Structural Optimization of Nanoclusters with Adaptive Tempering Monte Carlo Method

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ABSTRACT

The Adaptive Tempering Monte Carlo (ATMC) is proposed for the optimization of nanosystems. In this numerical simulation, the temperature of the system is changed adaptively such that the system selects the appropriate configuration. This method belongs to the family of multicanonical approaches. The system adaptive excursion in configuration space allows for rapid discovery of topological paths on the potential energy surface towards the global minimum. The method exists in serial and parallel versions. The ATMC has been applied to different types of nanosystems including nanoclusters under the Morse potential, tight-binding nanoclusters, and the characterization of the best folded structure of a polypeptide chain.

Keywords: Monte Carlo, Multicanonical, Tempering, Structural Optimization, Computational Nanomaterials Design

1 Introduction

The simulated tempering[1] and the method of expanded ensemble[2] are multi-canonical Monte Carlo methods also referred as "simulated tempering". In these simulated tempering approaches a Markov chain of configurational energies is built to link different canonical (NVT) ensemble partion functions Z_A and Z_B at temperatures T_A and T_B. An expanded canonical ensemble with partition function Z is thus formed by n of such sub-partition functions:

$$Z = \sum_{i=1}^{n} Z_i \exp(-\eta_i) \tag{1}$$

where Z_i is the partition function associated with the sampling distribution and η_i are weights.

In the simulated tempering, the Metropolis sampling is used to change configurations in each Z_i, and a second type of MC-move is applied for attempting changes between sub-ensembles. Each change from m to m' in Eq. 1 implies that the same point $\mathbf{q}$ in configuration space is sampled with probabilities $\pi_m = Z_m exp(-\eta_m)/Z$ and $\pi_{m'} = Z_{m'} \exp(-\eta_{m'})/Z$:

$$acc = \min[1, \frac{e^{-(H(\mathbf{q})/k_B T_{m'} + \eta_{m'})}}{e^{-(H(\mathbf{q})/k_B T_m + \eta_m)}}] \tag{2}$$

Thus $\mathbf{q}$ is an effective boundary configuration, and generally m' is chosen to be an adjacent sub-ensemble of m. It follows that the ratio $R_{m,m'}$ of the probabilities is:

$$\frac{\pi_m}{\pi_{m'}} = \frac{Z_m}{Z_{m'}} e^{-(\eta_m - \eta_{m'})} \tag{3}$$

The optimization of the best structure of nanoclusters is difficult because of the multitude of geometries associated with isomers that have energies very close to each other. This problem is encountered in both classical and quantum mechanical methods to represent the total energy of the system at zero temperature.

We propose a multi-canonical ensembles method that permits to optimize nanocluster structures and that can be either linked to calculation of energies through classical approaches based on model potentials or to a quantum tight-binding approach. This is the Adaptive Tempering Monte Carlo (ATMC) method[3] that we describe in the following section. The mid-section on this letter describes three applications of ATMC for optimization of Morse nanoclusters, and calculation of the energy of calcium nanoclusters and for the characterization of the best folded structure of a polypeptide. This work concludes with a summarizing section.

2 The Adaptive Tempering Monte Carlo

In the Adaptive Tempering MC method (ATMC)[3] the system accesses a multitude of NVT_i ensembles, where each T_i characterizes a different ensemble within a predetermined temperature range. Each canonical ensemble is simulated with the Metropolis acceptance criterion for a fixed number of configuration changes M_{fixed}. The various ensembles are connected along the simulation such that the temperature T is allowed to hop to either $T + \Delta T$ or $T - \Delta T$ ($\Delta T > 0$) with probabilities:

$$\pi_+ = \exp[-(E - \langle E \rangle)(\frac{1}{k_B(T + \Delta T)} - \frac{1}{k_B T})]/Q \tag{4a}$$

$$\pi_- = \exp[-(E - \langle E \rangle)(\frac{1}{k_B(T - \Delta T)} - \frac{1}{k_B T})]/Q \tag{4b}$$

Here E is the M^{th}_{fixed} instantaneous configuration energy at T, $\langle E \rangle$ is the MC average energy of the M_{fixed} configurations, and Q is a normalization factor. After some

algebraic rearrangements, a new temperature adapted to the location of the system in configuration space can be written as:

$$T_{adapt} = (T^2 - \Delta T^2)/\Delta T \quad (5)$$

where ΔT is:

$$\Delta T = \frac{T}{1 - \delta E/(ln(a)k_B T)} \quad (6)$$

Here δE is the standard deviation of the energy about the average $\langle E \rangle$ at temperature T over the M_{fixed} configuration trials. We introduce one parameter $ln(a)$ in terms of which T_{adapt} is readily obtained. A large $ln(a)$ quenches the system fast while a small $ln(a)$ leads the system to a larger number of temperature changes. In what follows, a "tempering event" will name the process of hopping from a temperature to a new temperature. Therefore, along the simulation there are many tempering events indicating how the system visits the range of temperatures spanned by the simulation. After a tempering event, the system evolves for another M_{fixed} configuration changes at either $T + \Delta T$ or $T - \Delta T$. In all simulations the system is started from an arbitrary initial configuration at high temperatures, close to the upper limit of the allowed temperature range. The simulation is stopped when the temperature is close to zero. The energy E is calculated consistent with the model used to simulate the system, which is not restricted to be a classical energy from a model potential.

In the ATMC, the system spends equal times in all the sub-ensembles. In Eq. 3, the weights η are locally assigned an adaptive constant based on the local T.

$$\eta_{\pm} \quad \cong \quad |E - < E > |/(3k_B T) \quad (7)$$

Implementation of the ATMC is straightforward. The NVT Metropolis MC with adaptive step size is run for M_{fixed} steps at the initial temperature T. At the M^{th}_{fixed} step, the $\langle E \rangle$ and δE are calculated and the instantaneous E and spatial configuration are recorded. Next, ΔT is calculated from Eq. 6 such that one of the two probabilities π_+ or π_- is selected. A random number uniformly distributed in $(0, 1)$ is thrown. If the chosen π is larger than the random number, the temperature is changed consistent with the chosen π. If the chosen π is smaller than the random number, then the other π is selected. In either case, the temperature is changed and the new temperature is $T + \Delta T$ or $T - \Delta T$. Subsequently the Metropolis MC simulation is restarted from the known M^{th}_{fixed} configuration but now at the new temperature $T \pm \Delta T$. New values of $\langle E \rangle$, δE, and E are calculated at the end of another set of M_{fixed} steps. A new ΔT is calculated and the above-discussed process is repeated to select another new temperature. This adaptive process is continued until the system reaches a final temperature close to zero, at which point the simulation should be stopped. Would the simulation be continued, it would reach negative temperatures, and basically the system does not return to high temperatures once the ground state is reached.

The tempering events are adaptive in the sense that both the ΔT and sign (π_+ or π_-) of the temperature change are determined adaptively in the simulation. The orginial ATMC is not a parallel algorithm. A multi-threaded ATMC on the other hand accelerates the learning of the energy landscape through parallel simulations. Such a parallel implementation is discussed in Section 3

3 Structural Optimizations with ATMC

ATMC simulations were carried out for Morse nanoclusters with 80 to 155 atoms.[3] Fig. 1a,b illustrates the evolution of the temperature and the binding energy as a function of tempering event for a Morse nanocluster with N=147 atoms.[3] There are 5326 tempering events in this case, showing clearly that the cluster is visiting a vast region of configuration space. The correlation between visited energies and accepted temperatures is shown in Fig.1c, which suggests an almost linear temperature-energy correlation along each of the two phases accessed along the tempering (liquid-like and solid-like). The more stable clusters in the studied size range are 105, 110, 115, 142 and 152 for the case of Morse parameter $\rho = 3.0$ and 105, 115, 135 and 147 for the case of $\rho = 3.68$. Only N=147 is a MacKay icosahedron. Additionally the Morse N=135 cluster with I_h symmetry is an energetically preferred structure.

Combined with a tight-binding model,[4] the ATMC was used to optimize calcium nanoclusters containing 14 to 32 atoms.[3] In this range, the magic numbers were determined to be 15, 21 and 23. Six novel structures were reported for Ca_{15}, Ca_{16}, Ca_{18}, Ca_{21}, Ca_{23} and Ca_{25}. These structures were not reported previously in the literature as energetically most stable under any model potential. The parallel version of ATMC was further implemented in a multi-thread way, such that a group of tempering threads are thrown simultaneously to explore the configuration space. If one temperature is repeated, then samplings of the two data segments are appended. This parallel implementation was tested for Ca_{21}. The simulation was run on an Altix®3700 Bx2 supercomputer. Built from random points on a $3 \times 3 \times 3$ simple cubic lattice, 8 random configurations were equilibrated at 800 K with 5000 iterations of NVT MC. Then, eight threads of ATMC were started with distinctive high temperature configurations. The ATMC parameters were $M_{fixed} = 100$ and $ln(a) = -1.0$. Seven of the threads lead their configurations to the global minimum. The correlation plot of potential energy-temperature at each tempering event

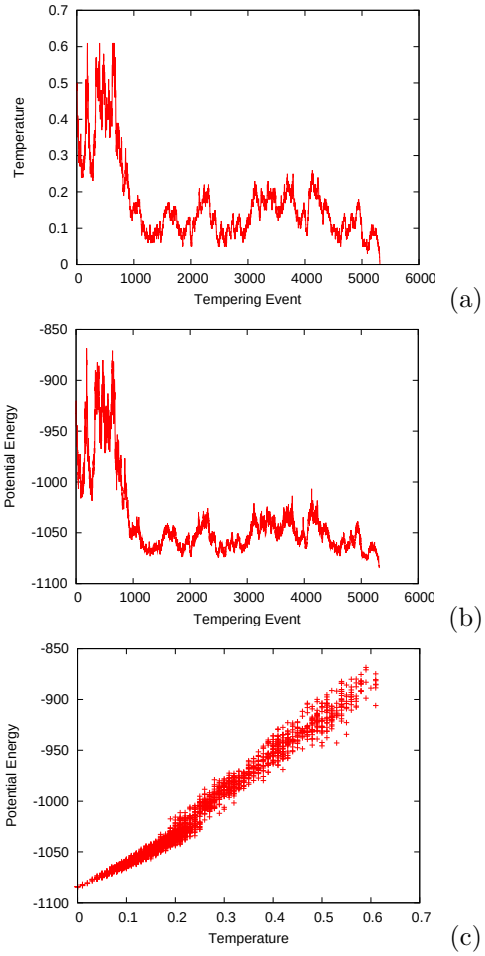

Figure 1: Evolution of the temperature (a) and the potential energy (b) as a function of tempering event for the 147-atom Morse cluster ($\rho = 3.68$); (c) correlation between potential energy and temperature during the tempering process. Energies are in reduced units of D_e and temperatures in units of D_e/k_B.

is illustrated in Fig. 2. Only one thread evolved into a local minimum structure in 102 tempering events and stopped. However, when continued, this simulation also reached the global minimum. The local minimum attained in this particular thread is only 0.06 eV above the global minimum. The structure of the global minimum of Ca_{21} and this close-by minimum are shown in Fig. 3. Local minimization with a steepest descent optimizer of the structures obtained in all threads at the end of the 500th tempering event showed that in about half of the cases the cluster was in the basin of the local minimum, whereas the other half was in the basin of the global minimum.

Application of the ATMC was further extended to the study of the folding of a polypeptide chain. The off-lattice continuum minimal model of this protein was developed by Veitshans and Klimov and Thirumalai.[5]

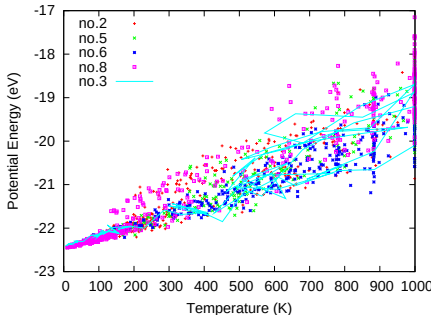

Figure 2: The correlation between energy and temperature during the tempering process of the Ca_{21} nanocluster.

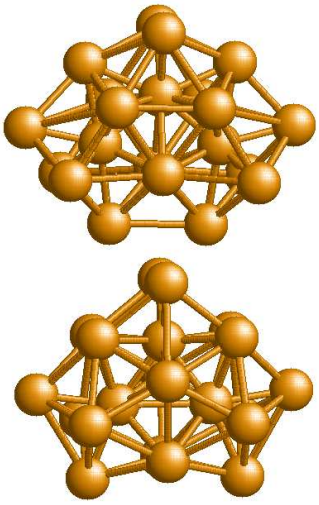

Figure 3: The global (top) and a local minimum (bottom) energy structures of Ca_{21} discovered by ATMC

Starting from a zigzag configuration, the polypeptide was equilibrated at temperature 1.5 before initiating the tempering process. Then the ATMC simulation was carried out with the parameters $M_{fixed} = 200$ and $ln(a) = -0.7$. An example is shown in Fig. 4 with the history of temperature, potential energy and order parameter of the polypeptide in the ATMC simulation. After 3000 tempering events, the polypeptide was fully folded and remained in the native state at low temperature. During tempering events 1500 to 2600, the polypeptide was partially folded at low temperatures. The ATMC was able to drive the polypeptide stretched chain at high temperature to the fully folded state at low temperatures.

Fig. 5 shows the correlation between the potential energy and temperature, and the correlation between the order parameter and temperature in the ATMC simulation. The correlations shown in Fig. 5 indicate that

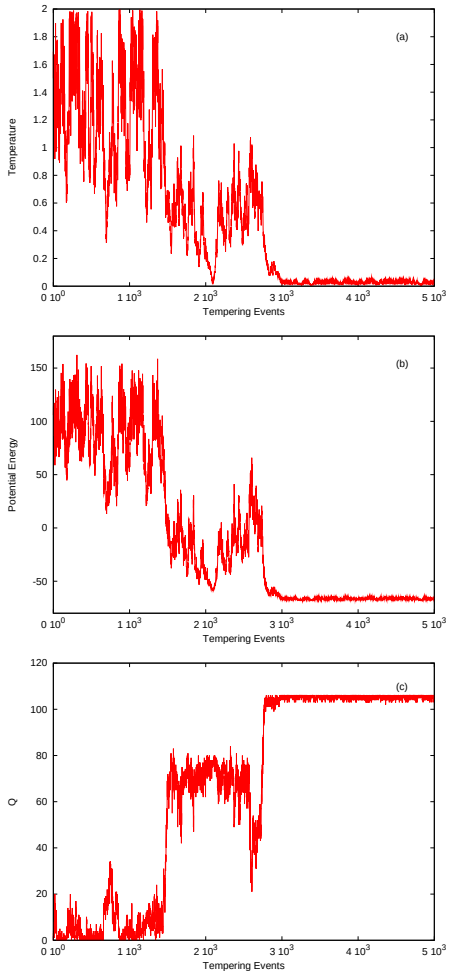

Figure 4: Evolution of temperature (a), potential energy (b) and order parameter (c) of the polypeptide as a function of tempering events. Energies and temepratures are in reduced units.

the ATMC guided the polypeptide chain in sampling various partially folded states before finding a path to the native state.

This application of ATMC shows that super cooled unfolded states at temperature 0.4 correspond to excursion over local minima. If a requlars quench is done, the system will be trapped in one of these metastable states. The native state first showed in the ATMC around temperature 0.4. However, the intelligent-search done by the ATMC avoided the local minima and found the fully folded state. Folding of the polypeptide was achieved in 3000 tempering events, which is altogher 6×10^5 iterations of NVT MC.

4 Conclusion

The Adaptive Tempering Monte Carlo method was applied for optimization of nanoclusters and folding of a polypeptide chain. The computational framework of the

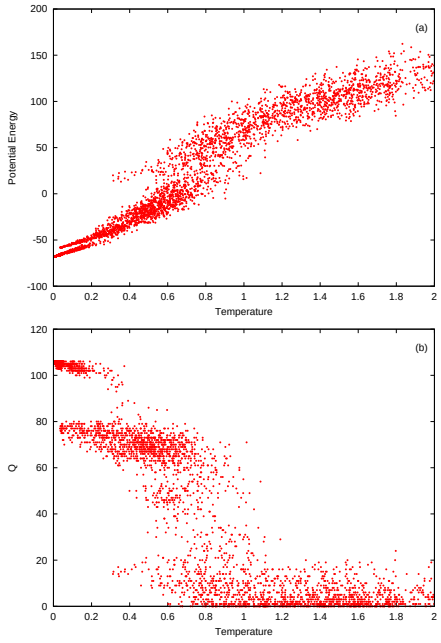

Figure 5: Correlation plots between potential energy and temperature (a) and between order parameter and temperature (b) during the evolution of an ATMC simulation

ATMC allows to use either phenomenological model potentials or quantum electronic structure approaches to predict the most ordered phase of a system. This is particularly interesting for finite systems in the nanoscale regime. In this algorithm all anharmonicities are treated without approximation. One of the advantages of the ATMC is the possibility to thermally excite all vibrations through the tempering mechanism. The strategic advantage of this algorithm allows the nanosystems to escape from metastable states, which otherwise require extreme long-time dynamics indicating that the way in which the MC algorithm was engineered to move around configuration space is quite effective.

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