Weights and acceptance ratios in generalized ensemble simulations

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This paper addresses issues related to weights and acceptance ratios in generalized ensemble simulation (GES), while comparing two algorithms of GES: serial (e.g., simulated tempering) and parallel (e.g., parallel tempering or replica exchange). We derive a cumulant approximation formula for optimal weights in the serial GES and discuss its effectiveness in practical applications. We compare the acceptance ratios of the serial and parallel GES and prove that provided optimal weights are used, the serial GES has higher acceptance ratios than does the parallel GES. The duality between forward and reverse transitions is at the heart of the derivations throughout the paper.

I. INTRODUCTION

Computer simulation, such as molecular dynamics and Monte Carlo, is a powerful technique for studying complex systems. However, simulations of complex systems are often hindered by trapping in local energy minima and slow relaxations. One method to overcome this difficulty is simulated tempering [1, 2], which attempts to reduce relaxation times at low temperatures by repeatedly heating and cooling the system.

The idea of simulated tempering can be readily extended to parameters other than temperature [2]. Here we will use the term generalized ensemble simulation (GES) to refer to this general context [3]. The motivation for running a GES is usually one or both of the following. First, as in simulated tempering, GES can be used to enhance sampling of microstates by performing a random walk among different ensembles. Second, GES provides a natural way to calculate relative free energies with respect to given parameters.

This paper focuses on two important elements of GES, weights and acceptance ratios. A successful GES requires rapid and uniform exploration of the given ensemble space. In order to satisfy this criterion, acceptance ratios must be not only high but also symmetric between forward and reverse transitions. These conditions can be achieved by assigning weights, that is, by performing weighted sampling of the ensemble space. In the context of free energy calculations, estimating the weights that lead to such optimal sampling is equivalent to calculating the relative free energies with respect to a given parameter.

To avoid the need to determine weights, researchers have developed a parallel version of GES [4, 5], known as parallel tempering or replica exchange. Not having to determine weights is an advantage of the parallel GES, whereas the serial GES has the advantage of being more robust in various computing environments because it does not require parallel simulation. The question remains: Which is more efficient? An important measure of efficiency in this case is the acceptance ratio. Based on empirical data, researchers have suggested that the serial GES may have higher acceptance ratios [6], but no definitive answer has been given so far.

This paper is organized as follows. In Section II, we describe the serial and parallel algorithms of GES. In Section III, we discuss the relationship between weights in the serial GES and the cumulant expansion of free energies, which leads to a derivation of the weight determination method of Ref. [7] from a different perspective. In Section IV, we derive general formulas for acceptance ratios and prove that, provided optimal weights are used, the serial GES indeed has higher acceptance ratios than does the parallel GES.

II. GENERALIZED ENSEMBLE SIMULATION

A generalized ensemble refers to a set of ensembles, each associated with different values of chosen parameters such as temperature or pressure. That is, the nth member of a generalized ensemble is described by the partition function

$$Z_n = \int dx \, \exp[-h_n(x)] \, , \tag{1}$$

where x denotes a microstate of the system and h_n is the reduced Hamiltonian for the nth ensemble.[1] Let us list a few examples. Simulated tempering deals with a generalized ensemble with respect to temperature:

$$h_n(x) = \beta_n H(x) \, , \tag{2a}$$

where $\beta_n = 1/k_B T_n$ is the nth inverse temperature and H is the original Hamiltonian of the system. We can also construct a generalized ensemble for pressure:

$$h_n(x) = \beta[H(x) + P_n V(x)] \, , \tag{2b}$$

where P_n is the pressure of the nth ensemble and $V(x)$ is the volume. When we want to calculate free energy

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[1] We use the terms such as reduced Hamiltonian and reduced free energy to denote quantities that have been divided by $k_B T$.

as a function of a parameter λ, a generalized ensemble with respect to λ can be useful:

$$h_n(x) = \beta H(x, \lambda_n) \ . \tag{2c}$$

It is also possible to construct a generalized ensemble for multiple parameters; for instance, we can combine the above three cases into

$$h_n(x) = \beta_n [H(x, \lambda_n) + P_n V(x)] \ . \tag{2d}$$

In this paper, we adhere to the most general context without specifying any form of $h_n(x)$, except when we discuss particulars of simulated tempering (Eq. 2a) and free energy calculation (Eq. 2c).

The idea of GES is to enhance the sampling of microstates by allowing the system to explore all the given ensembles. This is achieved by means of a random walk on the ensemble space (serial GES) or exchanges of ensembles (parallel GES). Below we describe these two algorithms.

A. Serial algorithm

Given K different ensembles, a generalized Hamiltonian for a serial GES is defined as

$$\mathcal{H}^S(x, n) = h_n(x) - g_n \ , \tag{3}$$

where $n = 1, \ldots, K$. The generalized partition function is then given as

$$\mathcal{Z}^S = \sum_{n=1}^{K} \int dx \, \exp[-\mathcal{H}^S(x, n)] = \sum_{n=1}^{K} Z_n e^{g_n} \ . \tag{4}$$

We use the superscript S to denote the serial algorithm. In this generalized ensemble, the nth ensemble is weighted by e^{g_n}; g_n is the logarithmic weight, but we call it the weight for simplicity.

With the generalized Hamiltonian of Eq. 3, a serial GES is performed as follows [1, 2]. A simulation is started in one of the K ensembles, and at regular intervals a transition is attempted to a randomly chosen ensemble.[2] Transitions are accepted according to the Metropolis criterion [8]; a transition from the mth to the nth ensemble, when the system is at microstate x, is accepted with probability

$$A^S_{m\to n}(x) = \min\left\{1, \exp[-\Delta\mathcal{H}^S_{m\to n}(x)]\right\} \ , \tag{5}$$

where

$$\Delta\mathcal{H}^S_{m\to n}(x) = h_n(x) - h_m(x) - (g_n - g_m) \ . \tag{6}$$

[2] Typically, one allows nearest-neighbor transitions only.

Notice that adding a constant to the weights has no effect; only the relative weights (differences of weights) matter.

A serial GES performs a random walk on the ensemble space. The frequency that the nth ensemble is visited, as can be seen from Eq. 4, is proportional to $Z_n e^{g_n}$. Therefore, a uniform sampling of ensembles is obtained if and only if

$$g_n = f_n + \text{const.} \ , \tag{7}$$

where f_n is the reduced free energy of the nth ensemble

$$f_n = -\ln Z_n \ . \tag{8}$$

The presence of an arbitrary constant means that the weights and the reduced free energies are equal up to an additive constant. The weights that satisfy this property will be referred to as the optimal weights and will be denoted by $\hat{g}_n$.

In free energy calculation with respect to a parameter λ (Eq. 2c), the reduced free energy f_n is related to the free energy $F_n = -k_B T \ln Z_n$ by $f_n = \beta F_n$. Thus, the relative reduced free energy $f_n - f_m$ is proportional to the relative free energy $F_n - F_m$, and finding the optimal weights is equivalent to calculating the free energy profile for λ. The free energy profile, therefore, naturally comes out of a serial GES with respect to λ.

B. Parallel algorithm

In a parallel GES, a generalized Hamiltonian is defined for a set of replicas:

$$\mathcal{H}^P(\boldsymbol{x}) = \sum_{n=1}^{K} h_n(x_n) \ , \tag{9}$$

where $\boldsymbol{x} := (x_1, \ldots, x_K)$ denotes microstates of the replicas; the nth replica is associated with the nth ensemble. The generalized partition function is then given as

$$\mathcal{Z}^P = \int d\boldsymbol{x} \, \exp[-\mathcal{H}^P(\boldsymbol{x})] = \prod_{n=1}^{K} Z_n \ . \tag{10}$$

The superscript P denotes the parallel algorithm.

A parallel GES proceeds as follows [4, 5]. A set of replicas is simulated in parallel, one replica for each ensemble. At regular intervals, an exchange is attempted between a chosen pair of ensembles. Exchanges are accepted according to the Metropolis criterion [8]; an exchange between the mth and the nth ensemble is accepted with probability

$$A^P_{m\leftrightarrow n}(\boldsymbol{x}) = \min\left\{1, \exp[-\Delta\mathcal{H}^P_{m\leftrightarrow n}(\boldsymbol{x})]\right\} \ , \tag{11}$$

where

$$\Delta\mathcal{H}^P_{m\leftrightarrow n}(\boldsymbol{x}) = h_m(x_n) + h_n(x_m) - h_m(x_m) - h_n(x_n) \ . \tag{12}$$

In this algorithm, no weighting is needed because the sampling of ensembles is already uniform; at any instant there is one replica for each ensemble.

III. CUMULANT APPROXIMATION FOR WEIGHTS

In this section, we derive an approximate formula for optimal weights from the cumulant expansion of reduced free energies and discuss the validity of the approximation in the context of simulated tempering and free energy calculation. This section, therefore, concerns only the serial GES, in which the weight is a relevant concept. Since transitions take place pairwise, namely from one ensemble to another, what we need for a serial GES is the relative weights between pairs of ensembles for which transitions are allowed. Therefore, without loss of generality, we consider transitions between ensembles 1 and 2.

As shown in Eq. 7, uniform sampling of the two ensembles is obtained with

$$\Delta\hat{g} = \Delta f \,, \tag{13}$$

where $\Delta\hat{g} := \hat{g}_2 - \hat{g}_1$ and $\Delta f := f_2 - f_1$. The relative reduced free energy Δf can be written as

$$\Delta f = -\ln\langle e^{-\Delta h}\rangle_1 \,, \tag{14}$$

where $\Delta h := h_2 - h_1$ and $\langle\cdot\rangle_1$ denotes an average over ensemble 1. This is known as the free energy perturbation formula [9] and is a special case of Jarzynski's equality [10]. The right-hand side can be expanded in terms of cumulants:

$$\begin{aligned}\Delta f &= -\sum_{k=1}^{\infty}\frac{(-1)^k}{k!}Q_1^k(\Delta h)\\ &= \langle\Delta h\rangle_1 - \frac{1}{2}\mathrm{var}_1(\Delta h) + \cdots \,,\end{aligned} \tag{15}$$

where $Q_1^k(\Delta h)$ is the kth-order cumulant of Δh over ensemble 1. This represents an expansion of Δf with respect to ensemble 1. Similarly, Δf can also be written in terms of ensemble 2:

$$\Delta f = \ln\langle e^{\Delta h}\rangle_2 \,, \tag{16}$$

which can be expanded as

$$\begin{aligned}\Delta f &= \sum_{k=1}^{\infty}\frac{1}{k!}Q_2^k(\Delta h)\\ &= \langle\Delta h\rangle_2 + \frac{1}{2}\mathrm{var}_2(\Delta h) + \cdots \,.\end{aligned} \tag{17}$$

Symmetrizing Eqs. 15 and 17 and using Eq. 13, we find

$$\Delta\hat{g} = \frac{1}{2}(\langle\Delta h\rangle_1 + \langle\Delta h\rangle_2) + \frac{1}{4}[\mathrm{var}_2(\Delta h) - \mathrm{var}_1(\Delta h)] + \cdots \,, \tag{18}$$

which, upon truncation, can be used for approximate estimation of optimal weights.

The effectiveness of this approximation scheme depends on whether we can truncate the cumulant expansions, Eqs. 15 and 17, at a low order without losing much accuracy. Cumulant expansion has been discussed previously in the context of Jarzynski's equality [10, 11, 12]. If the distribution in question is nearly Gaussian, cumulant expansion generally leads to a good approximation. One complication, however, is that the exponential average may be dominated by a distant tail region of the distribution. In such a case, cumulant expansion may yield a poor approximation if the distribution is far from Gaussian in the region that dominates the exponential average, no matter how close it is to Gaussian in the central region.

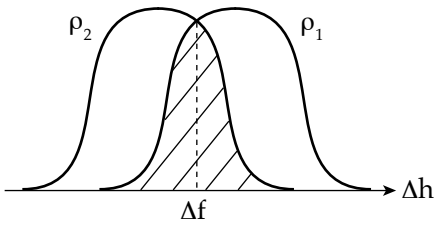

FIG. 1: Schematic diagram of ρ_1 and ρ_2, the distributions of Δh over ensemble 1 and 2. The two distributions intersect at a single point, Δf. As shown in Section IV, the acceptance ratio of the serial GES is identical to the shaded area of overlap.

In the present case, there are two relevant distributions: ρ_1 and ρ_2, the distributions of Δh over ensemble 1 and 2, respectively. These two distributions are not independent. In fact, one completely determines the other because they are related by

$$\begin{aligned}\rho_1(\epsilon) &= \frac{1}{Z_1}\int dx\, e^{-h_1(x)}\,\delta(\Delta h(x) - \epsilon)\\ &= \frac{e^{-\Delta f}}{Z_2}\int dx\, e^{-h_2(x)+\epsilon}\,\delta(\Delta h(x) - \epsilon)\\ &= e^{\epsilon-\Delta f}\,\rho_2(\epsilon) \,,\end{aligned} \tag{19}$$

which is a special case of Crooks' fluctuation theorem [13]. This duality relation implies that $\rho_1(\epsilon)$ and $\rho_2(\epsilon)$, where they are nonzero, intersect at a single point $\epsilon = \Delta f$. And, by applying Jensen's inequality to Eqs. 14 and 16, we find that $\langle\Delta h\rangle_2 \le \Delta f \le \langle\Delta h\rangle_1$. Thus, the two distributions must be situated as shown schematically in Fig. 1. In Section IV, we show that the acceptance ratio of the serial GES is identical to the area of overlap between ρ_1 and ρ_2.

These properties have important implications on the validity of the cumulant approximation for $\Delta\hat{g}$. Since $\rho_1(\epsilon)\,e^{-\epsilon}$ is proportional to $\rho_2(\epsilon)$, the region that dominates the exponential average $\langle e^{-\Delta h}\rangle_1$ coincides with the central region of ρ_2. Similarly, $\langle e^{\Delta h}\rangle_2$ is dominated by the central region of ρ_1. (This has been discussed by Jarzynski [14] in a more general context.) Now, since the overlap determines the acceptance ratio, the central regions of ρ_1 and ρ_2 cannot be far apart unless the two ensembles have been chosen so poorly as to yield very low acceptance ratios. In other words, the aforementioned situation in which an exponential average is dominated

by a distant tail region will not occur as long as we ensure (e.g., by adding intermediate ensembles if necessary) that reasonable acceptance ratios are obtained.

In simulated tempering, $\Delta h(x) = \Delta\beta\, H(x)$, where $H(x)$ is the original Hamiltonian of the system and $\Delta\beta := \beta_2 - \beta_1$. The cumulant approximation of Eq. 18 thus becomes

$$\Delta\hat{g} = \frac{\Delta\beta}{2}(\langle H\rangle_1 + \langle H\rangle_2) + \frac{\Delta\beta^2}{4}[\mathrm{var}_2(H) - \mathrm{var}_1(H)] + \cdots . \tag{20}$$

The first term is $O(\Delta\beta)$, but the second term is $O(\Delta\beta^3)$ because $\mathrm{var}_2(H) - \mathrm{var}_1(H)$ is $O(\Delta\beta)$; the absence of $O(\Delta\beta^2)$ terms is a consequence of the symmetrization of Eqs. 15 and 17. If we keep only the first term, we recover the method of Ref. [7], which was derived based on a heuristic argument of detailed balance. When the system contains many degrees of freedom, the distribution of H is likely to be nearly Gaussian at least in its central region. In such cases, assuming that there is significant overlap between the distributions of H at the two temperatures, the cumulant approximation is expected to be excellent, as was the case in Ref. [7]. Inclusion of higher orders in Eq. 20 could improve the estimate of $\Delta\hat{g}$, but it is generally unnecessary because weights are to be adjusted through adaptive weighting anyways.

The situation is not quite the same in free energy calculation where $\Delta h(x) = \beta H(x, \lambda_2) - \beta H(x, \lambda_1)$. Depending on how the parameter λ is coupled to the system, Δh may or may not contain a significant portion of the system's degrees of freedom. Consequently, the preceding argument for simulated tempering does not always apply in free energy calculation.

IV. ACCEPTANCE RATIOS

A successful GES requires rapid exploration of the given ensemble space, which means high acceptance ratios for transition attempts in the serial GES and exchange attempts in the parallel GES. In this section, we derive general formulas for the acceptance ratios in the serial and parallel GES and address the question of which algorithm has higher acceptance ratios. As in Section III, we focus on two ensembles, 1 and 2, without loss of generality.

A. Serial GES

An individual transition attempt in the serial GES is accepted with the probability of Eq. 5, expressed as a function of microstate x. Thus, the average acceptance ratio for the $1 \to 2$ transition is

$$\begin{aligned}\langle A^S\rangle_{1\to2} &= \int dx\, \frac{e^{-h_1(x)}}{Z_1}\, \min\left\{1, e^{-\Delta h(x)+\Delta g}\right\} \\ &= \int_- dx\, \frac{e^{-h_1(x)}}{Z_1} + \int_+ dx\, \frac{e^{-h_2(x)+\Delta g}}{Z_1} ,\end{aligned} \tag{21}$$

where $\int_-$ and $\int_+$ denote integrals restricted to the regions $\Delta h(x) < \Delta g$ and $\Delta h(x) > \Delta g$, respectively. This expression can be rewritten in terms of ρ_1 and ρ_2, the distributions of Δh over ensembles 1 and 2:

$$\langle A^S\rangle_{1\to2} = \int_{-\infty}^{\Delta g} d\epsilon\, \rho_1(\epsilon) + \frac{e^{\Delta g}}{e^{\Delta f}} \int_{\Delta g}^{\infty} d\epsilon\, \rho_2(\epsilon) . \tag{22}$$

The average acceptance ratio for the reverse transition can be written similarly:

$$\langle A^S\rangle_{2\to1} = \frac{e^{\Delta f}}{e^{\Delta g}} \int_{-\infty}^{\Delta g} d\epsilon\, \rho_1(\epsilon) + \int_{\Delta g}^{\infty} d\epsilon\, \rho_2(\epsilon) . \tag{23}$$

For an arbitrary choice of Δg, $\langle A^S\rangle_{1\to2}$ and $\langle A^S\rangle_{2\to1}$ are different. Only with the optimal choice $\Delta\hat{g} = \Delta f$ do they become identical:

$$\langle \hat{A}^S\rangle = \int_{-\infty}^{\Delta f} d\epsilon\, \rho_1(\epsilon) + \int_{\Delta f}^{\infty} d\epsilon\, \rho_2(\epsilon) , \tag{24}$$

where the hat indicates the use of optimal weights. The subscripts $1 \to 2$ and $2 \to 1$ have been dropped because the acceptance ratio now is the same in both directions. Since $\rho_1(\epsilon)$ and $\rho_2(\epsilon)$ intersect at a single point $\epsilon = \Delta f$, $\langle \hat{A}^S\rangle$ is identical to the area of overlap between the two distributions (Fig. 1). For reasonable acceptance ratios, significant overlap between ρ_1 and ρ_2 is required.

B. Parallel GES

In the parallel GES, individual exchange attempts are accepted with the probability given in Eq. 11. Therefore, the average acceptance ratio for the $1 \leftrightarrow 2$ exchange is

$$\begin{aligned}\langle A^P\rangle &= \int dx_1\, dx_2\, \frac{e^{-h_1(x_1)}}{Z_1}\, \frac{e^{-h_2(x_2)}}{Z_2}\, \min\left\{1, \frac{e^{\Delta h(x_2)}}{e^{\Delta h(x_1)}}\right\} \\ &= \int_* dx_1\, dx_2\, \frac{e^{-h_1(x_1)}}{Z_1}\, \frac{e^{-h_2(x_2)}}{Z_2} \\ &\quad + \int_\dagger dx_1\, dx_2\, \frac{e^{-h_1(x_2)}}{Z_1}\, \frac{e^{-h_2(x_1)}}{Z_2} .\end{aligned} \tag{25}$$

The subscript $1 \leftrightarrow 2$ has been dropped because it is the only exchange possible when we consider two ensembles. The integrals $\int_*$ and $\int_\dagger$ are restricted to the regions $\Delta h(x_1) < \Delta h(x_2)$ and $\Delta h(x_1) > \Delta h(x_2)$, respectively. The two integrals are in fact identical as we can verify by swapping the dummy variables x_1 and x_2:

$$\langle A^P\rangle = 2\int_* dx_1\, dx_2\, \frac{e^{-h_1(x_1)}}{Z_1}\, \frac{e^{-h_2(x_2)}}{Z_2} . \tag{26}$$

Using ρ_1 and ρ_2, we rewrite this as

$$\langle A^P\rangle = 2\int_{-\infty}^{\infty} d\epsilon_2 \int_{-\infty}^{\epsilon_2} d\epsilon_1\, \rho_1(\epsilon_1)\, \rho_2(\epsilon_2) . \tag{27}$$

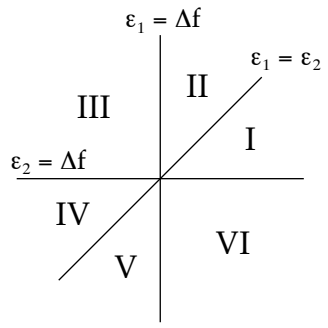

FIG. 2: Three lines, $\epsilon_1 = \Delta f$, $\epsilon_2 = \Delta f$, and $\epsilon_1 = \epsilon_2$, divide the (ϵ_1, ϵ_2) plane into six regions.

Geometrical interpretation of acceptance ratios is not as straightforward as in the serial GES, but it is clear that the parallel GES also requires significant overlap between ρ_1 and ρ_2 for reasonable acceptance ratios.

C. Comparison

We now prove $\langle \hat{A}^S \rangle \geq \langle A^P \rangle$. To compare Eq. 24 (a single-integral form) with Eq. 27 (a double-integral form), we convert Eq. 24 into a double-integral form:

$$\begin{aligned}\langle \hat{A}^S \rangle &= \int_{-\infty}^{\Delta f} d\epsilon_1\, \rho_1(\epsilon_1) + \int_{\Delta f}^{\infty} d\epsilon_2\, \rho_2(\epsilon_2) \\ &= \int_{-\infty}^{\infty} d\epsilon_2 \int_{-\infty}^{\Delta f} d\epsilon_1\, \rho_1(\epsilon_1)\, \rho_2(\epsilon_2) \\ &\quad + \int_{\Delta f}^{\infty} d\epsilon_2 \int_{-\infty}^{\infty} d\epsilon_1\, \rho_1(\epsilon_1)\, \rho_2(\epsilon_2)\,.\end{aligned} \tag{28}$$

We have thus expressed both quantities in terms of double integrals of $\rho_1(\epsilon_1)\,\rho_2(\epsilon_2)$. Let us examine what regions of the (ϵ_1, ϵ_2) plane each quantity covers. As illustrated in Fig. 2, three lines, $\epsilon_1 = \Delta f$, $\epsilon_2 = \Delta f$, and $\epsilon_1 = \epsilon_2$, divide the plane into six regions, labeled I through VI. The first term of Eq. 28 covers III, IV, and V, and the second term covers I, II, and III, which leads to

$$\langle \hat{A}^S \rangle = \left(\int_I + \int_{II} + 2\int_{III} + \int_{IV} + \int_V \right) dR\,, \tag{29}$$

where $dR := d\epsilon_1 d\epsilon_2\, \rho_1(\epsilon_1)\, \rho_2(\epsilon_2)$. And, Eq. 27 can be written as

$$\langle A^P \rangle = 2\left(\int_{II} + \int_{III} + \int_{IV} \right) dR\,. \tag{30}$$

The difference between the two quantities is

$$\langle \hat{A}^S \rangle - \langle A^P \rangle = \left(\int_I - \int_{II} - \int_{IV} + \int_V \right) dR\,. \tag{31}$$

Taking advantage of the symmetry between regions I and II (and regions IV and V) with respect to the reflection in the line $\epsilon_1 = \epsilon_2$, we compare $\int_I dR$ and $\int_{II} dR$ (and $\int_{IV} dR$ and $\int_V dR$) as follows. By swapping the dummy variables ϵ_1 and ϵ_2, $\int_I dR$ can be turned into an integral over II:

$$\int_I dR = \int_{II} d\epsilon_1 d\epsilon_2\, \rho_1(\epsilon_2)\, \rho_2(\epsilon_1)\,. \tag{32}$$

Then, we use the duality relation of Eq. 19 to obtain

$$\begin{aligned}\int_I dR &= \int_{II} d\epsilon_1 d\epsilon_2\, \rho_1(\epsilon_1)\, \rho_2(\epsilon_2)\, e^{\epsilon_2 - \epsilon_1} \\ &\geq \int_{II} d\epsilon_1 d\epsilon_2\, \rho_1(\epsilon_1)\, \rho_2(\epsilon_2) = \int_{II} dR\,,\end{aligned} \tag{33}$$

where the inequality holds because $e^{\epsilon_2 - \epsilon_1} \geq 1$ in region II. It can be shown similarly that

$$\int_{IV} dR \leq \int_V dR\,. \tag{34}$$

From Eqs. 31, 33, and 34, we obtain

$$\langle \hat{A}^S \rangle \geq \langle A^P \rangle\,, \tag{35}$$

which completes the proof.

The actual difference between $\langle \hat{A}^S \rangle$ and $\langle A^P \rangle$ depends on the specific forms of ρ_1 and ρ_2. As a typical example, let us consider the cases where they are Gaussian. Suppose ρ_1 is given as

$$\rho_1(\epsilon) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\epsilon - \mu)^2}{2\sigma^2} \right]\,. \tag{36}$$

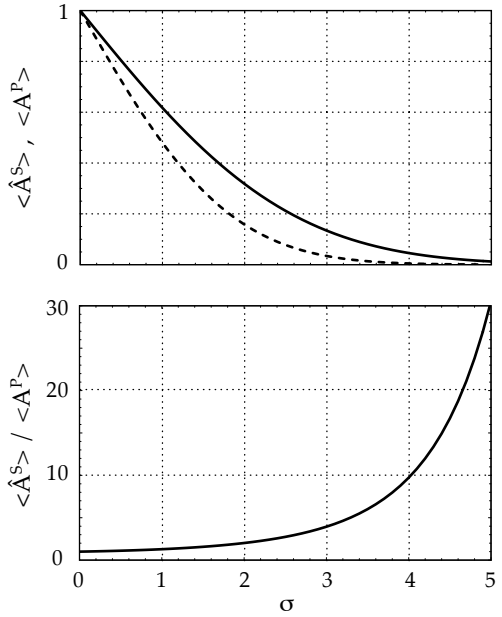

FIG. 3: Acceptance ratios, assuming Gaussian distributions. Top: $\langle \hat{A}^S \rangle$ for the serial GES (solid line) and $\langle A^P \rangle$ for the parallel GES (dashed line). Bottom: the ratio between the two acceptance ratios.

Then, Eqs. 14 and 19 yield

$$\Delta f = \mu - \sigma^2/2 \tag{37}$$

and

$$\rho_2(\epsilon) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\epsilon - \mu + \sigma^2)^2}{2\sigma^2}\right] . \tag{38}$$

Namely, if ρ_1 is a Gaussian distribution with mean μ and variance σ^2, then ρ_2 must be another Gaussian distribution with the mean shifted by $-\sigma^2$ and the same variance. Plotted in Fig. 3 are the acceptance ratios, $\langle \hat{A}^S \rangle$ (Eq. 24) and $\langle A^P \rangle$ (Eq. 27), calculated with these Gaussian distributions. Notice that since μ has no effect on the acceptance ratios, σ is the only relevant parameter. When $\sigma = 0$, two ensembles are identical and both acceptance ratios are unity. As σ increases, the overlap between ρ_1 and ρ_2 decreases; both acceptance ratios fall towards zero, but their ratio $\langle \hat{A}^S \rangle / \langle A^P \rangle$ diverges to infinity.

V. CONCLUSIONS

This paper has addressed two important issues of GES, weights and acceptance ratios. We have derived a cumulant approximation formula for optimal weights in the serial GES and argued why such an approximation is likely to be effective, especially in simulated tempering. We have also derived formulas for acceptance ratios and proved that the serial GES has higher acceptance ratios than does the parallel GES. Having higher acceptance ratios also means that a certain desired acceptance ratio can be achieved with fewer ensembles. It is interesting to note that the duality between forward and reverse transitions is at the heart of these derivations.

In contrast to the recent popularity of the parallel GES (e.g., parallel tempering), the serial GES (e.g., simulated tempering) has gained relatively little attention, possibly due to the difficulty of weight determination. As demonstrated in Ref. [7], however, optimal weights can be readily obtained by using the cumulant approximation formula combined with an adaptive weighting scheme. Now that we know it has higher acceptance ratios, the serial GES looks even more attractive.

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