On Monte Carlo and molecular dynamics methods inspired by Tsallis statistics: Methodology, optimization, and application to atomic clusters

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Generalized Monte Carlo and molecular dynamics algorithms which provide enhanced sampling of the phase space in the calculation of equilibrium thermodynamic properties is presented. The algorithm samples trial moves from a generalized statistical distribution derived from a modification of the Gibbs–Shannon entropy proposed by Tsallis. Results for a one-dimensional model potential demonstrate that the algorithm leads to a greatly enhanced rate of barrier crossing and convergence in the calculation of equilibrium averages. Comparison is made with standard Metropolis Monte Carlo and the J-walking algorithm of Franz, Freeman and Doll. Application to a 13-atom Lennard-Jones cluster demonstrates the ease with which the algorithm may be applied to complex molecular systems. © *1997 American Institute of Physics.* [S0021-9606(97)52045-9]

I. BACKGROUND

The ergodic hypothesis states that the time average of an observable equals the phase-space average. However, because of the finiteness of the simulation time, trajectories starting in different regions of the phase space may result in distinct time averages. Statistical theories of chemical systems are often faced by such problems of ''nonergodicity'' or ''broken ergodicity.''

Computer simulations of chemical reaction dynamics have demonstrated that the assumptions of statistical theories are often not met. For microcanonical (constant energy) reactions, in the KAM regime the reacting system may be ''nonergodic,'' due to impermeable barriers (invariant tori[1]) which limit the region of phase space a trajectory may explore, or ''quasiregular,'' due to semipermeable partitions (vague tori[2] or cantori[3]) which can greatly reduce the rate of travel through phase space. A statistical rate theory, which assumes that the phase space of the entire reaction region is accessible to any reactant regardless of its initial state, may greatly underestimate the reaction rate.[4]

The breakdown of statistical rate theory extends into the canonical (constant temperature) ensemble. An N-dimensional reaction system may be divided into a reaction coordinate and N-1 nonreactive coordinates. In the regime of fast intramolecular vibrational relaxation (IVR), the rate of energy equipartitioning between nonreactive coordinates and the reaction coordinate is fast compared with the reaction time scale and the reaction system is effectively N-dimensional. Due to damping of the nonreactive mode, or a change in the nonlinear coupling between modes, the rate of energy exchange between a nonreactive mode and the reaction coordinate can become slower than the reaction rate. In this regime of ''slow IVR,'' nonreactive modes are effectively eliminated from the reaction system and the dimensionality of the reaction system is reduced. This dynamical effect has been shown to lead to a significant decrease in the reaction rate in the energy diffusion regime.[5,6]

Calculation of equilibrium properties can be effected in similar ways. Nonergodicity can subvert the ergodic hypoth-esis (the indecomposable character of the measure) and averages derived from molecular dynamics computer simulation may differ greatly from the predictions of a statistical theory. However, the solution is straightforward. Using noisy molecular dynamics or Monte Carlo (MC) simulation it is possible to effectively sample nonergodic systems.[7]

Exploring systems whose phase space is partitioned by ''broken ergodicity'' is a much greater challenge. Broken ergodicity results when the time scale for measurement (a simulation or experimental average) is shorter than an important relaxation time scale for the system. In such cases the average which is calculated effectively ''breaks'' into sums of subaverages. Each subaverage is taken over a subset of the phase space. The problem is acute in complex disordered systems where the potential energy surface is rugged and regions of configurational space may be separated by energy barriers which are much greater than the thermal energy. For many systems of interest, such as proteins and glasses, the time scale for functionally important motions greatly exceeds that of molecular dynamics simulation.[8] Enhanced sampling algorithms which increase the frequency of barrier crossing allowing for an accelerated search of phase space are essential if reliable equilibrium averages are to be computed.

An important property of the sampling distribution is that it should include a significantly enhanced probability of making long range moves or simply visiting barrier regions. In systems such as proteins and glasses, it is difficult to make nonlocal moves which lead to thermodynamically important regions of phase space. A number of advances in Monte Carlo methodology which address the problem of broken ergodicity[9] have been reported in recent years. Rossky, Doll and Friedman[10] proposed the use of Brownian dynamics as a smart way of doing Monte Carlo simulations. Cao and Berne have developed an ''anti-force bias'' Monte Carlo method.[11] Anti-force bias Monte Carlo encourages the system to move toward minima in a convex region of the potential surface, or over barriers in a nonconvex region of the potential surface. The algorithm accelerates barrier crossing which may be an infrequent event. Frantz, Freeman and Doll[12] have proposed

the J-walking method which uses a high temperature MC run to generate trial moves. At high temperatures, barriers may be crossed easily, overcoming problems of broken ergodicity. The trial moves are accepted so as to compute averages at a lower temperature of interest. The J-walking method and a related method of Ferrenberg and Swendsen[13] have been employed by Tsai and Jordan to examine phase changes in small rare gas and water clusters.[14] Multicanonical Monte Carlo[15] and cluster move methods[16] have been developed to address problems of critical slowing down associated with phase transitions. These methods have also found some success in simulations of biomolecular systems[17] with moderate associated computational overhead.

In this paper we present an enhanced sampling algorithm based on the generalized thermodynamics proposed by Tsallis.[18] The algorithm generates a Monte Carlo walk through a well-defined generalized statistical distribution. An appropriately weighted average allows us to calculate equilibrium thermodynamic averages for the Gibbs–Boltzmann canonical ensemble. This generalized Monte Carlo algorithm is compared with standard Monte Carlo, and the J-walking algorithm of Franz, Freeman and Doll.[12] Application to a one-dimensional model potential and a 13-atom cluster modeled by Lennard-Jones interactions demonstrates the enhancement in sampling and efficiency in the computation of equilibrium thermodynamic averages.

II. GENERALIZED MONTE CARLO ALGORITHM

In this section we present a short introduction to the Tsallis statistical mechanics. Equilibrium distributions are derived and a Monte Carlo algorithm for sampling these distributions is defined. The properties of the algorithm and the general feature of enhanced frequency of barrier crossing are described in detail.

A. Tsallis statistics and generalized Monte Carlo methods

In the generalized statistical mechanics proposed by Tsallis, the ''generalized entropy'' for an N-body system is defined as[18,19]

$$S_q = \frac{k}{q-1} \int p_q(\mathbf{r}^N)(1 - [p_q(\mathbf{r}^N)]^{q-1}) d\mathbf{r}^N, \tag{1}$$

where q is a real number and S_q tends to the Gibbs–Shannon entropy $S = -k \int p(\mathbf{r}^N) \ln p(\mathbf{r}^N) d\mathbf{r}^N$ when $q=1$. To derive the configurational probability distribution function the generalized entropy is extremized subject to the constraints

$$\int p_q(\mathbf{r}^N) d\mathbf{r}^N = 1, \quad \int [p_q(\mathbf{r}^N)]^q U(\mathbf{r}^N) d\mathbf{r}^N = U_q, \tag{2}$$

where $U(\mathbf{r}^N)$ is the potential energy. The probability of a point in configuration space is found to be

$$p_q(\mathbf{r}^N) = \frac{1}{Z_q} [1 - (1-q)\beta U(\mathbf{r}^N)]^{1/(1-q)}, \tag{3}$$

where

$$Z_q = \int [1 - (1-q)\beta U(\mathbf{r}^N)]^{1/(1-q)} d\mathbf{r}^N \tag{4}$$

is the generalized configurational partition function.

We have proposed a Monte Carlo algorithm based on the acceptance probability

$$p = \min\left[1, \left(\frac{p_q(\mathbf{r}^N_{\text{new}})}{p_q(\mathbf{r}^N_{\text{old}})}\right)^q\right]. \tag{5}$$

This algorithm has been used to sample an equilibrium distribution proportional to $[p_q(\mathbf{r}^N)]^q$ in the conformational optimization of a tetrapeptide.[20] It was found that when $q>1$ the search of conformational space was greatly enhanced over standard Metropolis Monte Carlo methods. In this paper, we explore the use of this algorithm for the computation of equilibrium thermodynamic averages.

Note that by defining the effective potential

$$\bar{U} = \frac{q}{\beta(q-1)} \ln[1 - (1-q)\beta U] \tag{6}$$

the Monte Carlo acceptance probability Eq. (5) can be written in the familiar form

$$p = \min[1, \exp(-\beta \Delta \bar{U})]. \tag{7}$$

The standard Metropolis Monte Carlo method corresponds to the $q=1$ limit in which case the probability of accepting a new configuration of the system is

$$p = \min[1, \exp(-\beta \Delta U)], \tag{8}$$

where $\Delta U = U(\mathbf{r}^N_{\text{new}}) - U(\mathbf{r}^N_{\text{old}})$.

In the remainder of this section, we explore the properties of the Tsallis statistical Monte Carlo algorithm and a related molecular dynamics method.

B. Detailed balance and equilibrium averages

Equilibrium average properties are calculated using a statistical weighting of the probability $p_q(\mathbf{r}^N)$ of Eq. (3) raised to the power of q as required by the generalized statistical mechanics. The average of an observable O is *defined* by the so-called ''q-expectation value''

$$\langle O \rangle_q = \int [p_q(\mathbf{r}^N)]^q O(\mathbf{r}^N) d\mathbf{r}^N. \tag{9}$$

Consistently, the detailed balance condition is written as

$$[p_q(x)]^q W(x \to x') = [p_q(x')]^q W(x' \to x), \tag{10}$$

where $W(x \to x')$ is an element of the transition matrix.

The walk generated by Eq. (5) will sample the configuration space according to the distribution $[p_q(\mathbf{r}^N)]^q$. For most potentials, the moments of $p_q(\mathbf{r}^N)$ are well-defined and finite. In contrast, for certain values of q and a harmonic potential, the distribution $p_q(\mathbf{r}^N)$ can have infinite variance and higher moments. Still, this is of no practical concern for the simulation since a reweighting of the contribution of each phase point is performed (see Section II D) to obtain moments of the Gibbs–Boltzmann distribution. However, for all q the distribution $[p_q(\mathbf{r}^N)]^q$ is well-behaved for a harmonic

potential. This is important in the simulation of chemical systems where at low temperature the potential energy near a minimum is often effectively harmonic.

C. Dependence on the statistical distributions on the zero of energy

In contrast to our expectations developed in the Gibbs–Boltzmann statistical mechanics, in the $q \neq 1$ regime, the relative probability of two states depends on the choice of the zero of energy.[18] For example, for a constant potential shift ϵ

$$\frac{p_q(\mathbf{r}_{new}^N)}{p_q(\mathbf{r}_{old}^N)} = \left[\frac{1-(1-q)\beta(U(\mathbf{r}_{new}^N)+\epsilon)}{1-(1-q)\beta(U(\mathbf{r}_{old}^N)+\epsilon)} \right]^{1/(1-q)}, \quad (11)$$

Eq. (11) can be rewritten as

$$\frac{p_q(\mathbf{r}_{new}^N)}{p_q(\mathbf{r}_{old}^N)} = \left[\frac{1-(1-q)\beta' U(\mathbf{r}_{new}^N)}{1-(1-q)\beta' U(\mathbf{r}_{old}^N)} \right]^{1/(1-q)}, \quad (12)$$

where the potential shift ϵ has been absorbed in an effective temperature such that

$$\frac{1}{\beta'} = \frac{1}{\beta} - (1-q)\epsilon. \quad (13)$$

In the $q=1$ limit of Gibbs–Boltzmann statistics, the effective temperature equals the standard temperature. Otherwise, the potential shift has the effect of shifting the temperature at which the distribution is computed. For our purposes, we take ϵ to be an adjustable parameter which, like the acceptance ratio, may be optimized for a Monte Carlo run.

One might think that the larger the value of q (meaning a broader distribution function) the better for the enhancement of the phase space sampling. However, there is a weaker dependence on q of the acceptance probabiltiy. As q goes to infinity, the acceptance saturates

$$\lim_{q \to \infty} \frac{p_q^q(\mathbf{r}_{new}^N)}{p_q^q(\mathbf{r}_{old}^N)} = \frac{U(\mathbf{r}_{old}^N)}{U(\mathbf{r}_{new}^N)}. \quad (14)$$

This is reflected in the numerical simulation of a one dimensional potential discussed in a subsequent section.

D. Exact calculation of equilibrium averages by Tsallis statistical Monte Carlo method

Our enhanced sampling algorithm will be used to calculate standard, Gibbs–Boltzmann equilibrium thermodynamic averages over a trajectory which samples the generalized statistical distribution. The equilibrium average over configuration space for a given mechanical property $A(\mathbf{r}^N)$ in the Tsallis statistics is defined by the q-expectation value using Eq. (9) as

$$\langle A \rangle_q = \frac{1}{Z_q^q} \int A(\mathbf{r}^N)[1-(1-q)\beta U(\mathbf{r}^N)]^{q/(1-q)} d\mathbf{r}^N. \quad (15)$$

Using this definition, the equilibrium thermodynamic average of A in the $q=1$ canonical ensemble may be written as

$$\langle A \rangle_1 = \left\langle \frac{A e^{-\beta U(\mathbf{r}^N)}}{[1-(1-q)\beta U(\mathbf{r}^N)]^{q/(1-q)}} \right\rangle_q$$

$$\times \left\langle \frac{e^{-\beta U(\mathbf{r}^N)}}{[1-(1-q)\beta U(\mathbf{r}^N)]^{q/(1-q)}} \right\rangle_q^{-1}. \quad (16)$$

Using this expression, the standard $q=1$ equilibrium average properties may be calculated over a trajectory which samples the Tsallis statistical distribution for $q \neq 1$.

E. J-walking Monte Carlo and the histogram method

In the J-walking algorithm, a Monte Carlo trajectory is generated at a temperature $1/\beta$. With a probability $(1-P_J)$, a move is generated uniformly in a limited region leading to a change in potential energy of ΔU. The move is accepted with a probability

$$p = \min[1, \exp(-\beta \Delta U)]. \quad (17)$$

With a probability P_J, a "jump" move is randomly selected from an equilibrium Boltzmann distribution generated at a higher temperature $1/\beta_J$. The acceptance probability for the jump is

$$p = \min[1, \exp((\beta_J - \beta)\Delta U)]. \quad (18)$$

By allowing jumps chosen from a high temperature distribution, the J-walking algorithm encourages trajectories to overcome barriers which would be infrequently scaled at the lower sampling temperature.

As noted by Tsai and Jordan, the special case of the J-walking algorithm when the jump probability $P_J=1$ is equivalent to the single histogram method of Ferrenberg and Swendsen.[13] Thermodynamic averages at a given temperature $1/\beta$ may be calculated from a Monte Carlo trajectory generated at a higher temperature $1/\beta_J$. For example, if the average of $A(\mathbf{r}^N)$ over a high temperature trajectory at β_J is

$$\langle A \rangle_{\beta_J} = \frac{1}{Z_{\beta_J}} \int A(\mathbf{r}^N) \exp(-\beta_J U(\mathbf{r}^N)) d\mathbf{r}^N, \quad (19)$$

then the equilibrium thermodynamic average of A at β is[14]

$$\langle A \rangle_\beta = \langle A e^{(\beta_J - \beta)U(\mathbf{r}^N)} \rangle_{\beta_J} \langle e^{(\beta_J - \beta)U(\mathbf{r}^N)} \rangle_{\beta_J}^{-1}. \quad (20)$$

The key to an effective algorithm of the histogram/J-walking variety is to identify the optimal balance of the time spent in thermodynamically important basins of conformation space *versus* time spent in thermodynamically unimportant (high energy barrier) regions of the potential that are useful for traveling between basins. Choosing too low a sampling temperature $1/\beta_J$ will not overcome "broken ergodicity" or lead to enhanced barrier crossing. Choosing too high an effective temperature will bias the Monte Carlo walk away from the thermodynamically most important regions of phase space. Therefore, we can expect to identify an optimal choice of β_J and P_J which leads to the most rapid computation of equilibrium averages.

We adopt a protocol similar to that of the J-walking algorithm to implement with the Tsallis statistical Monte

Carlo. We dub it ''q-jumping.'' With probability P_q, we randomly sample from configurations distributed according to the Tsallis statistical distribution. With probability $1 - P_q$ we sample according to the Gibbs–Boltzmann distribution. When the move is suggested from the $q > 1$ distribution, it is accepted with the probability

$$p = \min\left[1, e^{-\beta\Delta U}\left(\frac{p_q(\mathbf{r}_{\text{old}}^N)}{p_q(\mathbf{r}_{\text{new}}^N)}\right)^q\right]. \tag{21}$$

The rest of the time, the acceptance probability is given by Eq.(8). The proof of detailed balance is straightforward. Denoting by $T_q(x \to x')$ the probability to suggest a move and $A_q(x \to x')$ the probability to accept it, for a given q, the transition matrix $W_q(x \to x') = T_q(x \to x')A_q(x \to x')$ and we have

$$P_q p(x) W_q(x \to x') + (1 - P_q) p(x) W_1(x \to x')$$
$$= P_q p(x') W_q(x' \to x) + (1 - P_q) p(x') W_1(x' \to x), \tag{22}$$

where $T_q(x \to x') = (1/Z_q^q)(1 - (1-q)\beta U(x'))^{q/(1-q)}$ when $q > 1$ and $T_q(x \to x') = 1/\Delta$ when $q = 1$, $A_q(x \to x')$ is given by Eq.(21) for $q > 1$ and $A_q(x \to x')$ is given by Eq.(8) for $q = 1$. Thus configuration space will be sampled according to the Gibbs distribution at temperature $1/\beta$.

F. Generalized molecular dynamics

As an alternative to MC sampling, one may sample the Tsallis probability distribution using an MD-based algorithm. For a given potential energy function $U(\mathbf{r}^N)$, the corresponding generalized statistical probability distribution which is generated by the generalized Monte Carlo algorithm is $P_q(\mathbf{r}^N) = [p_q(\mathbf{r}^N)]^q$. Consider the generalized distribution $P_q(\mathbf{r}^N)$ to be generated in the Gibbs–Boltzmann canonical ensemble ($q = 1$) by an effective potential $\mathscr{W}_q(\mathbf{r}^N; \beta)$ which is defined as

$$P_q(\mathbf{r}^N) = \exp(-\beta\mathscr{W}_q(\mathbf{r}^N; \beta)) \tag{23}$$

such that when $q = 1$, $\mathscr{W}(\mathbf{r}^N; \beta) = U(\mathbf{r}^N)$. For $q \neq 1$, the effective potential will depend on temperature as well as the coordinates.

Given this effective potential, it is possible to define a constant temperature molecular dynamics algorithm such that the trajectory samples the distribution $P_q(\mathbf{r}^N)$. The equation of motion takes on a simple and suggestive form

$$m_k\frac{d^2\mathbf{r}_k}{dt^2} = -\nabla_{\mathbf{r}_k}\bar{U} = -\nabla_{\mathbf{r}_k}U(\mathbf{r}^N)q[1 - (1-q)\beta U(\mathbf{r}^N)]^{-1} \tag{24}$$

for a particle of mass m_k and position $\mathbf{r}_k$ and $\bar{U}$ defined by Eq. (6).

The effective force derived from the effective potential $\mathscr{W}(\mathbf{r}^N)$ has a number of interesting properties. It is of the form $F_q(\mathbf{r}^N; \beta) = -\nabla_{\mathbf{r}_k}\bar{U} = F_1(\mathbf{r}^N)\alpha_q(\mathbf{r}^N; \beta)$ where $F_1(\mathbf{r}^N)$ is the ''exact'' force for standard molecular dynamics ($q = 1$) and $\alpha_q(\mathbf{r}^N; \beta)$ is a scaling function which is unity when $q = 1$ but can otherwise have a strong effect on the dynamics.
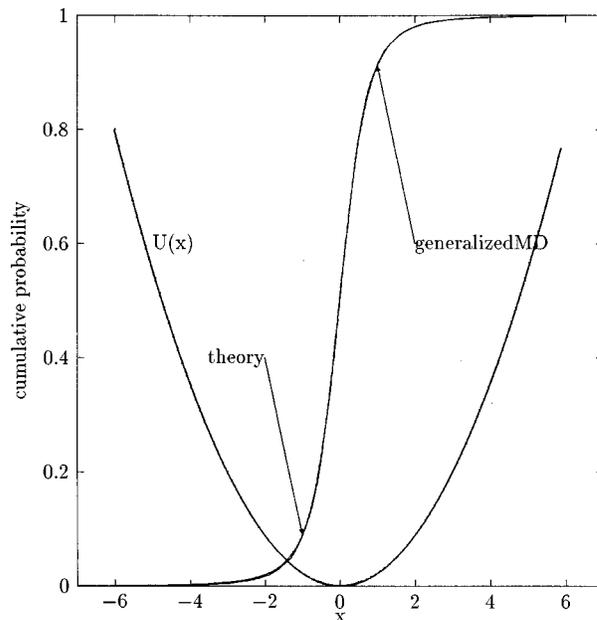

FIG. 1. The cumulative probability distribution generated by the generalized MD algorithm using the effective potential agrees well with the analytical distribution.

Assume that the potential is defined to be a positive function. In the regime $q > 1$, the scaling function $\alpha(\mathbf{r}^N, \beta)$ is largest near low lying minima of the potential. In barrier regions, where the potential energy is large, the scaling function $\alpha(\mathbf{r}^N, \beta)$ is small. This has the effect of reducing the magnitude of the force in the barrier regions. Therefore, a particle attempting to pass over a potential energy barrier will meet with less resistance when $q > 1$ then when $q = 1$. At equilibrium, this leads to more delocalized probability distributions with an increased probability of sampling barrier regions. This argument demonstrates that when $q > 1$ the generalized molecular dynamics or Monte Carlo trajectories will cross barriers more frequently and explore phase space more efficiently.

G. Proof of sampling distribution by the Kolmogorov–Smirnov test

We want to demonstrate that the generalized MD method samples the Tsallisian distribution. To do this, we employed the Kolmogorov–Smirnov test. We chose a harmonic potential, with temperature $T = 1$ and $q = 2$. The theoretical cumulative probability distribution can be obtained by integration of the probability in Eq. (23) for a harmonic oscillator. Using 1000 samples equidistantly sampled from a 10^4 step simulation, the significance level of agreement between the analytical distribution and that generated by solution of Eq. (24) was higher than 99.5%. A plot of the cumulative probability distribution obtained by the generalized MD simulation can be seen in Fig.1. The overlapped theoretical cumulative probability distribution is almost indistinguishable.

III. A MODEL POTENTIAL

In this section the properties developed in the previous section are explored for the case of a one-dimensional model potential $U(x)$ defined as

$$U(x) = x^2 - ae^{-b(x+2)^2} - ce^{-d(x-2)^2} - fe^{-g(x-3)^2} + \epsilon, \tag{25}$$

where ϵ is a constant potential shift that will make certain that the potential energy has positive values only. This energy function consists of four minima imposed on a harmonic background potential (see Fig. 2). We have used the parameters $a = f = 15, b = c = 10, d = g = 3$. The heights of the barriers separating the four minima vary greatly.

A. Tsallis statistical distributions and Monte Carlo walks

The generalized statistical distributions shown in Fig. 2 are compared with the standard $q = 1$ distribution. For $q > 1$ the distribution shows a significantly higher relative probability of being in the barrier region relative to the minima. This feature manifests itself during a Monte Carlo walk in a much higher frequency of barrier crossing. Fig. 3 shows a Monte Carlo walk for $q = 1$ which is characterized by infrequent hopping. For $q = 2$, the trajectory is much more delocalized as would be predicted for a jump diffusion process generated by a random sampling of the Tsallis statistical distribution.

B. Optimizing an algorithm

Throughout this study we employ as an indicator of the optimal values of the parameters the ergodic measure. The ergodic measure estimates the rate of self-averaging in an equilibrium MC or MD calculation.[21,22,8] Self-averaging is a necessary but not a sufficient condition for the ergodic hypothesis to be satisfied. The rate of self-averaging for a given property is expected to be proportional to the rate of phase space sampling. We have chosen to use the potential energy metric defined for two independent trajectories α and β. We define the ''move average'' over the Monte Carlo trajectory of the potential energy U for the jth particle along the α trajectory after n moves as

$$u_j^\alpha(n) = \frac{1}{\sum_k^n w(\mathbf{r}_k^N)} \sum_k^n w(\mathbf{r}_k^N) U_j(\mathbf{r}_k^N). \tag{26}$$

$w(\mathbf{r}_k^N)$ is a weighting factor for any property at a given position on the kth step $\mathbf{r}_k^N$. For a Metropolis Monte Carlo run the weighting factor is unity. For a generalized Monte Carlo run the weighting factor is given by Eq. (16). The ergodic measure is then defined as the sum over N particles

$$d_U(n) = \frac{1}{N} \sum_j [u_j^\alpha(n) - u_j^\beta(n)]^2. \tag{27}$$

For an ergodic system if $n \to \infty$, then $d_U(n) \to 0$. By analogy with molecular dynamics, for large n we expect the form of the convergence to be[23]
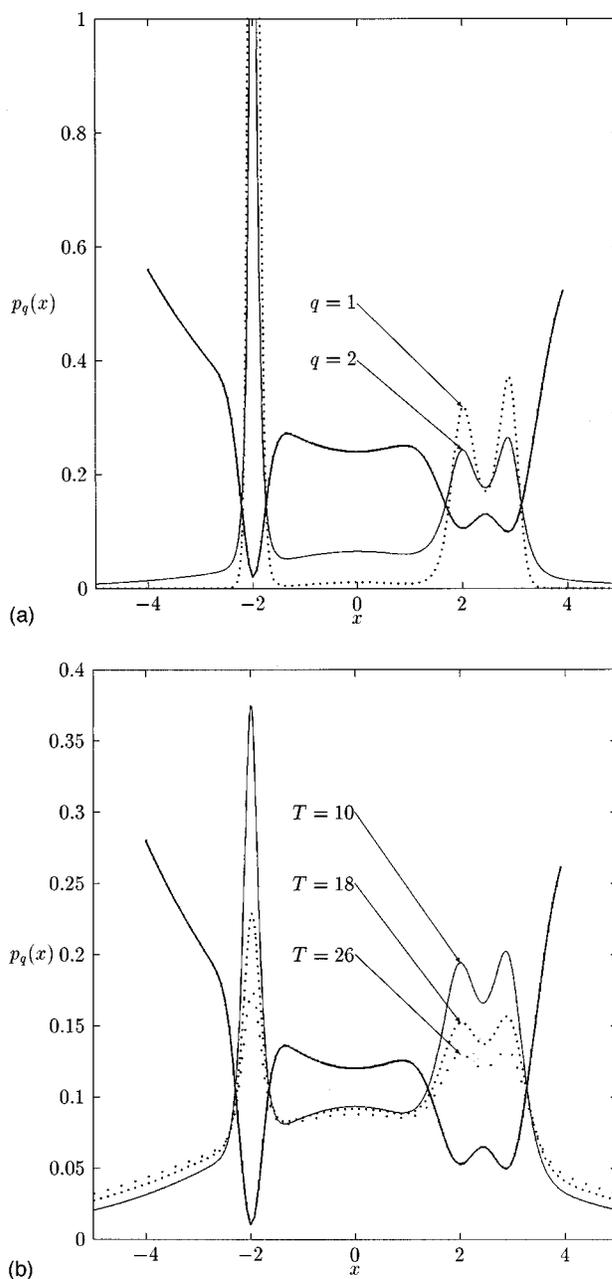

FIG. 2. (a) The one-dimensional model potential is drawn with a heavy line. The normalized equilibrium probability distributions are displayed over the model potential for $q = 2$ and $q = 1$ for the model potential. The Boltzmann distribution corresponds to $q = 1$. (b) Probability distributions for $q = 2$ at different temperatures. Note that even at the low temperature, the relative probability of being in the barrier region as opposed to the well region is significantly greater when $q > 1$ and does not level off with increasing temperature.

$$d_U(n) = d_U(0) \frac{1}{D_U n}, \tag{28}$$

where D_U is a rate for self-averaging of U over the two independent trajectories.

Throughout this study, we associate rapid and effective sampling of phase space with a large value of D_U. The choice of the potential energy metric is arbitrary. However, it
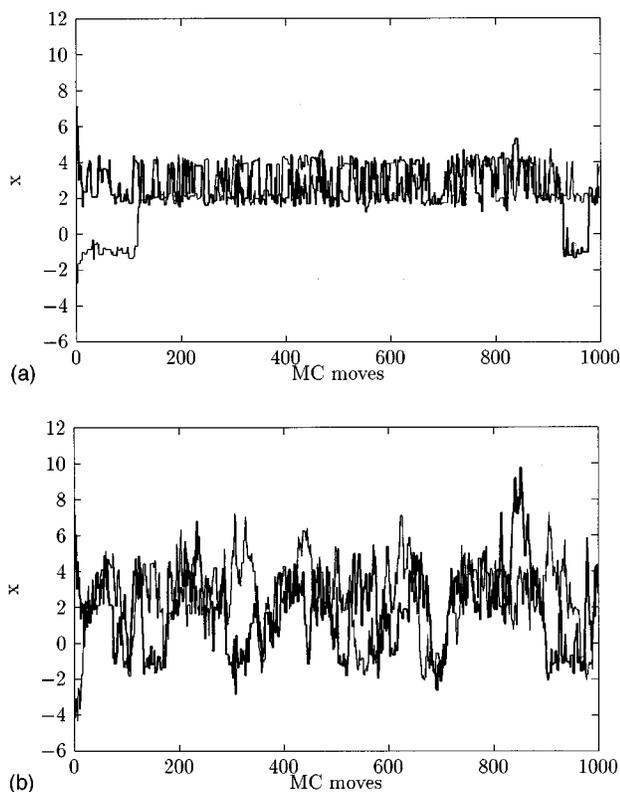
(a)

(b)

FIG. 3. Time series for Monte Carlo runs generated with (a) $q=1$ and (b) Tsallis statistical Monte Carlo ($q=2$). The number of barrier crossings and extent of conformation space explored is significantly greater for $q=2$. The qualitative features are the same for walks generated by the generalized molecular dynamics algorithm.

FIG. 4. The potential energy metric diffusion coefficient D_U generated by generalized Monte Carlo for $q=2$ as a function of the MC maximum step Δx for the one-dimensional model potential. The optimal value of Δx is that which maximizes the diffusion coefficient D_U and the rate of self-averaging of the potential energy. Each point's ordinate represents the average slope of the inverse metric calculated over 100 pairs of initial conditions. In each pair, one initial condition starts in the right well, the other in a left well.

has been shown to be a good measure of the extent of phase space sampling in a variety of systems. For the Monte Carlo algorithms studied, we vary the parameters of the algorithm to determine the optimal parameter set which maximizes D_U.

For all Monte Carlo algorithms there is the acceptance ratio which can be optimized. For the histogram/J-walking algorithm with fixed P_J, the sampling temperature $1/\beta_J$ should be optimized. One of the problems of the J-walking algorithm is the lack of *a priori* knowledge of the higher temperature distributions. For the generalized Monte Carlo algorithm, the two additional parameters (1) the potential energy shift ϵ and (2) the parameter q should be optimized. In this work, we take the optimal value of any parameter of the algorithm to be that which maximizes D_U— the rate of self-averaging of the thermodynamic potential energy.

In Fig. 4 the generalized diffusion coefficient D_U is shown to have a clear maximum as a function of the step size for the MC protocol. The optimal choice of the time step can be derived from an exploratory plot of this kind. Similarly, the potential energy shift ϵ (see Fig. 6) and the parameter q (see Fig. 5) may be optimized by maximizing D_U.

In general, we expect correlations in D_U between the values of Δx, ϵ and q and an iterative optimization is best performed. However, due to the simple behavior of D_U on each parameter, the correlation between parameters is ex-
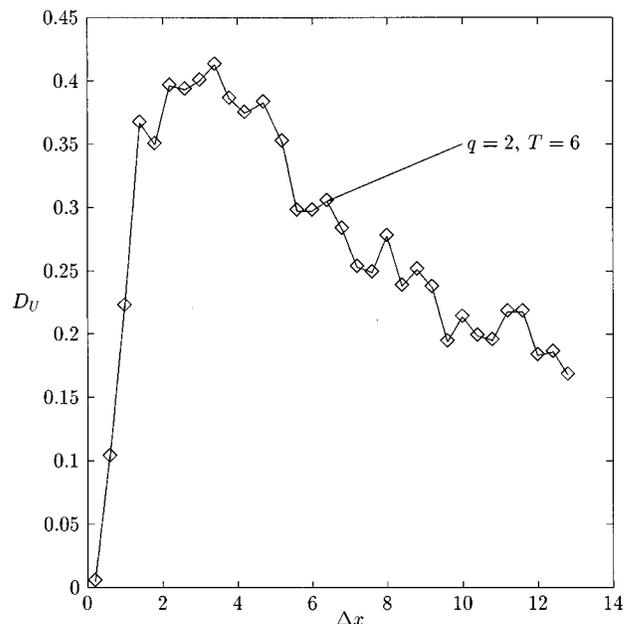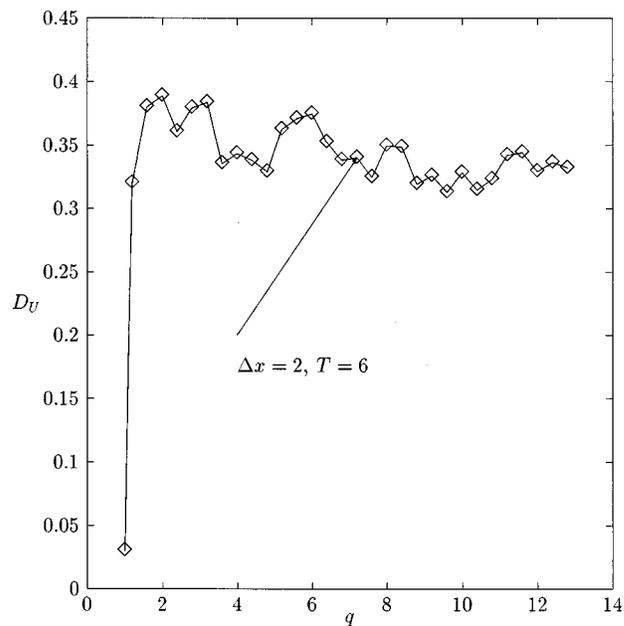

FIG. 5. The potential energy metric diffusion coefficient D_U generated by generalized Monte Carlo for $q=2$ as a function of the Tsallis ''q'' parameter for the one-dimensional model potential. The optimal value of ''q'' is that which maximizes the diffusion coefficient D_U and the rate of self-averaging of the potential energy. Note the saturation of the diffusion coefficient, paralleling the saturation of the acceptance in Eq. (5) for increasing q.
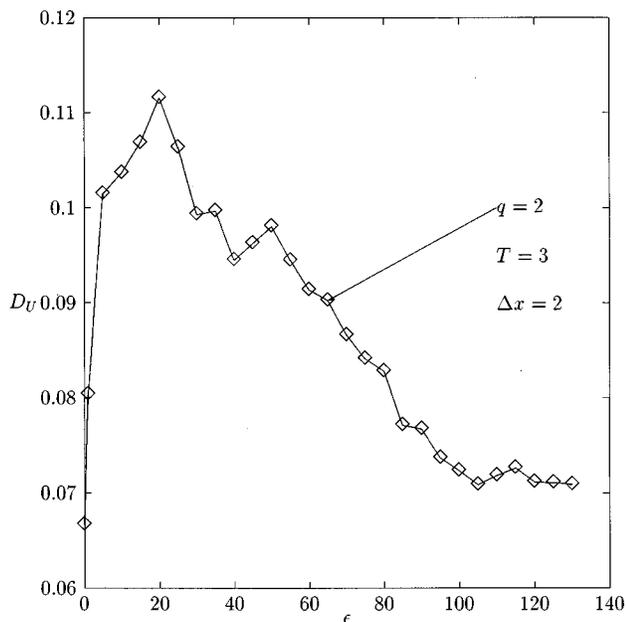
FIG. 6. The potential energy metric diffusion coefficient D_U generated by generalized Monte Carlo for $q=2$ as a function of the potential energy shift ϵ for the one-dimensional model potential. The optimal value of ϵ is that which maximizes the diffusion coefficient D_U and the rate of self-averaging of the potential energy.

FIG. 7. The convergence of the average potential energy in the case of a low temperature 13-atom cluster is shown for q-jumping Monte Carlo (lower curve) and standard Metropolis Monte Carlo (upper curve). There is essentially no convergence for the standard Monte Carlo trajectories which are trapped in their initial basins. The q-jumping Monte Carlo method is effective in allowing for transitions between basins leading to rapid convergence of the average potential energy.

pected to be weak which allows for a rapid convergence to a set of optimal parameter values. In accordance with Eq. (13) the temperature dependence of D_U is expected to behave as the dependence on potential shift ϵ. This is seen in Fig. 6.

IV. APPLICATION TO A 13-ATOM CLUSTER

We have applied the algorithm to a cluster of 13 atoms. The potential is pairwise additive, each pair interaction consisting of a Lennard-Jones potential expressed in energy units of the well depth and length units of the pair equilibrium distance

$$V(r) = \frac{1}{r^{12}} - \frac{2}{r^6}, \tag{29}$$

where r is the interatomic distance. To confine the atoms during the conjugate gradient search, we have also added to the Lennard-Jones pairwise interaction a confining boundary potential of the type $(r/r_0)^{\alpha}$, where $r_0 = 5$. Because of the shape of such a confinement, it has a negligible effect on the small interatomic distances. We have chosen a value of $\alpha = 20$.

A. Low temperature dynamics

To show the breakdown of ergodicity at low temperatures, we show in Fig. 7 the energy metric for our method in comparison with the normal Metropolis Monte Carlo. Our method consists of the q-jumping algorithm described earlier with $q=2$. The simulation was performed at a temperature of 0.2 reduced units (Boltzmann's constant is unity).

The energy metric is computed by starting from two configurations that are different in the sense that conjugate
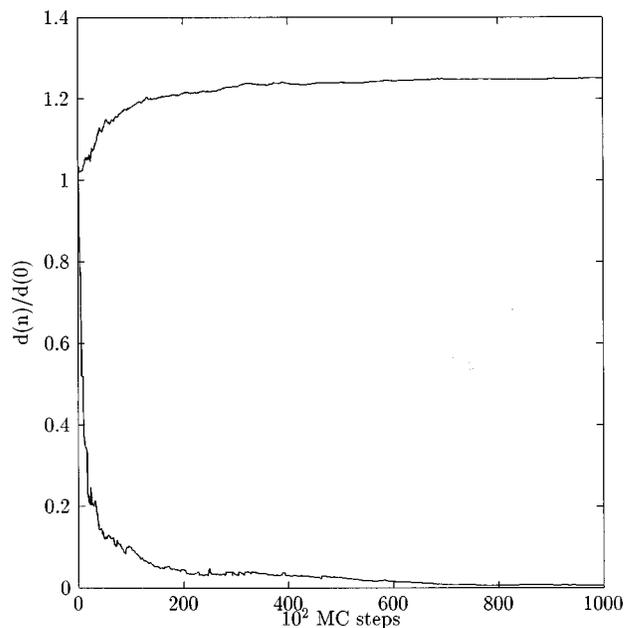
gradient minimization applied to each configuration leads to different minimized configurations. That is, the initial configurations were in different ''catchment regions'' (or ''basins of attraction''). In this range of temperature (0.2–0.4 reduced units) it is known that the argon clusters, for example, exist in a region of coexistence between liquid-like and solid-like structures. The coexistence region is defined by the temperature range bounded by the melting and freezing temperatures. The minimum energy geometry is an icosahedron. This so-called ''magic number'' cluster is a standard because it exhibits a large energy gap between the ''ground state'' of potential energy and the ''first-excited'' state, and a time-scale difference exists between inter- and intrawell motions. As a consequence it has a sizeable coexistence region.

The q-jumping Monte Carlo algorithm provides for rapid convergence of the equilibrium average of the potential energy while the standard Monte Carlo simulation shows little or no convergence over the length of the runs. In this case, the q-jumping MC algorithm is effective in overcoming the broken ergodicity encountered at low temperatures.

B. Comparison of algorithms

In Fig. 8 we show the comparison of the rate of self-averaging of the potential energy for a 13-atom cluster using the q-jumping and the J-walking MC methods. The q-jump method has a self-averaging rate roughly twice that of the J-walking algorithm. In the J-walking method, because the distributions at higher temperatures do not overlap with the
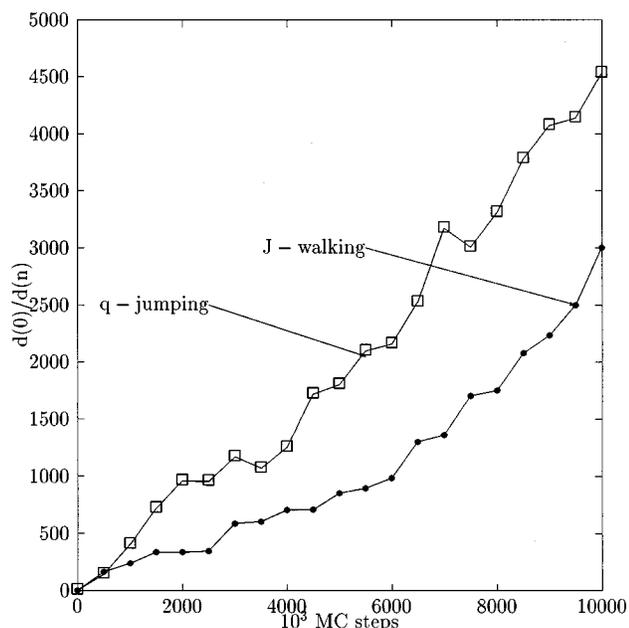
FIG. 8. The inverse of the energy metric for the 13-atom cluster for q-jumping and the J-walking algorithm with $P_q = P_J = 0.1$. The q-jumping Monte Carlo algorithm leads to a more rapid convergence of the thermodynamic average with a smaller associated computational overhead.

distributions at much lower temperatures, a stepwise decrease of temperature is used; configurations are stored at the higher temperature steps to be used for the lower temperature steps. For the case of the 13-atom cluster, Frantz *et al.* used temperatures of 50, 40, and 30 K to calculate equilibrium properties at 20 K. Following those authors, the J-walking data presented for comparison are generated at the same temperatures. As seen in Fig. 2, the Tsallisian distributions overlap in the barrier region. Therefore, no intermediate storage is needed. The q-jump method has the advantage over the J-walking method that no previously stored configurations are needed for intermediate q values. Only a single run at elevated q is required to generate configurations for trial ''jumps.'' An advantage over the multicanonical Monte Carlo algorithm[15] is that the q-jumping method does not require a previous estimation of the weight. For the q distributions the Tsallis weight is known. In instances where the delocalization (broadening) of the distribution function in the Tsallis ensemble is not sufficient, additional temperature increase can be performed.

V. CONCLUSION

We have presented algorithms to perform enhanced sampling of phase space for systems which suffer from broken ergodicity. One method is based on Monte Carlo, the other on molecular dynamics. Both algorithms sample phase space according to the generalized statistical distribution of Tsallis. Because of the delocalized character of these distributions for $q > 1$, sampling of the phase space is greatly enhanced. This allows for fast convergence of the equilibrium average in the canonical ensemble when appropriate reweighting is performed, even if the sampling is done in the Tsallis statistical ensemble.

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