Random Walk Based Scaling for Optimizing Replica Exchange Molecular Dynamics

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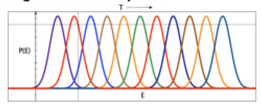
Abstract:

The adequate sampling over configurations can be a challenge for molecular simulations. Replica exchange is a commonly used method to help overcome this problem, but it becomes inefficient for large systems. In this work, we implement a replica exchange variant which is much better for larger systems (replica exchange with dynamical scaling, or REDS) and explore methods to make it easier for the user and more efficient in general. We implemented our method in GROMACS, which is an open source molecular dynamics software whose source code is freely available, and the system we considered consisted of Alanine Dipeptide with 450 water molecules.

The Idea:

Replace a large number of replicas



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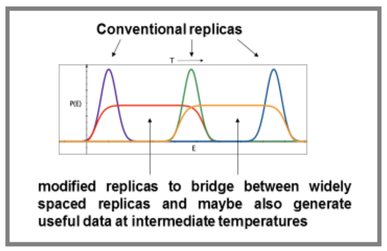

Basics:

Put a replica in the middle with b_m and potential

$$U_m(r) = [lb_1+(1-l)b_2]/b_m\ U(r)$$

The Boltzmann factor for the middle replica is

$$\exp(-\ b_m\ [lb_1+(1-l)b_2]/b_m\ U(r)\ ) = \exp(-\ [lb_1+(1-l)b_2]\ U(r)\ )$$

The actual exchange probability between j and m will depend on

$$\Delta_{jm}=\beta_j[U(r_j)-U(r_m)]-\ [lb_1+(1-l)b_2][U(r_j)-U(r_m)]$$

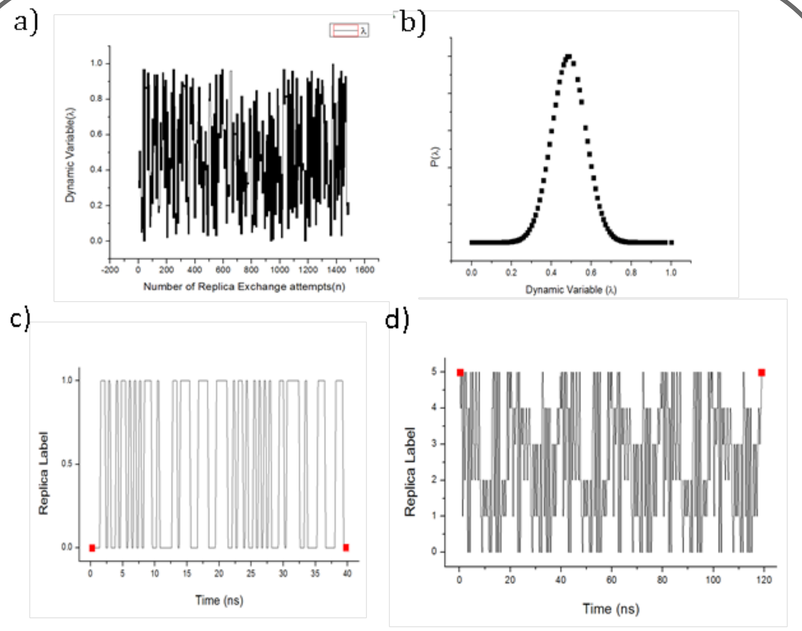

Figure 1. a) The variation of λ as a as a function of the number of attempted replica exchanges. b) The probability distribution of λ between 0 and 1. c) and d) represents the transitions between replicas at different temperatures, c) is the transition curve for the replica at temperature 298.0k and 500k, and d) is the transition curve for the replicas at temperature 500k. As we can see, the transition occurs quite rapidly, for instance for d) the replicas go down to zero and come back in under 10 ns.

Methodology:

Gromacs, an open source software whose code is written in C/C++, can perform REMD simulations. We updated it to include the replica exchange with dynamical scaling (REDS) algorithm. This involved introducing new variables and parameters, including l and the terms to describe the biasing potentials, as well as modifying the energy and the forces the particles feel by adding the scaling of Eq. 1. A routine to propagate l using the Monte Carlo algorithm and modification of the exchange criteria were also added. Given a system with temperatures T_{-m} and T_n, where $T_{-m} < T_{-n}$, and their corresponding energies be: $E_m(\{r_1\},l_1) = [l_1\ b_{m1}+(1-\ l_1)b_{m2}]/b_m\ E(\{r_1\}) + E_{bias}^m(l_1)$, and $E_n(\{r_2\},l_2) = [l_2\ b_{n1}+(1-\ l_2)b_{n2}]/b_n\ U(r_2) + E_{bias}^n(l)$, where $b_1=1/k_BT$

Algorithm Details:

The REDS method was implemented in Gromacs as follows:

1. Scale the forces and energies in the do_force routine after the sum_epot routine has been called.
2. Perform random walk on the dynamic variable l.
3. Attempt a replica swap after a specified number of time steps and accept the swap as described above, using the calc_delta routine.

We performed the simulations on 6 replicas of Alanine Dipeptide with 450 water molecules at temperatures equal to 298.0, 308.0, 318.3, 329.0, 440.0 and 500.0K, and attempted a replica exchange every 100 steps. Also, we conduct REMD between temperatures 298K and 500K, for which conventional REMD does not work.

Conclusion:

From the experiments we conducted on Alanine Dipeptide system, we conclude that our method is able to conduct replica exchanges between temperatures where the conventional REMD does not work. We were able to successfully conduct exchanges between 298K and 500K. Also, it was seen that the exchanges between different temperatures occurred rather efficiently. Further work will add an adaptive method for automatically including an optimal biasing potential to the program.

References

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