New Monte Carlo Iteration Method for Generalized Ensembles

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We present a new and general Monte Carlo iteration method for generalized ensembles. It consists of two elements: (1) a simple algorithm to distinguish between distributions arising from respectively equilibrium- and non-equilibrium processes, and (2) a selfconsistent maximum-likelihood estimation of the unknown thermodynamic quantities, based on the information obtained at all previous iterations. We demonstrate the efficiency of the method by calculating the density of state function of a homopolymer with $16^3$ monomers. This represents an improvement of at least an order of magnitude compared to previous studies.

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The method of Monte Carlo (MC) integration has proven successful for calculating thermodynamic properties of model systems with moderate number of degrees of freedom \cite{1}. The basic idea is to sample the phase space by generating a Markov chain of states through a fixed matrix of transition probabilities. These probabilities are chosen such that the condition of detailed balance is fulfilled for the statistical ensemble in concern. For instance, the traditional Metropolis algorithm \cite{1} samples directly in the canonical ensemble (CE) by the choice of Boltzmann transition probabilities.

A generic deficiency of the Metropolis sampling technique is the slow relaxation of the Markov chain which typically appears at points of phase transitions or at low temperatures. For systems with a rugged energy landscape, such as spin glasses \cite{3}, random heteropolymers \cite{4} or even spin-interacting homopolymers \cite{5}, this problem effectively causes results which are erroneously sensitive to the initial states of the Markov chain.

In the past decade, a variety of MC-methods, based on non-Boltzmann probability distributions, have been developed to improve the phase space sampling. They are commonly referred to as broad energy ensemble or generalized ensemble (GE) methods \cite{6} corresponding to the generalization of the partition function, $Z$:

$$Z = \sum_{\phi} \Gamma(\phi) \omega(\phi).$$

(1)

Here, $\phi$ is some coarse-grained state variable, $\Gamma$ is the density of states and $\omega(\phi)$ are the ensemble-defining weights. Different choices have been proposed in the literature. In the multicanonical approach (MU) \cite{8}, $\phi$ is simply the energy, $E$, of the system and $\omega_{MU}(E) = \Gamma(E)^{-1}$. This approach also includes the entropic sampling \cite{9}. In the so-called $\ell/k$-ensemble \cite{8} the weights are defined as $\omega_{\ell/k}(E) = k(E)^{-1}$, with $k(E) = \sum_{E' \leq E} \Gamma(E')$. Finally, for Simulated Tempering (ST) \cite{10,11} $\phi$ also contains a temperature index $l$, i.e. $\phi = \{E, l\}$, and $\omega_{ST}(E, l) = \exp(-\beta_l E + f_l)$, where $f_l$ is the reduced free energy at the inverse temperature $\beta_l$,

$$e^{-f_l} = Z_{CE}(\beta_l) = \sum_{E} \Gamma(E) e^{-\beta_l E}.$$

Here, $Z_{CE}(\beta)$ is the usual canonical partition function. By inspection of eq. (1) it is clear that MU is equivalent to uniform energy sampling and ST is equivalent to a uniform temperature sampling in the preassigned set of values $\{1/\beta_l\}$. The last method practically corresponds to a uniform entropy sampling \cite{8}.

Unlike the canonical ensemble, the probability weights are not a priori known in the generalized ensembles, since $\omega$ in all cases is a function, $g$, of the density of states (or the free energy), $\omega = g(\Gamma)$, and the knowledge of $\Gamma$ corresponds exactly to solving the thermodynamics. The standard solution to this problem is to determine $\omega$ through an iterative procedure, $\omega_{i+1} = F_1(N_i, \omega_i)$, where $N_i = N_i(\phi)$ is the observed histogram over $\phi$ obtained in the $i$th simulation with the weights $\omega_i$. The map, $F_1$, is constructed to have the desired fixed point, $F_1(N, g(\Gamma)) = g(\Gamma)$, where $N = N(\phi)$ is the expected number of counts in a simulation with weights $g(\Gamma)$. Typically, the iteration process is stopped when the observed histogram and the weights are sufficiently close to the fixed point requirement. A large run is then performed in which the physical quantities of interest are studied.

Despite several successful applications of this iteration scheme (see eg. \cite{1, 8, 12}), it suffers from the loss of statistics inherent in the updating rule for the weights. Since $\omega_{i+1}$ only depends on the last histogram, $N_i$, a necessary
requirement to insure convergence is that the set $S(N_i) = \{ \phi | N_i(\phi) > 0 \}$ encloses at least the same region of the (coarse-grained) phase space as the previously obtained set $S(N_{i-1})$, i.e. $S(N_i) \supseteq S(N_{i-1})$. Otherwise, the iteration $F_l(N_i, \omega_i)$ will lead to a worse estimate of $\theta(\Gamma)$ for such regions of the phase space. This is clearly a strong statistical requirement. In particular, it prevents for a more adiabatic updating of the weights, which otherwise could speed up the convergence.

In this letter we propose a new iteration scheme which accounts for the information obtained from in principle all previous iterations. More precisely, a selfconsistent map $\omega_{i+1} = F_M(\{N_{i-j}, \omega_{(i-j)}\}_{j=0}^{M-1})$, will be derived where the 'memory' $M$ can be chosen arbitrary large. As such there will not be any specific statistical requirement to insure the convergence, and it therefore allows for an extension of the GE-analysis to systems of much greater complexity or size.

The scheme is based on a maximum-likelihood estimate of the density of state consistent with the set of distributions $\{N_i\}_i$. In order not to overestimate metastable states, it is important, however, to distinguish between statistics arising from respectively equilibrium and non-equilibrium processes. Therefore we will first discuss a simple but general algorithm for doing so. Its basic principle is to assign a number $\theta = \theta(\phi)$ and a set $\Theta(\phi)$ to each $\phi$-bin during the simulation. This pair, $(\theta, \Theta)$, is updated on the same MC-rate as the distribution $N_i$, say after each timestep $\Delta t$. If $\phi_t$ denotes the state of the system at time $t$ and $\phi'_t$ is the test state for the last move (in case of acceptance, $\phi'_t = \phi_t$) the quantities $(\theta, \Theta)$ are given by the following rules:

1. Initially, $(\theta, \Theta)(\phi) \ DEFINES (0, \{\})$ for all states $\phi$ except for the first one $\phi_0$, for which $(\theta, \Theta)(\phi_0) \ DEFINES (1, \{\})$.

2. If the transition $\phi_t \ TO \ \phi_{t+\Delta t}$ takes the Markov chain into a new state, $\theta(\phi_{t+\Delta t}) = 0$, one puts $(\theta, \Theta)(\phi_{t+\Delta t}) \ DEFINES (\theta(\phi_t) + 1, \Theta(\phi_{t+\Delta t}) \cup \{\theta(\phi_t) + 1\})$.

3. If the transition $\phi_t \ TO \ \phi_{t+\Delta t}$ takes the Markov chain into an old state, $\theta(\phi_{t+\Delta t}) > 0$, one redefines $(\theta, \Theta)$ for all states $\phi$ for which $\theta(\phi) > \theta(\phi_{t+\Delta t})$ as $\theta(\phi_{t+\Delta t})$ and $\Theta(\phi) \ DEFINES \{\theta(\phi_{t+\Delta t})\} \cup \{m \in \Theta(\phi) \mid m \leq \theta(\phi_{t+\Delta t})\}$.

4. After the value $\theta(\phi_{t+\Delta t})$ has been determined by (2) or (3), $\Theta(\phi'_{t+\Delta t})$ is seperately updated as $\Theta(\phi'_{t+\Delta t}) \ DEFINES \Theta(\phi'_{t+\Delta t}) \cup \{\theta(\phi_{t+\Delta t})\}$.

It follows, that the $\theta$-value of the present state $\phi_t$ of the simulation always equals the maximum value. The purpose of the $\theta$-function is to partition the phase space into the kinetically connected or locally equilibrated regions. Each set $\Phi_m = \{ \phi | \theta(\phi) = m \}$ defines such a region, whereas the transition $\Phi_m \ TO \ \Phi_{m'}$ with $m' > m$, corresponds to a process which, within the total simulation time $\tau_i$ spent at iteration $i$, effectively is out of equilibrium. The time-step $\Delta t$ for this analysis should be large enough to reflect the local properties of the free energy landscape, $f(\phi) \sim \log(\Gamma(\phi)\omega(\phi))$, i.e. $\Delta t$ should be comparable to the (local) decorrelation time. Depending on the choise of $\Delta t$, some of the regions generated by the values of $\theta$ might contain only very few counts. This will for instance be characteristic for the transition region between two minima of the free energy landscape. After the completion of the $i$'th simulation, a simple minimums criteria on the statistical content can be applied to discard such values of $\theta$. Hereafter, $\theta$ can be considered as a way of labelling the different effective 'macro-states' or basins observed in the simulation.

The 'adjoint' quantity, $\Theta$, keeps track of the neighbourhood of each basin as well, $\Phi_m = \{ \phi | m \in \Theta(\phi) \} \supseteq \Phi_m$, by the inclusion of the observed but possibly rejected states (rule 4). The necessity for this rather tedious book-keeping is that the rejection of a state may indicate that the corresponding free energy previously has been underestimated. The algorithm is schematically illustrated in fig. 1.

Following the line of arguments, the distribution $N_i(\phi)$ resulting from iteration $i$ must be partitioned, $N_i \ TO \ \{N_{im}\}_m$, according to the different equilibrium regions $\{ \Phi_m \}_m$. If the simulation is done in the ST-ensemble, a natural further partitioning, $m \ TO \ m' = ml$, is defined by the different temperatures, $T_i$; such that $\{\Phi_{im'}\}_m$ and $\{N_{im'}\}_m$ can be considered as sets and functions in energy space alone. For all types of ensembles, let $M_i$ denote the total number of partitions at iteration $i$ and let $m_l$ be the corresponding index variable. Furthermore, put $s = \{i, m_l\}$ such that a particular set or histogram obtained at a given iteration can be referred to simply as $\Phi_s$ or $N_s$ respectively.

The map, $F_M$, is readily constructed in the following way. The probability $p_s(E \mid \Gamma)$ of observing the energy $E$ within the domain $\Phi_s$, given the density of states $\Gamma$ and the weights $\omega_s(E)$, is defined by

$$p_s(E \mid \Gamma) = \frac{\Gamma(E)\omega_s(E)}{Z_s}, \quad Z_s \ DEFINES \sum_{E \in \Phi_s} \omega_s(E)\Gamma(E).$$
Under the assumption of (restricted) statistical independence, the histogram \( N_s(E) \) will be a member of the multinomial probability distribution \( P_s \):

\[
P_s(N_s|\Gamma) = n_s! \prod_{E \in \Phi_s} \frac{p_s(E|\Gamma)^{N_s(E)}}{N_s(E)!},
\]

where \( n_s = \sum_E N_s(E) \) is the total number of counts in \( \Phi_s \). The likelihood \( \mathcal{L} \) for observing the set of histograms \( \{N_s\}_{s=1}^M \) \((M = \sum_i M_i)\), is given by the product of the \( P_s \)'s, i.e. \( \mathcal{L}(\{N_s\}_{s=1}^M|\Gamma) = \prod_{s=1}^M P_s(N_s|\Gamma) \). An efficient estimate, \( \tilde{\Gamma} \), of the true density of states can now be obtained by maximizing \( \mathcal{L} \) with respect to \( \Gamma \). This leads to the expression,

\[
\tilde{\Gamma}(E) = \frac{\sum_{s=1}^M N_s(E)}{\sum_{s=1}^M \delta(E \in \Phi_s)n_s\omega_s(E)Z_s^{-1}},
\]

where \( \delta(E \in \Phi) = 1 \) if \( E \in \Phi \) and zero otherwise. The partition functions \( Z_s \) must be estimated selfconsistently from eq. (2). This set of estimates \( \{Z_s\} \) can be expressed as the solution to the following \( M \) equations, \( y_s = 1, \ldots, M \):

\[
y_s \overset{\text{def}}{=} \sum_{E \in \Phi_s} \frac{\sum_{t=1}^M N_t(E)}{\sum_{t=1}^M \delta(E \in \Phi_t)n_t\omega_t(E)Z_t^{-1}} = 1.
\]

In fact, these equations contain the multihistogram equations as a special case. This comparison together with the different numerical solving procedures mentioned below, will be discussed in details in a separate paper.

By inspection of eq. (3) it is clear that each disconnected region of \( \Phi_{\text{tot}} = \bigcup_{s=1}^M \Phi_s \) will introduce a zero mode in the Jacobian \( \frac{\partial y}{\partial y} \), corresponding to a (local) normalization constant in terms of an entropy or free energy, which can be chosen freely. In particular, an overall normalization constant has to be fixed in order to define a unique solution. A way around the problem of multiple zero modes, is to solve eq. (3) separately for each connected region and estimate the relations between the normalization constants afterwards by interpolating the slope of the entropy function \( S(E) = \log(\tilde{\Gamma}(E)) \). Obviously, a reliable estimate of \( \Gamma \) is not obtained before \( \Phi_{\text{tot}} \) constitutes one overall connected set.

The weights for simulation \( i + 1 \) is obtained by inserting the solution \( \{Z_s\}_{s=1}^M \) \((M = \sum_{i=1}^L M_i)\) of eq. (3) into expression (2) and use \( \omega_{i+1} = g(\tilde{\Gamma}) \). Contrary to the standard GE-iteration method, the Markov chain does not have to be reinitialized for the next iteration, not even if the Markov chain at iteration \( i \) ends in a trapped region of the phase space. Since the iteration scheme for \( \omega \) keeps all the information previously obtained and since the new weights \( \omega_{i+1} \), by construction improves the phase space sampling, one can simply continue the next iteration from the final state \( \phi_f \) of the last one. This makes the scheme very efficient in optimization problems. For the sake of completeness it should also be noted, that both the ‘equilibrium sorting’ algorithm and eq. (2)-(3) can be directly applied to multidimensional state variables \( \phi \) as well.

As a demonstration of the method we calculate the density of states of a self-avoiding homopolymer with a nearest-neighbour (non-bonded) potential of energy \( \epsilon = -1 \) in a simple cubic lattice. Homopolymer models of this type have recently been the subject of extensive studies, both on-lattice and off-lattice. Order parameter related quantities have been calculated up to rather long on-lattice chains \((L = 5000)\), but estimates of heat-capacities or densities of states have been limited to much shorter chains (in all cases \( L < 400 \)), due to the normal difficulty associated with obtaining converged results for these quantities.

In this study, we have chosen \( L = 16^3 \) and performed three independent runs in the multicanonical ensemble, \( g(\Gamma) = \Gamma^{-1} \), with the parameters \( \tau_{\text{tot}} = \sum_i \tau_i \approx 4 \times 10^9 \) and \( \Delta t = 4 \times 10^3 \). The energies are binned with \( \Delta E = 8 \) which implies that \( \sim 8 \times 10^2 \) independent values of \( \Gamma \) has to be estimated. For each run the system is initialized by a random self-avoiding walk and with the infinite temperature weights \( \omega_{i=1}(E) = 1 \). The simulation time \( \tau_i \) in each iteration within a run is defined dynamically, roughly proportional to the size of the phase space observed. The maximal 'memory' of the iteration scheme is set to \( M_{\text{max}} = 100 \), which has turned out to be sufficient to contain the full history of each run.

The results are shown in fig. 2. In the large figure the change of entropy \( \Delta S \) compared to the random coil is plotted as function of the total energy \( E \), for the three runs. Deviations can be observed for energies \( E < -5500 \), but otherwise the differences are less than the size of the data points. In the inset, these differences are depicted in terms of \( \Delta \Delta S = \Delta S - (\Delta S)_{\text{av}} \), where \( (\Delta S)_{\text{av}} \) is the weighted average of the three runs. For energies \( E > -5500 \) the relative uncertainties are generally observed to be of the order \( \sim 10^{-3} \). No thermodynamical transitions takes place below
$E = -5500$, and the results have converged in the sense that they are sufficiently accurate to reproduce the sensitive thermodynamic quantities such as the temperature dependence of the heat capacity. We refer to a forthcoming publication [26] for this analysis. Keeping in mind the level of convergence and relating the size of the system to the total simulation time, the iteration method constitutes an improvement of at least one order of magnitude compared to previous studies.

In fig. 3, a typical state of the homopolymer in the energy region $E < -5500$ is depicted. The state is completely compact, and its difference to the ground state (the box $16^3$) is only due to the particular arrangement of the ‘rigid’ surface. The structure of the state testifies to the fact that the method is capable of investigating most of the coarse grained phase space, even within the relatively short MC-time $\tau_{\text{tot}}$ available.

In summary, we have presented a new and general Monte Carlo iteration scheme for generalized ensembles (GE), which allows for an extension of the GE-analysis to systems of much greater size or complexity. In the future, we plan to test the method on off-lattice polymers and spin-glasses.

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FIG. 1. Schematic illustration of the equilibrium sorting algorithm. (a) shows the free energy landscape $f(\phi)$ (in arbitrary units) with two minima as function of the state variable $\phi$ (arbitrary numbers) for some system, which is initialized in state $\phi_0$. (b) shows a possible time evolution of the system in a MC-simulation. The full line is the actual history, whereas the marks (+) show the test states of the Markov chain. Two non-equilibrium transitions are observed, $\phi_0 \rightarrow \tilde{\Phi}_1$ and $\tilde{\Phi}_1 \rightarrow \tilde{\Phi}_2$. Here, $\tilde{\Phi}_1$ and $\tilde{\Phi}_2$ are the basins defined by the statistical relevant values of $\theta$ (see text). The figure also shows the extended regions $\Phi_1$ and $\Phi_2$ obtained by the inclusion of the test states within each basin.

FIG. 2. The change of entropy $\Delta S$ compared to the random coil for a homopolymer with $16^3$ monomers, as function of the total energy $E$. Three independent simulations have been performed with $\sim 4 \cdot 10^9$ MC-steps. In the inset the differences between the results are shown in therms of $\Delta \Delta S = \Delta S - (\Delta S)_{av}$, where $(\Delta S)_{av}$ is the weighted average of the three runs. The relative uncertainty of $\Delta S$ is generally observed to be of the order $\sim 10^{-3}$ for energies $E > -5500$.

FIG. 3. An example of a typical homopolymer state with $L = 16^3$ monomers in the low energy region ($E < -5500$). Only the particular arrangement of the ‘rigid’ surface makes it different from the true ground state. The structure of the state testifies to the fact, that the simulation is capable of investigating most of the relevant phase space within a relatively short MC-time $\sim 4 \cdot 10^9$.

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