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Molecular dynamics, Langevin and hybrid Monte Carlo simulations in a multicanonical ensemble

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Abstract

We demonstrate that the multicanonical approach is not restricted to Monte Carlo simulations, but can also be applied to simulation techniques such as the molecular dynamics, Langevin and hybrid Monte Carlo algorithms. The effectiveness of the methods is tested with an energy function for the protein folding problem. Simulations in the multicanonical ensemble by the three methods are performed for a penta peptide, Met-enkephalin. For each algorithm, it is shown that from only one simulation run one cannot only find the global minimum energy conformation but also obtain probability distributions in the canonical ensemble at any temperature, which allows the calculation of any thermodynamic quantity as a function of temperature.

1. Introduction

Simulations in a system with many degrees of freedom by conventional methods such as molecular dynamics (MD) and Monte Carlo (MC) can sample only a small portion of the entire phase space, rendering the calculations of various thermodynamic quantities inaccurate. This is because the energy function has many local minima, and at low temperatures simulations will necessarily get trapped in the configurations corresponding to one of these local minima. In order to overcome this multiple minima problem, many methods have been proposed. For instance, simulated annealing [1] is one of the most widely used algorithms for locating the global minimum state out of the multitude of local minimum states. The multicanonical approach [2,3] is another powerful technique. The advantage of this algorithm lies in the fact that from only one simulation run one cannot only find the energy global minimum but also calculate various thermodynamic quantities at any temperature. The method was originally developed to overcome the supercritical slowing down of first-order phase transitions [2,3], and then proposed to be used for systems that suffer from the multiple minima problem such as spin glasses [4] and the protein folding problem [5]. The same method was later referred to as entropic sampling [6], but a proof of the equivalence of the two methods was given to clarify the matter [7]. In the context of the protein folding problem, the effectiveness of multicanonical algorithms was compared with that of simulated

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annealing [8]. It was also used to study the coil–globular transitions of a model protein [9], helix–coil transitions of amino acid homo-oligomers [10], and conformational sampling of a constrained peptide [11].

In all of the previous works the multicanonical ansatz was used in the context of Monte Carlo simulations utilizing mostly the Metropolis algorithm [12] to generate a Markov chain of configurations. However, other simulation techniques such as molecular dynamics [13] are also widely used. The purpose of the present work is to demonstrate that these techniques can be used for simulations in a *multicanonical ensemble*. Here, we consider three common algorithms: molecular dynamics, Langevin [14] and hybrid Monte Carlo [15]. The performances of the algorithms are tested with the system of an oligopeptide, Met-enkephalin.

2. Methods

2.1. Multicanonical ensemble

Simulations in the canonical ensemble at temperature T weigh each state with the Boltzmann factor

$$w_B(E, T) = e^{-\hat{\beta}E}, \tag{1}$$

where the inverse temperature is given by $\hat{\beta} = 1/k_B T$ with Boltzmann constant k_B. This weight factor gives the usual bell-shaped canonical probability distribution of energy:

$$P_B(E, T) \propto n(E) w_B(E, T), \tag{2}$$

where $n(E)$ is the density of states.

In the *multicanonical ensemble* [2], on the other hand, the probability distribution of energy is *defined* to be constant:

$$P_{mu}(E) \propto n(E) w_{mu}(E) = \text{const}. \tag{3}$$

The multicanonical weight factor for each state with energy E is then given by

$$w_{mu}(E) \propto n^{-1}(E) = e^{-S(E)}, \tag{4}$$

where $S(E)$ is the microcanonical entropy (with $k_B = 1$):

$$S(E) = \ln n(E). \tag{5}$$

With the uniform probability distribution of Eq. (3), a simulation in the multicanonical ensemble leads to a 1D random walk in energy space, allowing itself to escape from any energy barrier and to explore a wide range of the phase space.

Unlike in a canonical simulation, however, the multicanonical weight $w_{mu}(E)$ is not a priori known, and one has to obtain its estimator for a numerical simulation. Hence, the multicanonical ansatz consists of three steps. In the first step the estimator of the multicanonical weight factor $w_{mu}(E)$ is calculated (for details of the method of finding $w_{mu}(E)$ for the case of the Metropolis Monte Carlo algorithm, see Refs. [3,8]). Then one makes with this weight factor a production run with high statistics. In this way information is collected over the whole energy range. Finally, by examining the history of this simulation, one cannot only locate the energy global minimum but also obtain the canonical distribution at any inverse temperature $\hat{\beta}$ for a wide range of temperatures by the re-weighting techniques [16]:

$$P_B(E, T) \propto P_{mu}(E) w_{mu}^{-1}(E) e^{-\hat{\beta}E}. \tag{6}$$

This allows one to calculate the expectation value of any physical quantity $\mathcal{O}$ by

$$\langle \mathcal{O} \rangle_T = \frac{\int dE \mathcal{O}(E) P_B(E, T)}{\int dE P_B(E, T)}. \tag{7}$$

In the following subsections, we describe how to implement multicanonical simulations for the Langevin, molecular dynamics and hybrid Monte Carlo algorithms.

2.2. Langevin algorithm in a multicanonical ensemble

The Langevin algorithm [14] is used to integrate the following differential equation:

$$\dot{q}_i = -\hat{\beta} \frac{\partial E(q)}{\partial q_i} + \eta_i, \tag{8}$$

where q_i $(i = 1, \ldots, N)$ are the (generalized) coodinates of the system, $E(q)$ is the potential energy and η_i is a set of independent Gaussian distributed random variables with a unit variance:

$$\langle \eta_i(t_l) \eta_j(t_m) \rangle = \delta_{ij} \delta(t_l - t_m). \tag{9}$$

It can be shown that the dynamics based on the Langevin algorithm yields a canonical distribution

$P_B(E, T) \propto n(E)e^{-\hat{\beta}E}$. For numerical work one integrates the above equation by discretizing the time with step Δt:

$$q_i(t+\Delta t) = q_i(t) + \Delta t\left(-\hat{\beta}\frac{\partial E(q)}{\partial q_i(t)} + \eta_i(t)\right). \tag{10}$$

A straightforward generalization of this technique to simulations in a multicanonical ensemble can be made by replacing the $\hat{\beta}E$ in Eq. (8) by the microcanonical entropy $S(E)$:

$$\dot{q}_i = \frac{-\partial S(E(q))}{\partial q_i} + \eta_i. \tag{11}$$

The above equation now describes dynamics which will yield a *multicanonical* distribution $P_{mu}(E) \propto n(E)e^{-S(E)} = \text{const}$ (see Eq. (4)). (A similar consideration of the multicanonical Langevin algorithm is given in Ref. [17].) Hence, for the actual simulations we use the following difference equation:

$$q_i(t+\Delta t) = q_i(t) + \Delta t\left(-\frac{\partial S(E(q))}{\partial q_i(t)} + \eta_i(t)\right). \tag{12}$$

We remark that Eq. (11) can be written as

$$\dot{q}_i = -\frac{\partial S}{\partial E}\frac{\partial E(q)}{\partial q_i} + \eta_i = -\beta(E)\frac{\partial E(q)}{\partial q_i} + \eta_i, \tag{13}$$

where $\beta(E)$ is an energy-dependent effective inverse temperature. In this notation the term "multicanonical" becomes obvious (compare Eq. (13) with Eq. (8)).

2.3. Molecular dynamics algorithm in a multicanonical ensemble

The expectation value of a physical quantity $\mathcal{O}$ is calculated by

$$\langle \mathcal{O} \rangle_T = \frac{\int \mathrm{D}q\, \mathcal{O}(q) e^{-\hat{\beta}E(q)}}{\int \mathrm{d}q e^{-\hat{\beta}E(q)}}, \tag{14}$$

where the integration measure is defined by $\mathrm{D}q = \prod_{i=1}^{N} \mathrm{d}q_i$ and q_i $(i = 1, \ldots, N)$ are again the (generalized) coordinates of a system. $E(q)$ is the potential energy of the system. The above equation is mathematically identical with

$$\langle \mathcal{O} \rangle_T = \frac{\int \mathrm{D}q\, \mathrm{D}\pi \mathcal{O}(q) \exp\left[-\sum_{i=1}^{N} \pi_i^2/2m_i - \hat{\beta}E(q)\right]}{\int \mathrm{D}q\, \mathrm{D}\pi \exp\left[-\sum_{i=1}^{N} \pi_i^2/2m_i - \hat{\beta}E(q)\right]}, \tag{15}$$

where we used the notation $\mathrm{D}\pi = \prod_{i=1}^{N} \mathrm{d}\pi_i$. Identifying the auxiliary variables π_i with the conjugate momenta corresponding to the coordinates q_i, we can describe our system with a Hamiltonian

$$H(q, \pi) = \frac{1}{2}\sum_{i=1}^{N} \pi_i^2 + \hat{\beta}E(q_1, \ldots, q_N), \tag{16}$$

where we have set all the masses m_i equal to 1 for simplicity.

The classical molecular dynamics algorithm uses Hamilton's equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial \pi} = \pi_i,$$
$$\dot{\pi}_i = -\frac{\partial H}{\partial q_i} = -\hat{\beta}\frac{\partial E}{\partial q_i}, \tag{17}$$

to generate representative ensembles of configurations. For numerical work the time is discretized with step Δt and the equations are integrated according to the *leapfrog* (or other time reversible integration) scheme:

$$q_i(t+\Delta t) = q_i(t) + \Delta t \pi_i\left(t + \tfrac{1}{2}\Delta t\right),$$
$$\pi_i\left(t + \tfrac{3}{2}\Delta t\right) = \pi_i\left(t + \tfrac{1}{2}\Delta t\right) - \Delta t \hat{\beta}\frac{\partial E}{\partial q_i(t+\Delta t)}. \tag{18}$$

The initial momenta $\{\pi_i(\frac{1}{2}\Delta t)\}$ for the iteration are prepared by

$$\pi_i\left(\tfrac{1}{2}\Delta t\right) = \pi_i(0) - \tfrac{1}{2}\Delta t \hat{\beta}\frac{\partial E}{\partial q_i(0)}, \tag{19}$$

with appropriately chosen $q_i(0)$ and $\pi_i(0)$ ($\pi_i(0)$ is from a Gaussian distribution).

In order to generalize this widely used technique to simulations in a multicanonical ensemble, we again propose to replace $\hat{\beta}E$ by the entropy $S(E)$ in Eqs. (17), (18) and (19) (just as we did for the

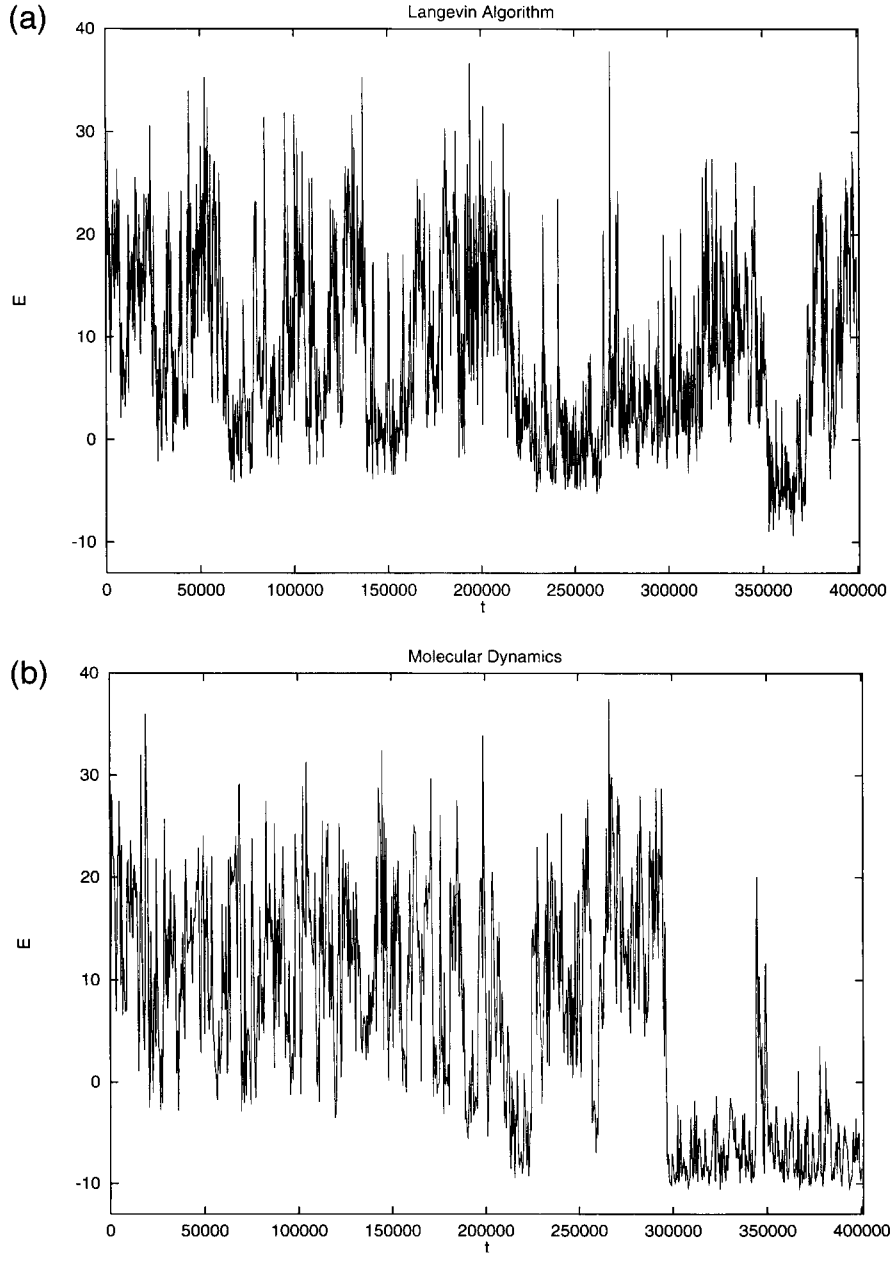

Fig. 1. (a) Time series of the total potential energy E (kcal/mol) from a multicanonical Langevin simulation of 400000 × 19 time steps with step size $\Delta t = 0.0001$. (b) Time series of E from a multicanonical molecular dynamics simulation of 400000 × 19 time steps with step size $\Delta t = 0.005$. (c) Time series of E from a multicanonical hybrid Monte Carlo simulation of 200000 MC steps. For each MC step an MD run of 19 time steps was made with step size $\Delta t = 0.01$.

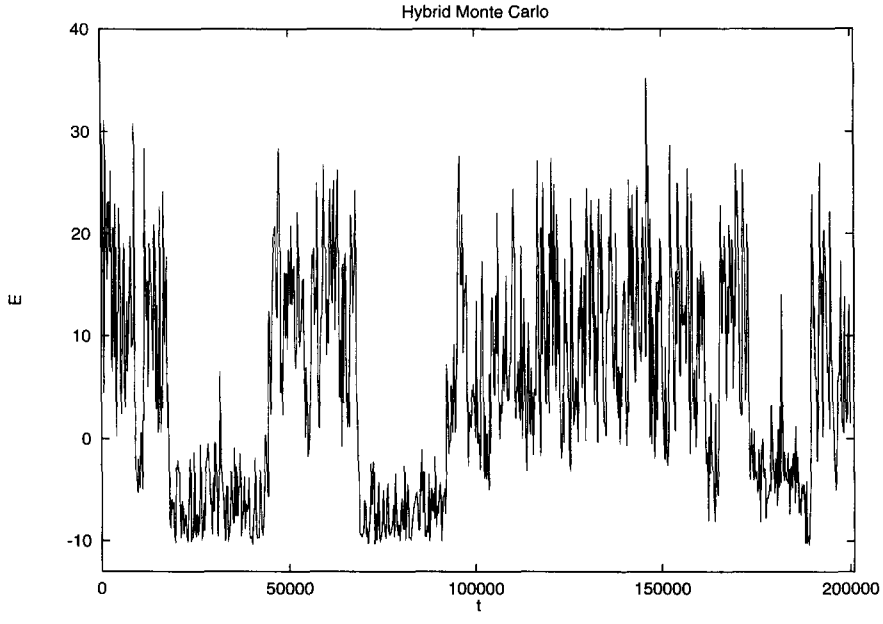

Fig. 1. (continued).

Langevin algorithm). Hence, we have a new "Hamiltonian"

$$H(q, \pi) = \frac{1}{2} \sum_{i=1}^{N} \pi_i^2 + S(E(q)), \tag{20}$$

and a new set of Hamilton's equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial \pi_i} = \pi_i,$$
$$\dot{\pi}_i = -\frac{\partial H}{\partial q_i} = -\frac{\partial S(E(q))}{\partial q_i} = -\frac{\partial S}{\partial E}\frac{\partial E(q)}{\partial q_i}. \tag{21}$$

This is the set of equations we adopt for multicanonical MD simulations. Formally, it can be understood as a rescaling of the usual force term by the derivative of the entropy. For numerical simulations the Hamilton equations are again discretized in time and integrated by a *leapfrog* scheme. In analogy to the case of canonical MD, convergence to the multicanonical ensemble can be proven if $\frac{1}{2}\sum_{i=1}^{N}\pi_i^2$ is kept fixed.

2.4. Hybrid Monte Carlo algorithm in a multicanonical ensemble

The hybrid Monte Carlo algorithm [15] is based on a combination of the molecular dynamics and Metropolis Monte Carlo algorithms; namely, each proposal for the Metropolis method is prepared by a short MD run starting from the actual configuration. Hence, this algorithm is based on a global update, while in the conventional Metropolis method one is usually restricted to a local update. Furthermore, the Metropolis step ensures that the sampled configurations are distributed according to the chosen ensemble, while conventional molecular dynamics simulations are hampered by difficult-to-control systematic errors due to finite step size in the integration of the equations of motion.

Given the set of coordinates $\{q_i\}$ of the previous configuration and choosing the corresponding momenta $\{\pi_i\}$ from a Gaussian distribution, a certain number of MD steps are performed to obtain a candidate configuration $\{q_i', \pi_i'\}$. This candidate is accepted according to the Metropolis Monte Carlo criterion with probability

$$p = \min\{1, e^{-(H(q',\pi') - H(q,\pi))}\}, \tag{22}$$

where H is the Hamiltonian in Eq. (16). The time reversibility of the *leapfrog* integration scheme ensures detailed balance and therefore convergence to the correct distribution. The whole process is re-

peated for a desired number of times (Monte Carlo steps). The number of integration (*leapfrog*) steps N_{LF} and the size of the time step Δt are free parameters in the hybrid Monte Carlo algorithm, which have to be tuned carefully. A choice of too small N_{LF} and Δt means that the sampled configura-

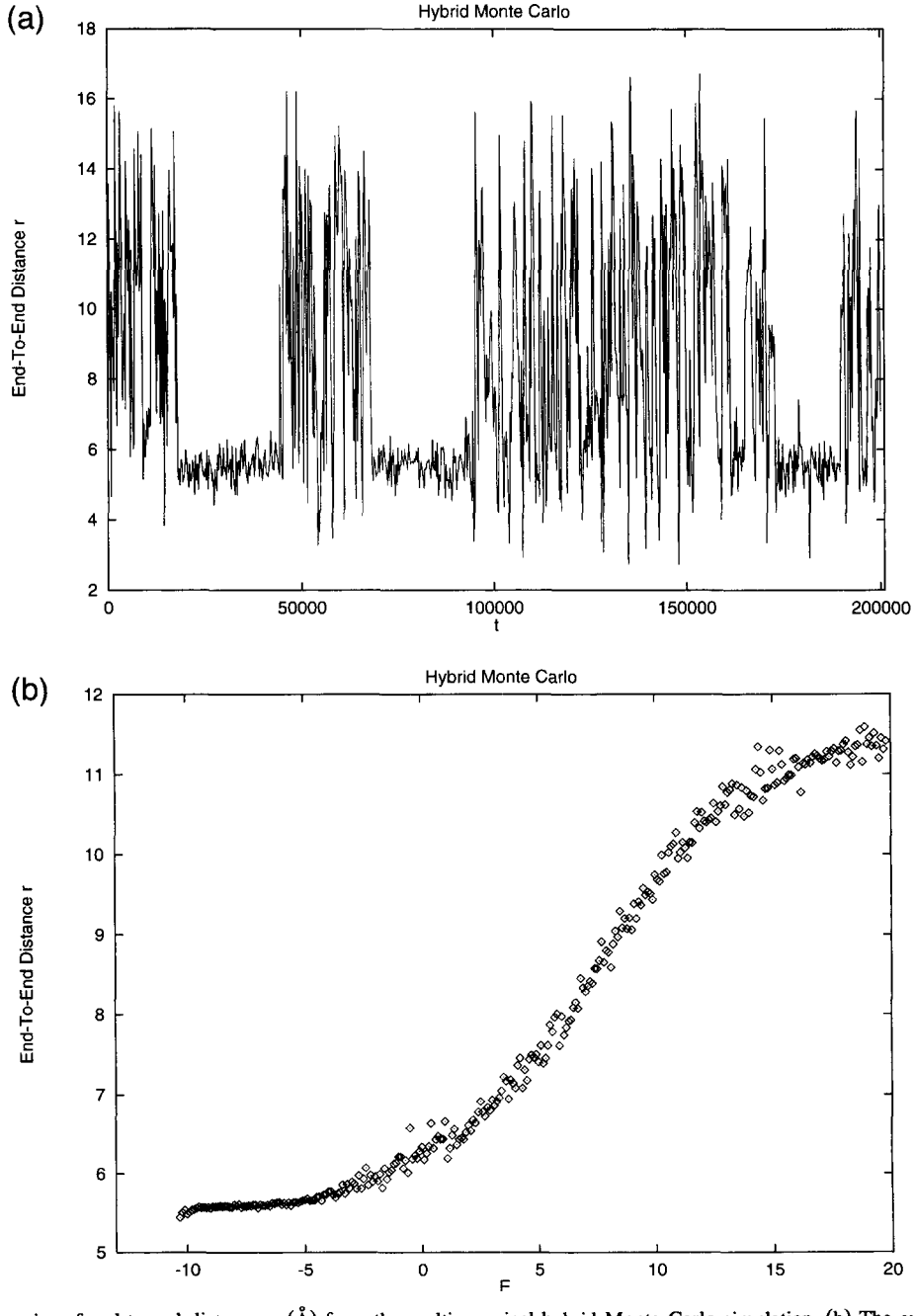

Fig. 2. (a) Time series of end-to-end distance r (Å) from the multicanonical hybrid Monte Carlo simulation. (b) The average end-to-end distance r as a function of potential energy E obtained from the multicanonical hybrid Monte Carlo simulation.

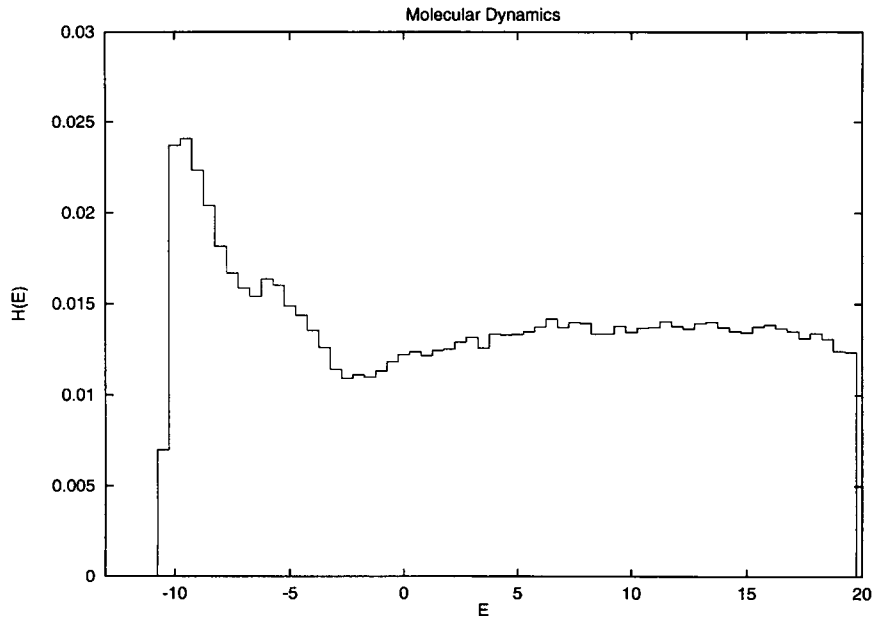

Fig. 3. Probability distribution of potential energy E obtained from the multicanonical molecular dynamics simulation.

tions are too much correlated, while too large N_{LF} (or Δt) yields high rejection rates. In both cases the algorithm becomes inefficient.

The generalization of this technique to simulations in a multicanonical ensemble can again be made by replacing the Hamiltonian of Eq. (16) with the multicanonical Hamiltonian of Eq. (20), i.e. replacing $\hat{\beta}E$ by the entropy $S(E)$ in the equations of motion.

3. Results and discussion

The effectiveness of the algorithms presented in the previous section is tested for the system of an oligopeptide, Met-enkephalin. This peptide has the amino acid sequence Tyr–Gly–Gly–Phe–Met. The potential energy function that we used is given by the sum of an electrostatic term, a Lennard-Jones term and a hydrogen-bond term for all pairs of atoms in the peptide together with the torsion term for all torsion angles. The parameters for the energy function were adopted from ECEPP/2 [18–20]. The computer code SMC [1] was modified to accommodate the multicanonical ensemble.

For the coordinates $\{q_i\}$ we used the dihedral angles. (We remark that it was recently claimed that convergence is faster for the dihedral coordinates [22]. We could have used Cartesian coordinates as well with the same set of equations.) The peptide-bond dihedral angles ω were fixed to be 180° for simplicity. This leaves 19 dihedral angles as generalized coordinates. By the definition of a multicanonical ensemble, one cannot obtain information on the real dynamics of the system by the MD algorithm, and only static thermodynamic quantities can be calculated. For this reason we need not consider the equations of motion for a dihedral space as presented in Ref. [23], but can use the much simpler form as given in the previous section. However, we remark that this may not be the optimal choice. Often it may be more suitable to distinguish between "soft" and "hard" degrees of freedom and introduce appropri-

[1] The program SMC was written by Eisenmenger [21].

ately chosen "masses" in the equations of motion [22].

For the multicanonical MD simulations, we made a single production run with the total number of time steps $N_{LF} = 400000 \times 19$ and the time-step size $\Delta t = 0.005$ (in arbitrary units), after the optimal estimate for the multicanonical weight factor $w_{mu}(E)$, or entropy $S(E)$, was obtained. For the multicanonical Langevin algorithm, a production run with the same number of time steps ($N_{LF} = 400000 \times 19$) as in the MD simulation, but our optimal time-step size was only $\Delta t = 0.0001$. This indicates that the simulation moves more slowly through phase space, and we expect slower convergence to the multicanonical distribution than in the MD case. For the multicanonical hybrid Monte Carlo algorithm, an MD simulation with 19 leapfrog steps was made for each Monte Carlo step and a production run with 200000 MC steps was made. Since the Metropolis step in hybrid Monte Carlo corrects for errors due to the numerical integration of the equation of motion, the time-step size can be large for this algorithm. We chose $\Delta t =$ 0.01 in our units. The initial conformation for all three simulations was the final (and therefore equilibrized) conformation obtained from a multicanonical Monte Carlo simulation of 200000 sweeps, following 1000 sweeps for thermalization with the same weights (in each sweep all of the 19 angles were updated once).

In Fig. 1 the time series of the total potential energy are shown for the three multicanonical simulations. They all display a random walk in energy as they should for a simulation in a multicanonical ensemble. All the lowest-energy conformations were essentially the same (with only a small amount of deviation for each dihedral angle) as that of the global minimum energy conformation previously obtained for the same energy function (with $\omega = 180°$) by other methods [5,24,25]. The global minimum potential energy value obtained by minimization is -10.7 kcal/mol [25]. The random walks of the MD and hybrid MC simulations visited the global minimum region ($E < -10$ kcal/mol) three times and five times, respectively, while that of the Langevin

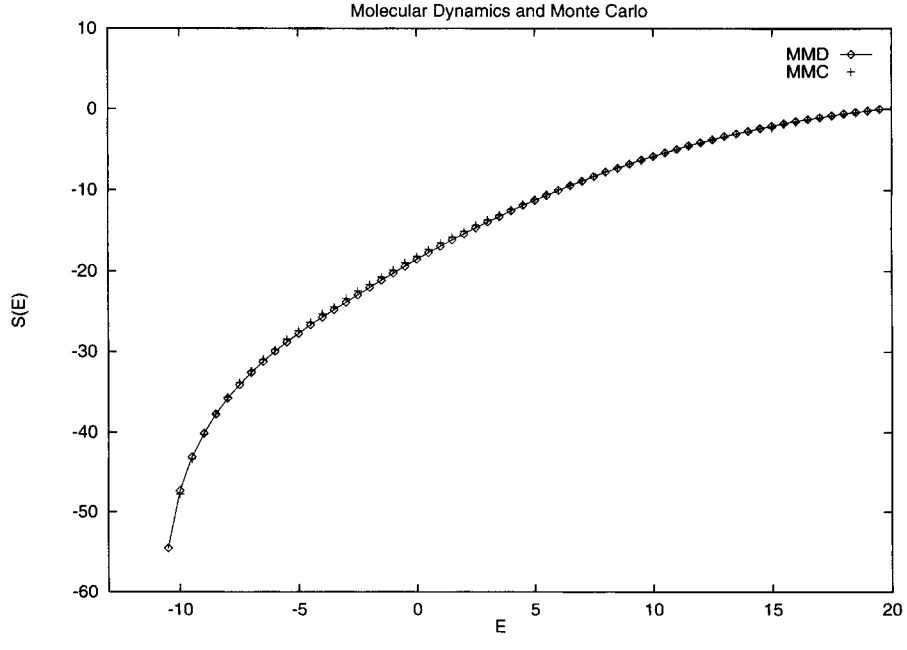

Fig. 4. Microcanonical entropy $S(E)$ as a function of potential energy E obtained from the multicanonical molecular dynamics simulation (MMD) and multicanonical Monte Carlo simulation (MMC).

simulation reached the region only once. These visits are separated by walks towards the high energy region much above $E = 16$ kcal/mol, which corresponds to the average energy at $T = 1000$ K [5]. We remark that the random walk for a regular multicanonical Monte Carlo simulation reached the global minimum region about four times in 200000 MC sweeps [8]. Hence, the rate of convergence to the multicanonical ensemble is of the same order for all four methods (with the MD and Langevin algorithms being slightly slower). As discussed below, however, the results of thermodynamic quantity calculations all agree with each other, implying that the methods are equally reliable.

In Fig. 2a the time series of the end-to-end distance r is plotted. Here, the distance was measured from N of Tyr 1 to O of Met 5. Only the result from the multicanonical hybrid Monte Carlo simulation is given, since the other two simulations give similar results. Note that there is a positive correlation between potential energy E and end-to-end distance r (compare Figs. 1c and 2a), indicating that a folded structure generally has a lower potential energy than a stretched one. This becomes even clearer in Fig. 2b, where we display the average end-to-end distance r as a function of potential energy E.

In Fig. 3 we demonstrate that the probability distribution $P_{\mathrm{mu}}(E)$ of potential energy E obtained from the multicanonical MD simulation is essentially flat (of the same order of magnitude) over the whole energy range. Similar figures can be drawn for the other two algorithms.

In Fig. 4 the entropy $S(E)$ calculated from the probability distribution $P_{\mathrm{mu}}(E)$ is displayed (see Eqs. (3) and (4)), where we set $S(20) = 0$ for normalization. The result from the multicanonical MD simulation is given, since the other two simulations give essentially the same results. It is a monotonically increasing function. Note that there is a sudden drop of $S(E)$ near $E = -10$ kcal/mol, suggesting that the global minimum conformation is "unique". The result from the earlier MC run in a multicanonical ensemble [8] is also shown in Fig. 4 for comparison. They are in complete agreement, indicating that both algorithms converged to the same distribution.

Simulations in a multicanonical ensemble cannot only find the energy global minimum but also any thermodynamic quantity as a function of temperature

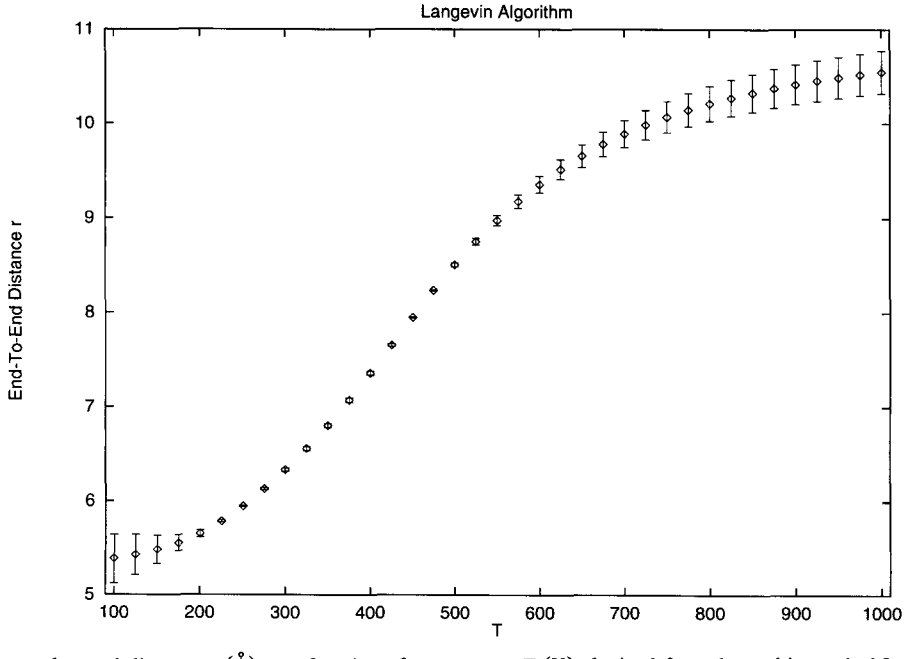

Fig. 5. The average end-to-end distance r (Å) as a function of temperature T (K) obtained from the multicanonical Langevin simulation.

from a single simulation run. We have calculated the specific heat and average potential energy as functions of temperature for the three algorithms. The results all agreed within errors with those from our previous multicanonical MC runs (see, for instance, Refs. [5,8]). Here, we just show another example of such a calculation, the average end-to-end distance as a function of temperature. The results are essentially the same for the three algorithms. That from the multicanonical Langevin algorithm is shown in Fig. 5. We see that the average end-to-end distance becomes smaller as the temperature is lowered, indicating that the peptide has a compact structure at low temperatures.

4. Conclusions

In this article we have shown that the multicanonical ansatz is not restricted to Monte Carlo simulations, but can also be used in combination with other simulation methods such as the molecular dynamics, Langevin and hybrid Monte Carlo algorithms. In fact, any algorithm that creates a canonical ensemble can be generalized to simulations in multicanonical ensemble by simply replacing the potential energy βE by the microcanonical entropy $S(E)$. We have tested the performances of these above three methods in a multicanonical ensemble for a simple peptide, Met-enkephalin. The results were comparable to those of the original Monte Carlo version [5] in that the rate of convergence to the multicanonical ensemble is of the same order and the thermodynamic quantities calculated as functions of temperature all agreed with each other. We believe that there is a wide range of applications for multicanonical versions of molecular dynamics and related algorithms. For instance, multicanonical MD simulations may prove to be a valuable tool for the refinement of protein structures inferred from X-ray and/or NMR experiments.

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