumed; from the energy-temperature data we find $C_V/Nk=0.78$.

The results are presented in Fig. 2, where the observed acceptance rate is plotted against the entropy difference for the exchange pair. It is clear from the figure that for a fixed system size, the acceptance rate correlates strongly with the entropy. However, it is equally clear that there is an additional system-size dependence that is not captured by the extensive nature of entropy. The decay of the acceptance probability with increasing system size is attenuated, such that a system-size increase does not lead to a full exponential decay in the acceptance indicated by Eq. (2). To fully uncover this dependence we must proceed with a more detailed model of the calculation, going beyond the qualitative picture presented so far.

III. ENERGY-DISTRIBUTION MODEL

We define energy distributions $p_i(U)=p(U;\beta_i)$ such that $p_i(U)dU$ is the likelihood to observe a system of temperature β_i to have energy in the range U to $U+\mathrm{d}U$. The acceptance probability is simply the sum over all values of the system energies U_0, U_1, taking the probability that the two systems will have the given energies times the probability that a trial that exchanges them will be accepted [Eq. (1)]. Thus,

$$\overline{p}_{\mathrm{acc}}=\int_{U_m}^{\infty}dU_1p_1(U_1)\int_{U_m}^{\infty}dU_0p_0(U_0)\times\min[1,\exp(-(\beta_0-\beta_1)(U_1-U_0))], \tag{4}$$

where U_m is the lowest possible energy. The energy distributions can be decomposed as follows:

$$p_i(U)=\frac{1}{Q(\beta_i)}\Omega(U)\exp(-\beta_iU), \tag{5}$$

where $\Omega(U)$ is the density of states, independent of β, and $Q(\beta_i)$ is the canonical-ensemble partition function. Without loss of generality, we require $\beta_0>\beta_1$ ($T_0<T_1$), which permits us to evaluate the min function in terms of whether U_1 is greater or less than U_0. Then substituting Eq. (5) for the distributions in Eq. (4), after a few steps we can arrange the result,

$$\overline{p}_{\mathrm{acc}}=2\int_{U_m}^{\infty}dU_1\int_{U_m}^{U_1}dU_0\frac{\Omega(U_1)\Omega(U_0)}{Q(\beta_1)Q(\beta_0)}e^{-\beta_0U_1}e^{-\beta_1U_0} \tag{6}$$

which can in turn be expressed back in terms of the distribution functions

$$\overline{p}_{\mathrm{acc}}=2\int_{U_m}^{\infty}dU_0p_0(U_0)\int_{U_m}^{U_0}dU_1p_1(U_1). \tag{7}$$

A casual inspection of the integral finds that it is a quantification of the overlap of the distribution functions, inasmuch as it ranges from zero to unity for the cases ranging between no overlap and complete overlap $[p_0(U)=p_1(U)]$, respectively. Note that the inner integral is for the high-temperature distribution function p_1, which peaks at larger values of U than p_0 does. So if p_0 peaks and returns to zero before p_1 begins to rise (i.e., the distributions do not overlap), there is no contribution to the integral.

It is possible to proceed further if we are willing to make assumptions about the systems being simulated. In particular, we will assume that the heat capacity is constant across the temperature range between β_0 and β_1. Then the density of states across this range is

$$\Omega(U)=\left(1+\frac{1}{C}\beta_r(U-U_r)\right)^C\Omega(U_r), \tag{8}$$

where the r subscript indicates an arbitrary reference state where the energy is U_r and the temperature is T_r. Here C is the extensive, constant-volume heat capacity in units of the Boltzmann constant, $C\equiv C_V/k$. This result is derived by eliminating β between constant-C expressions for the entropy $S(\beta)=S_r+kC\ln(\beta_r/\beta)$ and energy $U(\beta)=U_r+C(1/\beta-1/\beta_r)$, along with the bridge equation $S=k\ln\Omega$. For this density of states, the normalized energy distribution function is

$$p_i(U)=\frac{\beta_i}{C\Gamma(C)}[\beta_i(U-U_m)]^C\exp[-\beta_i(U-U_m)], \tag{9}$$

and we now identify specifically $U_m=U_r-C/\beta_r$ as the minimum possible energy for this model of the density of states.

The average acceptance probability is obtained by combining Eqs. (7) and (9). The double integral can be simplified using the variable substitutions

$$\kappa \equiv \frac{\beta_1(U_1-U_m)}{\beta_0(U_0-U_m)},$$

$$\gamma \equiv \beta_1(U_1-U_m)+\beta_0(U_0-U_m),$$

with the result,

$$\overline{p}_{\mathrm{acc}} = 4\frac{\Gamma(2C)}{[\Gamma(C)]^2}\frac{2C+1}{C}\int_0^{\beta_1/\beta_0} d\kappa \frac{\kappa^C}{(1+\kappa)^{2(C+1)}}. \quad (10)$$

Remembering our convention that $\beta_1 < \beta_0$, the range of the integral is zero to unity, at most. As the difference in temperature grows, the upper limit of integration decreases, and the acceptance probability is diminished. It is notable that the acceptance probability depends on the temperatures only through their ratio. This observation provides a direct connection to the entropy difference, because for constant heat capacity,

$$\Delta S/k = -C\ln(\beta_1/\beta_0). \quad (11)$$

Figure 2 demonstrates that Eq. (10)—with the integral evaluated numerically and the entropy given by Eq. (11)—describes the full behavior of the average acceptance probability with quantitative accuracy.

Consistent with the simulation data there is a further size dependence beyond what is captured by the extensive entropy, as the heat capacity appears in many other places in the formula. An asymptotic analysis can reveal the additional size dependence. Expressed partially in terms of the entropy difference via Eq. (11), the result is (for β_1/β_0 not too close to unity)

$$\overline{p}_{\mathrm{acc}} \sim \frac{\exp(-\Delta S/k)}{(\pi C)^{1/2}}\left[\frac{4}{(1+B)^2}\right]^{C+1}\left[\frac{1+B}{1-2B+B^2}\right] \times (1+O(C^{-1/2})) \quad C\to\infty, \quad (12)$$

where $B \equiv \beta_1/\beta_0 < 1$. Note that the term in square bracket with the $C+1$ exponent is greater than unity, so it is largely responsible for attenuating the decay of the acceptance probability with increasing system size. The acceptance probability indicated by this formula [with Eq. (11)] is included in Fig. 2.

We finish the analysis by emphasizing the importance of working with the correct form of the energy distributions, as described in Eq. (5). In particular, it is not a good idea to treat these distributions as Gaussians, as is the common (and largely appropriate) practice in statistical mechanical analyses in other contexts. The reason is that we are concerned with the overlap of the distributions, and thus the behavior at their tails. The Gaussian form is not consistent with the exponential decay on the high-energy side of the distribution, nor the algebraic decay on the other side, so it will fail to capture well the dependence of the acceptance probability on the tail overlap. Such an analysis leads via Eq. (7) to the following:

$$\overline{p}_{\mathrm{acc}} = \mathrm{erfc}[(\tfrac{1}{2}C)^{1/2}(1-\beta_1/\beta_0)], \quad (13)$$

for which an example is included in Fig. 2.

IV. CONCLUSION

The primary results of this work include identifying the acceptance probability with the entropy [Eq. (2)], quantifying the dependence on the overlap [Eq. (7)], and developing within an approximation of constant heat capacity exact [Eq. (10)] and asymptotic [Eq. (12)] formulas for the acceptance probability. This work provides an analytical justification for the empirical observation[18,22] that the acceptance probability can be made uniform across a multireplica partition by selecting temperature intervals such that all adjacent temperatures are in a fixed ratio.

The present analysis has considered parallel tempering in its original form, in which the replicas differ in temperature only. Generalizations such as hyperparallel tempering[19] that employ replicas differing in chemical potential or in Hamiltonian[18] can also be subject to the analysis developed here. However, the connection of the acceptance probability to the entropy is less certain, because in these extensions we are not assured that the relevant regions of configuration space exhibit the subset relation shown in Fig. 1(b); the arguments given in Sec. II might not apply. Nevertheless, the distribution-function analysis can be extended in a straightforward way, and we expect it would show that the acceptance probability depends on the ratio of the relevant field variable for the exchange systems, and the appropriate susceptibility.

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