Multicanonical jump walking: A method for efficiently sampling rough energy landscapes

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(Received 5 January 1999; accepted 4 March 1999)

The multicanonical sampling and jump walking methods are combined to provide a new, effective means of overcoming quasiergodicity in Monte Carlo simulations. In this new method, configurations generated during a long multicanonical sampling are stored infrequently and a modified jump walking procedure is implemented using this set of configurations to sample phase space at low temperature. Multicanonical jump walking, as this new method is called, is compared with regular jump walking and with straight multicanonical ensemble sampling on two systems: a one-dimensional random potential and an Ar_{13} cluster. It is shown that for the same number of MC steps, the multicanonical jump walking method more efficiently samples the phase space than either the regular jump walking or the pure multicanonical ensemble sampling method. © *1999 American Institute of Physics.* [S0021-9606(99)51920-X]

I. INTRODUCTION

In the study of protein folding,[1,2] first-order phase transition phenomena in clusters[3,4] and spin glasses,[5–7] potential energy minima are often separated by high energy barriers, which are exponentially suppressed because of the Boltzmann factor. Consequently, in a simulation of finite length, the high energy barriers will be crossed very rarely. The system can get trapped in some of the local energy basins and the sampling method fails to sample large regions of the thermally accessible phase space. For this reason ordinary sampling methods are often quasiergodic.[8] Considerable effort has been devoted to address the quasiergodicity problem in the past decade, and a variety of powerful methods have been proposed to circumvent the local energy trap. (For a recent review, see Ref. 9) Frantz *et al.* have invented the jump walking[4] (J-walking) method. In this method, which we will call the canonical J-walk method, the normal Monte Carlo simulation is infrequently interrupted by attempts to jump into configurations sampled at a higher temperature. Since quasiergodicity is not a problem at a sufficiently high temperature, the jumps can lead the system to travel between local energy minima and more efficiently sample the phase space. Another attempt to reduce quasiergodicity is the multicanonical ensemble method,[10] invented by Berg *et al.*, and the equivalent entropic sampling method,[11] independently invented by J. Lee. In the multicanonical method, the system performs a random walk in the one-dimensional energy space, and the sampled configurations are uniformly distributed in energy, leading to more frequent barrier crossings. The canonical distribution can be reconstructed by using a reweighting of the multicanonical results.

The canonical J-walk method and the multicanonical sampling method represent significant progress toward reducing the quasiergodic problems. Nonetheless, these two methods have certain attendant problems. The canonical J-walk method depends on jumping into configurations generated at a high enough temperature to circumvent quasiergodicity. But the configurations at the high temperature tend to have high energies, and attempts to jump into such configurations from low temperature configurations (therefore normally with low energies) are often rejected. If the difference between the high and low temperatures becomes large, the attempts are rejected most of the time, and this method will become inefficient. To avoid this, the J-walk is sometimes implemented in several temperature stages to assure reasonable jump acceptance rate. This, however, entails a large extra computational cost. In multicanonical ensemble sampling, on the other hand, a single run can provide information for a whole range of temperatures. One drawback of multicanonical sampling, as is partially shown in this work, is that the low energy end is not sufficiently sampled, resulting in poor statistics at low temperatures. In addition, since the configurations are uniformly distributed over a wide energy range, one must generate a large number of configurations to obtain good statistics on the states accessible in the narrower energy range of a finite temperature canonical distribution.

In this work we devise a multicanonical J-walk method that bypasses the need to use several temperature stages in the canonical J-walk method. In this new method a low temperature MC walk is interrupted by attempts to accept configurations generated in a multicanonical MC walk. The acceptance probability for these attempted moves is constructed in such a way as to guarantee detailed balance and to generate the correct low temperature Boltzmann distribution. In this paper we test the multicanonical J-walk (MJW) method on a one-dimensional rugged random potential to demonstrate its validity. Then a comparative study of the new method with canonical jump walking (CJW) and pure multicanonical ensemble sampling is carried out on an Ar_{13} cluster.

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II. METHODS

A. Canonical jump walking (CJW)

In one variant of the canonical jump walking scheme (CJW) proposed by Frantz *et al.*,[4] a standard Metropolis sampling is first carried out at a sufficiently high temperature $T_J=1/k_B\beta_J$, high enough to reduce the quasiergodicity problem. This sampling is run for a large number of MC steps (e.g., 10^7 steps), and configurations are stored in an external file infrequently (e.g., every 1000 steps). Then a Metropolis sampling is carried out at the desired low temperature $T=1/k_B\beta$. With probability P_J, the Metropolis sampling at low temperature is interrupted by attempts to randomly jump into one of the configurations stored during the preceding sampling at high temperature. Since the stored high temperature configurations are distributed according to the Boltzmann factor $\exp(-\beta_J V)/Z_J$ where $Z_J=\int d^N\mathbf{r}e^{-\beta_J V(\mathbf{r})}$ is the canonical partition function at T_J, the MC sampling distribution of the configurations to be jumped into is thus

$$\Gamma_J(\mathbf{r}'|\mathbf{r})=\frac{\exp(-\beta_J V(\mathbf{r}'))}{Z_J}. \tag{1}$$

Since the aim is to sample states at the low temperature, the detailed balance condition,

$$\mathrm{acc}_J(\mathbf{r}'|\mathbf{r})\Gamma_J(\mathbf{r}'|\mathbf{r})\rho(\mathbf{r})=\mathrm{acc}_J(\mathbf{r}|\mathbf{r}')\Gamma_J(\mathbf{r}|\mathbf{r}')\rho(\mathbf{r}'), \tag{2}$$

where $\mathrm{acc}_J(\mathbf{r}'|\mathbf{r})$ is the acceptance probability for the jump $\mathbf{r}\rightarrow\mathbf{r}'$, and $\rho(\mathbf{r})=\exp(-\beta V(\mathbf{r}))/Z$ is the Boltzmann distribution at the low temperature, leads to the acceptance probability for the jumping attempts

$$\mathrm{acc}_J(\mathbf{r}'|\mathbf{r})=\min(1,q_J(\mathbf{r}'|\mathbf{r})), \tag{3}$$

where

$$q_J(\mathbf{r}'|\mathbf{r})=\frac{\Gamma_J(\mathbf{r}|\mathbf{r}')\rho(\mathbf{r}')}{\Gamma_J(\mathbf{r}'|\mathbf{r})\rho(\mathbf{r})}=\exp\{(\beta_J-\beta)[V(\mathbf{r}')-V(\mathbf{r})]\}.$$

This acceptance criterion will thus generate the desired low temperature distribution. One of the problems encountered in the CJW method is that for the jumps to be accepted with a reasonable acceptance probability, the energy distribution at low and high temperatures must have adequate overlap. For this reason, multiple temperature stages are often required in CJW.

B. Multicanonical ensemble

The energy distribution in the canonical ensemble (constant temperature) is

$$P_C(E;\beta)\propto\Omega(E)\exp(-\beta E). \tag{4}$$

This is a narrow distribution at low temperatures, since the density of states $\Omega(E)$ increases with energy rapidly but at low temperature the Boltzmann factor $\exp(-\beta E)$ quickly drops to zero. Therefore, in a canonical Monte Carlo simulation, very high energy and very low energy configurations are rarely sampled, and if energy minima are separated by high barriers, this leads to quasiergodicity.

The multicanonical (mu) ensemble,[10,12] on the other hand, is defined by the condition that its energy probability distribution function, $P_{\mathrm{mu}}(E)$, is constant throughout a certain energy range so that,

$$P_{\mathrm{mu}}(E)\propto\Omega(E)w_{\mathrm{mu}}(E)=\text{constant}. \tag{5}$$

This implies that the multicanonical weight factor is

$$w_{\mathrm{mu}}(E)\propto\Omega^{-1}(E). \tag{6}$$

$w_{\mathrm{mu}}(E)$, however, is not known *a priori*, and needs to be estimated via iterated numerical simulations. An effective approach to estimating the multicanonical weight factor, and the approach followed in this paper, is given in detail by Okamoto *et al.*[12]

In the following we summarize the essential ideas. The multicanonical weight factor can be written in the form $w_{\mathrm{mu}}(E)=\exp(-S(E))$ where $S(E)=\ln(\Omega(E))$ is the microcanonical entropy of the system with energy E. A canonical Monte Carlo simulation at a sufficiently high temperature $T_0=1/k_B\beta_0$ is first performed. The energy histogram $H^{(0)}(E)$ is constructed during the sampling, which is proportional to the sampled canonical energy distribution

$$H^{(0)}(E)\propto\Omega(E)\exp(-\beta_0 E). \tag{7}$$

Based on the determined $H^{(0)}(E)$, estimates of the entropy,

$$S^{(0)}(E)=\ln(\Omega(E))=\ln(H^{(0)}(E))+\beta_0 E+\text{const}, \tag{8}$$

and the weight factor,

$$w_{\mathrm{mu}}^{(0)}(E)=\exp(-S^{(0)}(E)), \tag{9}$$

are made. The constant in $S(E)$ can be taken to be zero since in a Monte Carlo simulation only the ratio of weight factors matters. Once this first estimate of the weight factor $w_{\mathrm{mu}}^{(0)}(E)$ has been determined, a new Monte Carlo simulation is performed to sample states with this distribution. The energies of these sampled states are then used to construct an energy histogram $H^{(1)}(E)$. This histogram can now be expressed as

$$H^{(1)}(E)\propto\Omega(E)w_{\mathrm{mu}}^{(0)}(E), \tag{10}$$

from which the following new estimates of the entropy and the weight factor can be made:

$$\begin{aligned}S^{(1)}(E)&=\ln(\Omega(E))\\&=\ln(H^{(1)}(E))-\ln(w_{\mathrm{mu}}^{(0)}(E))\\&=\ln(H^{(1)}(E))+S^{(0)}(E),\end{aligned} \tag{11}$$

and

$$w_{\mathrm{mu}}^{(1)}(E)=\exp(-S^{(1)}(E)). \tag{12}$$

This new weight factor is then used to carry out another simulation and the procedure is iterated until the obtained energy histogram $H(E)$ is reasonably flat within certain range. In each iteration, the weight factor is updated by

$$S^{(k)}(E)=S^{(k-1)}(E)+\ln(H^{(k)}(E)), \tag{13}$$

and

$$w_{\mathrm{mu}}^{(k)}(E)=\exp(-S^{(k)}(E)), \tag{14}$$

where $H^{(k)}(E)$ is the energy histogram in the kth simulation.

Once $w_{\mathrm{mu}}(E)$ has been obtained, one can devise a Monte Carlo procedure for sampling the phase space with a multicanonical distribution. Essentially, multicanonical ensemble sampling generates a random walk in the one-dimensional energy space, and energies within a certain prescribed range are sampled with equal probability. High energy configurations are now sampled amply and barrier crossing ceases to be a rare event, thus reducing quasiergodic behavior. The canonical average of any property A can be computed from the multicanonical sampling by using umbrella sampling so that

$$\langle A\rangle = \frac{\int d^N\mathbf{r} A(\mathbf{r}) e^{-\beta V(\mathbf{r})}}{\int d^N\mathbf{r} e^{-\beta V(\mathbf{r})}} = \left\langle A(\mathbf{r}) \frac{e^{-\beta V(\mathbf{r})}}{w_{\mathrm{mu}}(V(\mathbf{r}))} \right\rangle_{\mathrm{mu}} \Bigg/ \left\langle \frac{e^{-\beta V(\mathbf{r})}}{w_{\mathrm{mu}}(V(\mathbf{r}))} \right\rangle_{\mathrm{mu}}, \quad (15)$$

where $\langle\cdots\rangle_{\mathrm{mu}}$ denotes the average over the multicanonical distribution, $w_{\mathrm{mu}}(V(\mathbf{r}))$.

One problem with the multicanonical sampling concerns the convergence of the simulation. When the estimated density of states $\Omega(E)$ (or the reciprocal of the weight factor $1/w_{\mathrm{mu}}(E)$) differs too much from its correct value, then the updated weight factor according to Eqs. (13) and (14) can change either too much or too little in a certain configurational region in an iteration. Consequently the estimated weight factor will oscillate instead of steadily approaching the exact function. Interestingly, Hao and Scheraga[13] have used jump walking method to overcome this problem in multicanonical sampling.

Another problem with multicanonical sampling, as is shown in this work, is that it fails to sample the low energy range sufficiently. Therefore, it gives inadequate statistics at low temperatures.

C. Multicanonical jump walking (MJW)

Because the multicanonical ensemble generates an energy distribution that is uniform throughout a certain energy range, this energy distribution should adequately overlap the canonical energy distribution at many temperatures (see Fig. 3). Thus, in principal, multicanonical ensemble sampling can be used in a jump walking scheme in place of the costly multiple temperature stages often required in canonical jump walking. In this approach, configurations sampled from the multicanonical distribution are stored and a standard canonical MC walk at the desired low temperature is interrupted by trial moves to these stored multicanonical configurations. Because a whole energy range is covered, this multicanonical jump walking scheme should reduce the quasiergodicity efficiently while avoiding the costly multistage temperature runs of canonical jump walking. We thus expect that this new scheme will lead to considerable savings in CPU time over the CJW method.

In this new multicanonical jump walking (MJW) method, the multicanonical weight factor $w_{\mathrm{mu}}(E)$ is first estimated via a set of iterations as outlined in Sec. II B. A long production run is then carried out with the obtained weight factor. During the long sampling, configurations and their corresponding energies are stored infrequently (e.g., every 1000 MC steps). A canonical Monte Carlo sampling run at the desired temperature is interrupted with probability P_J by attempts to jump into one of the previously stored multicanonical configurations (randomly selected from the set). The sampling distribution for the jumps is then

$$\Gamma_J(\mathbf{r}'|\mathbf{r}) = \frac{w_{\mathrm{mu}}(V(\mathbf{r}'))}{Z_{\mathrm{mu}}}, \quad (16)$$

where $Z_{\mathrm{mu}} = \int dE \Omega(E) w_{\mathrm{mu}}(E)$ is the partition function for the multicanonical ensemble. To satisfy the detailed balance in Eq. (2), the jumps are accepted with the probability

$$\mathrm{acc}_J(\mathbf{r}'|\mathbf{r}) = \min\{1, q_{\mathrm{MJ}}(\mathbf{r}'|\mathbf{r})\}, \quad (17)$$

where

$$q_{\mathrm{MJ}}(\mathbf{r}'|\mathbf{r}) = \exp(\beta(V(\mathbf{r}) - V(\mathbf{r}'))) \frac{w_{\mathrm{mu}}(V(\mathbf{r}))}{w_{\mathrm{mu}}(V(\mathbf{r}'))}.$$

III. RESULTS AND DISCUSSION

In the following, we apply the multicanonical jump walking method to two extensively studied systems, the 1D random potential and the Ar_{13} cluster, and we compare the results with those of the canonical jump walking method and the pure multicanonical ensemble method.

A. One-dimensional random potential

The one-dimensional random potential[8] is defined by a Fourier sum of sine waves

$$V(x) = \sum_{n=1}^{N} C_n \sin\left(\frac{2n\pi x}{L}\right). \quad (18)$$

The coefficients C_n are generated randomly on $[-1,1]$. In our study, $N=20$ and $L=4.0$. The potential surface is shown in Fig. 1. The choice of units are arbitrary. Here units are chosen such that the Boltzmann constant $k_B=1.0$ and thermodynamic properties at temperature $T=0.1$ are determined. This model is useful for testing methods because it is pos-

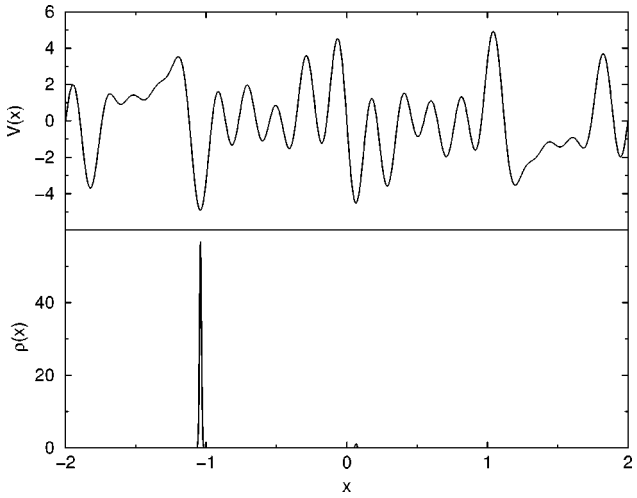

FIG. 1. The one-dimensional random potential surface [cf. Eq. (18)] used in the simulations is given in the top plate. The exact configurational distribution function, $\rho(x) = \exp(-\beta V(x))/Z$, at $T=0.1$ is given in the bottom plate.

sible to calculate the thermodynamic properties corresponding to this potential exactly. The one-dimensional potential is useful as a test that each of the methods gives the correct results.

1. Canonical jump walking (CJW)

In canonical jump walking (CJW) on this potential surface it is necessary to choose a J-walk temperature of $T_J=3.0$ to assure ergodicity. In this one-dimensional model there is sufficient overlap between the energy distributions at this high temperature and the very low temperature ($T=0.1$) so that CJW with only one stage will suffice. This overlap is due to the fact that the density of states of this one-dimensional system is pathological, in that it does not increase rapidly with energy. To demonstrate the power of the new MJW method it will be necessary to study multidimensional systems as we do in the next subsection. Nevertheless, it is still of some interest to compare the methods on a system which can be calculated exactly.

The CJW run was done as follows: A Metropolis sampling was carried out at $T_J=3.0$ for 200 000 steps, and configurations were stored every 20 steps. Then a Metropolis walk was carried out at the temperature $T=0.1$ and with probability $P_J=0.03$ an attempt was made to move the low temperature walker to one of the saved configurations of the high temperature walker. This attempt was accepted or rejected with the probability given in Eq. (3). The density distribution $\rho(x)=e^{-\beta V(x)}/Z$ and its deviation from the exact values were computed. The deviation in the density distribution is defined here as[8]

$$\chi=\int dx[\rho(x)-\rho_{\text{exact}}(x)]^2. \tag{19}$$

2. Multicanonical sampling and multicanonical jump walking (MJW)

The multicanonical weight factor $w_{\text{mu}}(E)$ was computed via five iterations, with 100 000 MC steps in each iteration. In the first iteration a completely random sampling was used. The weight factor determined in this run was then used in the following pure multicanonical sampling and then in multicanonical jump walking (MJW). A production run of 200 000 steps was carried out. In pure multicanonical sampling, the canonical distribution for $T=0.1$ was reconstructed by the following reweighting formula,

$$\rho_C(x;\beta)\propto\rho_{\text{mu}}(x)\frac{e^{-\beta V(x)}}{w_{\text{mu}}(V(x))}, \tag{20}$$

and thermodynamic quantities were computed using Eq. (15). In the MJW production run, configurations were stored every 20 steps (a total of 10 000 configurations were stored) and a Metropolis sampling at $T=0.1$ was carried out, punctuated by attempted jumps with probability $P_J=0.03$ to these stored configurations, which were accepted or rejected with the probability given in Eq. (17).

3. Results for the one-dimensional system

The results for the random potential using the three different methods are presented in Fig. 2. It can be seen that the density distributions computed by the three methods all converge to the exact values. The two jump walking methods (MJW and CJW) converge faster and yield more accurate distributions than pure multicanonical sampling. This is because both jump walking methods sample the energy space with the actual Boltzmann distribution, while the pure multicanonical ensemble method samples all energies with equal probability and the Boltzmann distribution is reconstructed by reweighting. As a result, the jump walking methods have better statistics in the thermally important regions than the pure multicanonical sampling method. This advantage of jump walking methods (both MJW and CJW) becomes even more pronounced as the size of the system gets larger, as will be shown in the next section.

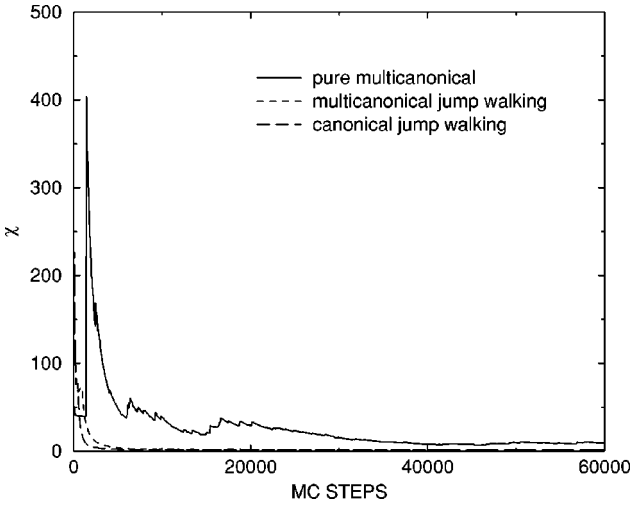

FIG. 2. The decay of the square deviation χ of Eq. (19) as a function of the number of Monte Carlo steps for the one-dimensional random potential shown in Fig. 1. The MC steps in the two jump walking methods are steps in the Metropolis samplings at $T=0.1$, while the MC steps in the pure multicanonical sampling are steps in the production run.

B. Ar_{13} cluster

''Phase transitions'' in atomic clusters have been extensively studied by computer simulation.[14,15] Quasiergodicity due to large energy barriers has been a troublesome problem in Monte Carlo studies of cluster melting, a fact which has led to controversy concerning the solid–liquid transition in small rare gas clusters.[15,16] A good example is the cluster Ar_{13}.[17,18] Another problem in the study of small clusters is that thermodynamic properties of finite systems differ in different ensembles. Doye *et al.* addressed such differences between microcanonical and canonical ensembles in their study of small Lennard-Jones clusters.[19,20] In this paper, we calculate the canonical thermodynamic properties, and the temperature we use is the canonical temperature.

In what follows, the potential energy of the cluster is taken to be the pairwise additive Lennard-Jones potential,

$$V(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{21}$$

with $\varepsilon=119.4\,\text{K}$ and $\sigma=3.45\,\text{Å}$ for argon.[21] Following Straub,[22] to eliminate the translational and rotational degrees of freedom, the first atom is fixed at the origin of the coor-

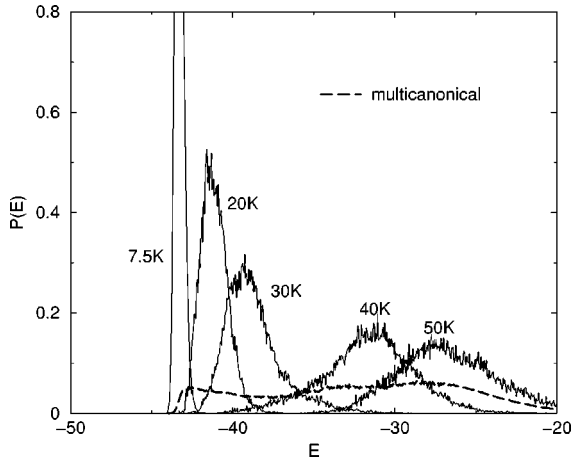

FIG. 3. Histograms of the energy distribution function of Ar_{13}. The histograms are obtained from multicanonical jump walking simulations. The long dashed line is the multicanonical energy distribution obtained on the basis of five iterations as described in the text. The multicanonical distribution is roughly flat over most of the energy range and overlaps significantly with canonical distributions at the five temperatures shown. Note that there is very little overlap between the energy distributions at temperatures more than 10 K apart.

dinate system, a second one is constrained to move along x-axis, and a third one is constrained to move on xy-plane. To prevent the cluster from evaporating, a spherical, perfectly reflecting wall is imposed at radius 4σ from the origin.

1. Canonical jump walking (CJW)

Canonical jump walking (CJW) was implemented using four temperature stages, starting at 50 K to assure ergodicity and descending at 10 K intervals to 20 K. At each of these temperatures the Metropolis sampling was interrupted by attempts to jump into configurations at the next higher temperature stage as described in Sec. II A. At each stage, configurations were stored every 1000 MC steps to diminish correlation. The necessity of using multiple temperature stages in the CJW method can be understood by looking at Fig 3. For the jumps to be accepted with a reasonable acceptance probability, the energy distribution at low and high temperatures must have adequate overlap. In the study of Ar_{13}, we see that sufficient overlap exists only for temperatures no more than 10 K apart. Thus to simulate the system at $T=20\,\mathrm{K}$, we have to adopt a multistage scheme, starting from 50 K to assure ergodicity, and running CJW at 40, 30, and finally 20 K. This becomes increasingly expensive as the system gets larger and the canonical energy distribution gets relatively narrower, entailing more and more intermediate stages. In addition, since in a simulation of finite length the obtained distribution is only an approximation of the true distribution and there's always some statistic error, the errors will accumulate through the temperature stages, compromising the accuracy of the simulation.

After the configurations were stored at the four temperature stages, a Metropolis sampling was carried out at each temperature from 2.5 to 50.0 K at 2.5 K intervals, interrupted with probability $P_J=0.1$ by attempts to jump into the configurations stored at the next higher temperature stage. (i.e., in sampling temperatures $\leqslant 20.0\,\mathrm{K}$, the jumps were attempted into configurations stored at 20.0 K, for temperatures in the 20.0–30.0 K range, the jumps were attempted into configurations stored at 30.0 K, etc.) At each temperature, a random initial configuration was used. The system was first thermalized for 100 000 steps and then the thermodynamic quantities were computed in the following 200 000 MC steps.

2. Multicanonical sampling and multicanonical jump walking (MJW)

The multicanonical weight factor $w_{\mathrm{mu}}(E)$ was determined from five iterations (see Sec. II B.) with 2 000 000 MC steps in each iteration, and then a long production run using this weight factor was carried out. In the pure multicanonical ensemble simulation, thermodynamic quantities were calculated using Eq. (15) during the production run. In multicanonical jump walking (MJW), configurations were stored every 1000 MC steps during the multicanonical ensemble production run, then a Metropolis MC sampling at desired temperatures was interrupted with probability $P_J=0.1$ by attempted jumps into a randomly chosen configuration of the stored set, and this new configuration was accepted with the probability given in Eq. (17). As in the CJW simulation, the system was initialized randomly, thermalized for 100 000 steps, and the thermodynamic data were accumulated in the following 200 000 steps.

3. Results

In order to compare the performance of the three methods, we first implemented each method with the same number of total MC steps. In CJW, we used 12 500 000 MC steps with configurations stored every 1000 steps at each temperature stage. Since four stages were used, the total number of MC steps was 50 000 000. In MJW, the weight factor was calculated via five iterations with 2 000 000 MC steps in each iteration, then a production run of 40 000 000 MC steps was carried out and configurations were stored every 1000 steps. Therefore the total number of MC steps involved was also 50 000 000. In both jump walking methods, a Metropolis sampling of 300 000 MC steps was implemented and thermodynamic quantities calculated for each temperature from 2.5 to 50 K at 2.5 K intervals, so that a total number of 6 000 000 MC steps were required for the accumulation of the thermodynamic data after the configurations had been stored. Therefore in CJW and MJW, the total number of MC steps used for generating stored configurations and for calculating thermodynamic quantities was 56 000 000. In pure multicanonical sampling, the weight factor was estimated via five iterations with 2 000 000 MC steps in each iteration for a total of 10 000 000 and a production run of 50 000 000 MC steps was carried out during which the thermodynamic quantities were accumulated. Therefore the total number of MC steps used for the pure multicanonical sampling was 60 000 000, approximately the same as the number of steps in CJW and MJW.

The average energy and heat capacity of Ar_{13} and their standard deviations were calculated from 20 parallel simulations. Figures 4 and 5 show the caloric curve and heat capacity curve of Ar_{13} obtained by the three methods. The

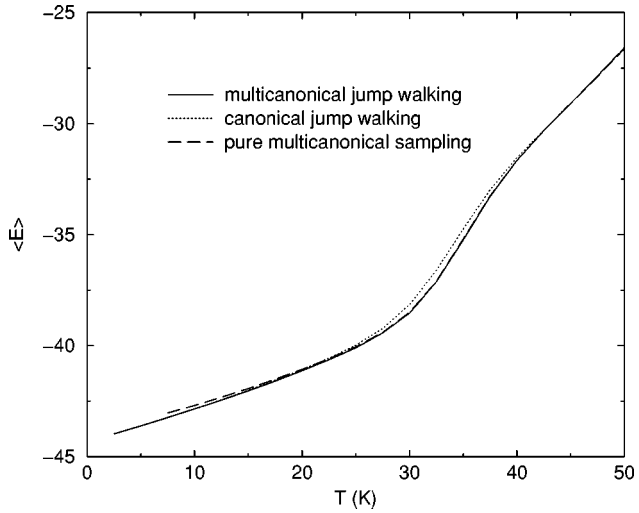

FIG. 4. The caloric curve of Ar_{13}. The energies are expressed in reduced unit E/ε. It can be seen that overall the three methods give consistent results. But pure multicanonical sampling results deviate from the other two at low temperatures, while CJW results differ from the other two in the transition region. This suggests that MJW gives the most consistent results over all the temperature range. The same number of total MC steps were used in each method.

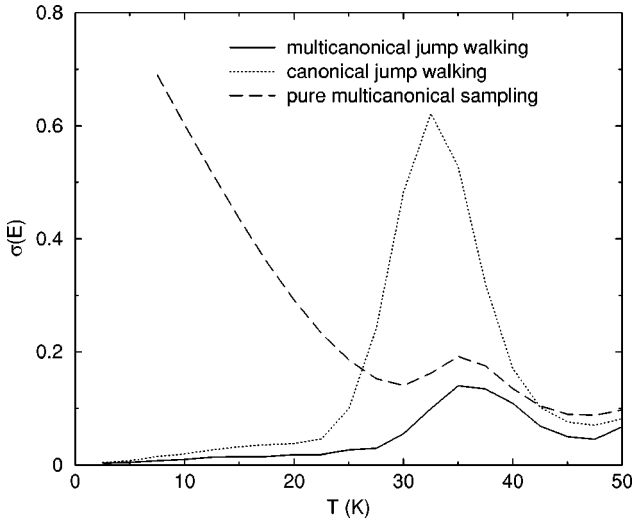

FIG. 6. The standard deviation in the average energy of Ar_{13}. $\sigma(E) = \sqrt{\langle E^2\rangle - \langle E\rangle^2}$. The deviation is calculated from 20 parallel simulations. It can be seen that for the same number of total MC steps MJW gives the best precision of the three. CJW behaves poorly in the transition region while pure multicanonical sampling is very inaccurate at low temperatures.

three methods agree fairly well, except that the pure multicanonical simulation fails to yield results at temperatures below 7.5 K. (There is no data point for the pure multicanonical curve at temperatures lower than 7.5 K.) This is because when reweighting using Eq. (15) at very low temperature, $e^{-\beta E}$ becomes too small and leads to numerical underflows. The pure multicanonical sampling results deviate slightly from the other two at low temperatures, while the CJW results differ from the other two in the transition region (25–40 K). This suggests that MJW gives the most consistent results over the whole temperature range. The standard deviations of average energy and heat capacity are used as measures of the precision of each method and are presented in Fig. 6 and Fig. 7. It can be seen that for the same number of total MC steps, the new MJW method gives the best precision of the three. MJW and CJW have similar precision at low temperatures, but in the transition region MJW gives much better precision than CJW. On the other hand, the pure multicanonical sampling gives as good precision as MJW in the transition region, but behaves very poorly at low temperatures. The reason for this is that the pure multicanonical sampling samples energies within a certain range with roughly equal probability, but at the two ends of the range, the probability drops precipitously. Therefore at low energies, (correspondingly at low temperatures,) very few configurations are sampled, re-

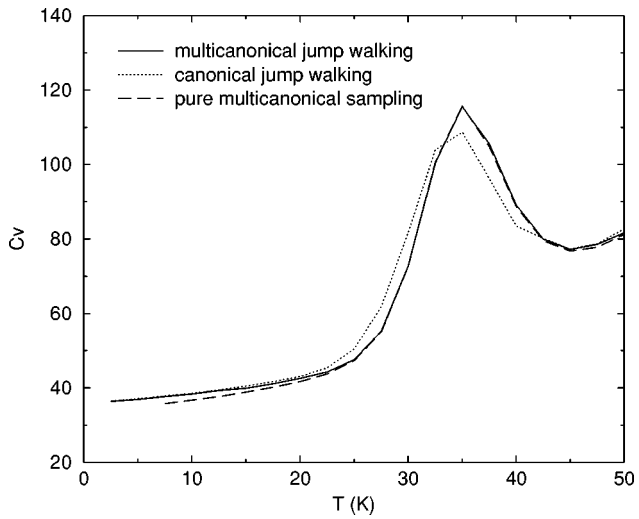

FIG. 5. The heat capacity curve for Ar_{13}. The results obtained from the three methods agree reasonably well. But pure multicanonical sampling results deviate from the other two at low temperatures, while CJW results differ from the other two in the transition region, suggesting that MJW gives the most consistent result over all the temperature range studied.

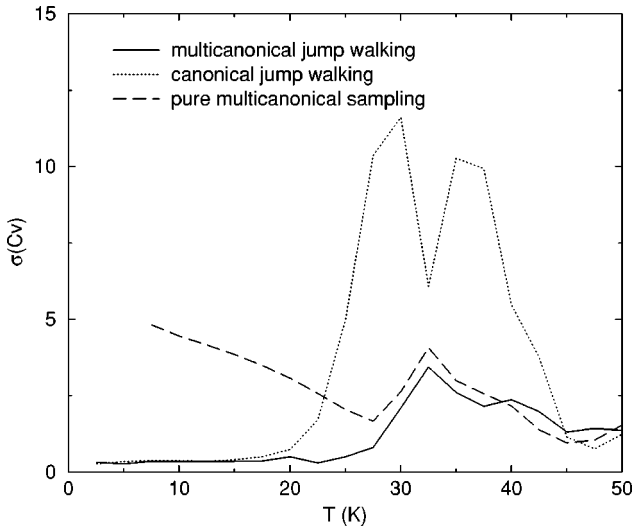

FIG. 7. The standard deviation in the heat capacity of Ar_{13}. $\sigma(Cv) = \sqrt{\langle Cv^2\rangle - \langle Cv\rangle^2}$. The deviation is calculated from 20 parallel simulations. It can be seen that for the same number of total MC steps MJW gives the best precision of the three. CJW behaves poorly in the transition region while pure multicanonical sampling is inaccurate at low temperatures.

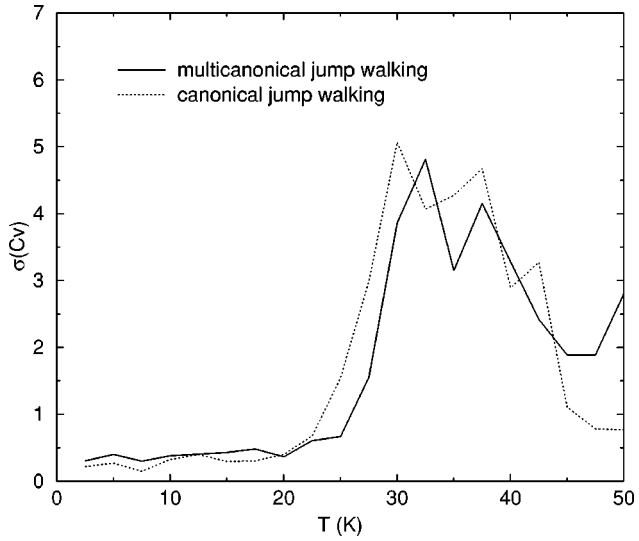

FIG. 8. The standard deviation in the heat capacity of Ar_{13}. Six times more total MC steps were used in CJW than in MJW. In this case, CJW and MJW give comparable precision.

sulting in poor statistics. The energy histograms in Fig. 3 show that pure multicanonical sampling fails to cover a significant part of the canonical distribution at $T=7.5$ K, causing low accuracy at this temperature. In MJW, on the other hand, an individual Metropolis sampling of configurations coupled with jumps to the states generated by the multicanonical sampling is carried out at every temperature, therefore a large number of configurations are sampled and ample statistics is achieved. From this we can see that for the MJW method to give accurate results, it is enough that the multicanonical distribution overlaps with part of the canonical distribution at the temperature in question, while for pure multicanonical sampling to give accurate results, the multicanonical distribution must cover the whole range of the canonical distribution. Therefore MJW is advantageous over pure multicanonical sampling, especially at low temperatures.

Having established the fact that for the same number of MC steps MJW gives the highest precision of the three methods, we further compared the CJW and MJW methods by determining the number of steps required to obtain essentially the same accuracy for these two methods. For this purpose, we used 40 000 000 MC steps at each temperature stage in CJW for storing the high temperature canonical configurations and only 10 000 000 MC steps in the production run in MJW to store multicanonical configurations. In this case six times more total MC steps were used in CJW than in MJW. The thermodynamic quantities and their standard deviations were calculated from 20 parallel simulations. The standard deviation in heat capacity is used as the measure to compare the precision of each method and is presented in Fig. 8. CJW and MJW have comparable precision in this case, but CJW costs six times more than MJW for the system of Ar_{13}.

In comparing the CPU time for the three different methods we note that MJW and CJW involve writing external files when a configuration is stored (1 out of 1000 MC steps in our study) and reading external files when a jump is accepted (1 out of about 30 steps on average), whereas pure multicanonical sampling does not require this. This added file I/O overhead, however, is quite small and thus for the same number of configurations generated, pure multicanonical sampling does not cost noticeably less than MJW or CJW method. Moreover, the file I/O overhead only scales as N, where N is the size of the system, while the cost of each MC step scales as N^{α} with $\alpha \geqslant 1$ for most systems. Therefore MJW is more advantageous for large systems than pure multicanonical sampling.

In fact, as the number of atoms in the system increases, the advantage of MJW over the other two methods should become more pronounced. As the system is made larger, the density of states $\Omega(E)$ increases more rapidly with energy E, leading to a relatively narrower peak in energy distribution. This may lead to the necessity of employing more temperature stages in CJW and is expected to yield poorer statistics for each temperature in pure multicanonical simulation. MJW, on the other hand, should be immune from such problems because (a) there is always sufficient overlap between the multicanonical distribution and the canonical distribution at any temperature, therefore adequate jump success ratio, and thus good ergodicity, are assured; (b) individual sampling at each temperature generates a large number of configurations to give enough statistics. As a result, MJW should always have good accuracy at all temperatures. A comparative study of these three methods using CPU times and various ergodic measures is being performed on larger systems such as peptides.

IV. CONCLUSION

A multicanonical jump walking (MJW) method based on combining jump walking and multicanonical ensemble sampling methods has been introduced and tested on two simple systems: a one-dimensional random potential and an Ar_{13} cluster. This new method was compared with pure multicanonical sampling and with canonical jump walking (CJW) methods for sampling rugged energy landscapes. These latter two methods have already proved very useful for lessening quasiergodicity in the sampling of configurations on rough energy landscapes. In this paper we show that multicanonical sampling very inefficiently samples the low energy configurations which contribute so prominently at low temperatures. CJW on the other hand often requires the use of many temperature stages to sample the low temperature distributions. In this paper we show that the new MJW method, which only requires two stage sampling, one using multicanonical sampling and the other at the desired temperature, gives better precision than either the canonical jump walking (CJW) method or pure multicanonical ensemble sampling at the same cost. The advantage of the new MJW method over the CJW method arises from the fact that there is a large overlap in the energy distribution of the multicanonical ensemble and the canonical ensemble at any temperature. The MJW method is better than pure multicanonical sampling because it samples each temperature individually and therefore has better statistics. We can conclude from this paper that the MJW method provides a very promising alternative to the

other methods for the sampling of configurations on rough energy landscapes. It remains to demonstrate this conclusion on systems of current interest like peptides and proteins.

ACKNOWLEDGMENTS

H.X. would like to thank K. Bernacki for inspiring discussions. The work was supported by a grant from the NSF. The computational resources of the NIH Biotechnology Resource Center for Biomolecular Simulations at Columbia University are gratefully acknowledged.

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