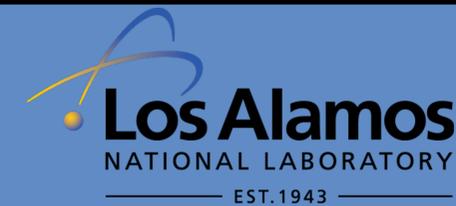




Generalizations of the Parallel Replica Dynamics method for long-timescale atomistic simulations



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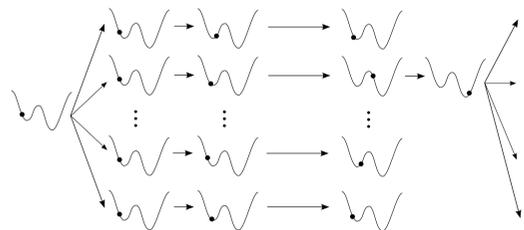
Long-Timescale Atomistic Simulations

Since its introduction, Molecular Dynamics (MD) has become one of the most important computational techniques for the study of the dynamical behaviour of matter at the atomic scale, enabling significant advances in physics, chemistry, biology and materials science. Despite its enormous success, MD suffers from an important limitation: while it can be efficiently parallelized in space, its original formulation is essentially **serial in time**. This severely limits the timescales that are amenable to direct simulation and leave many important physical processes out of reach, specially those of thermally activated nature that occur only rarely on vibrational timescales.

This problem was the subject of intense investigation during the past decade and, largely following pioneering work carried out at LANL, significant progress was made in the development of Accelerated Molecular Dynamics (AMD) methods [1]. AMD methods have greatly expanded the horizon of timescales amenable to MD simulations. The basic philosophy of these methods is to let MD trajectories (which are often “smarter” than we are) identify proper evolution pathways, but to trick them into doing so faster than they would normally do (using statistical physics considerations). This is possible when there is a significant separation of timescales between vibrations and persistent changes in the topology of the system.

This separation of timescales can be exploited in different ways (by correcting for changes in temperature as in Temperature Accelerated Dynamics, or in potential energy as in hyperdynamics). It can also be used to parallelize the evolution of the system in the time domain. This is the basis of the **Parallel Replica Dynamics** method [2].

The Parallel Replica Dynamics Method



A Parallel Replica Dynamics simulation proceeds as follows:

1. Replicate the current state of the system onto every available processor
2. Prepare an ensemble of the replica by randomizing the momenta and integrating the equations of motion for a correlation time (dephasing step)
3. Let every replica do MD independently from one another, but periodically monitor for any change in state (transition)
4. As soon as one replica observes a transition, stop all other replicas
5. Let the replica that found the transition run until it spends at least one correlation time within a state (decorrelation step)
6. Sum the total MD time spent on every replica, *excluding the dephasing time*, and add it to the MD clock
7. Go to 1

The Parallel Replica Dynamics method relies on the fact that rare events have *exponential* escape-time statistics (i.e., that kinetics are of first order). Therefore, the probability to observe any given transition on any given replica is a (time-independent) constant and the total elapsed time before the first escape of any of the replicas is drawn from the same distribution as that of a serial MD simulation. The discrete state-to-state dynamics of the system is arbitrarily well reproduced by a Parallel Replica Dynamics simulation (modulo a correct choice of the correlation time).

While the method is very powerful and useful in practice, its practical scaling is limited by the presence of low barriers (fast rates). In this case, the overhead due to the dephasing step becomes significant and adding more replicas does not significantly improve the performance of the method.

Super-State Parallel Replica Dynamics

The initial formulation of Parallel Replica Dynamics was based on sound physical arguments, but its deeper mathematical structure was left somewhat unexplored. We recently carried out an in-depth mathematical analysis of the method based on an overdamped Langevin description of the dynamics [3].

Our analysis revealed the crucial underpinning role of the quasi-stationary distribution (QSD). The QSD can be defined as the distribution ν , supported within a given state A , such that if X is distributed according to ν at time 0, it is still distributed according to ν at time t , conditioned on not having left A before t . The QSD corresponds to the first eigenvector of the generator of the dynamics with absorbing boundary conditions around A .

The QSD possesses two important properties:

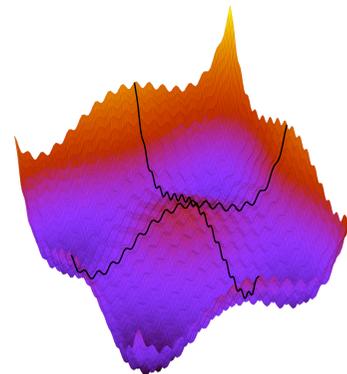
1. Absorption (escape) times are exponentially distributed with a rate λ_1 , which is the eigenvalue corresponding to the QSD
2. In the QSD, the absorption rate on any element of the boundary is constant and independent of time

The dephasing step of the original algorithm can therefore be interpreted as a preparation of the QSD. Starting from a QSD initial state, the Parallel Replica Method would be *exact* in selecting the next escape path and the corresponding escape time. In the general case, escapes can (and will) occur before the QSD is perfectly established. The role of the decorrelation step can be understood as allowing capture of these non-QSD events. At the end of the decorrelation step, one can assume that an ensemble of replica running in the current state would by then be distributed according to the QSD. For any finite value of the correlation time, this assumption will introduce an approximation, but we showed that the error is bounded by

$$C \exp((\lambda_1 - \lambda_2) \tau_{\text{corr}})$$

where λ_2 is the second eigenvalue of the generator, and hence can be controlled **arbitrarily well** by choosing an appropriate τ_{corr} .

This general analysis has an important consequence: it shows that the error in the algorithm can be arbitrarily controlled for **any** definition of the states, not only for the commonly used one based on individual basins of attraction of the potential energy landscape.



The definition of states can be optimized by lumping individual shallow states into super-states

This implies that we are free to define states as we wish, as long as we can estimate a proper τ_{corr} . This opens the door to the development of sophisticated time-wise multiscale schemes, where the definition of states can be adjusted on-the-fly in order to maximize the efficiency of the method. This can be done by building **super-states** by lumping of shallower states so as to maximize the spectral gap $\lambda_2 - \lambda_1$ (the separation of timescales between equilibrating inside of a state and escaping from the state) [4].

The optimal way to reliably identify super-states remains to be developed, but existing strategies can be leveraged.

Diffusion-Reaction Parallel Replica Dynamics

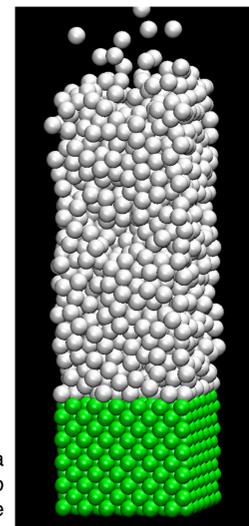
Parallel Replica Dynamics is able to accelerate the evolution of a system when the dynamics proceeds through a sequence of rare, activated events. While this is true of many solid-state systems, it is obviously not the case for liquids. In cases where a solid phase is in contact with a non-reacting liquid we demonstrated that Parallel Replica Dynamics can be adapted to provide an accurate description of the slow kinetics perturbed by the fast degrees of freedom [1]. Imagine that the liquid contains reactive agents moving diffusively until they react with the solid (e.g., a corrosive solution in contact with a metallic surface). This case is no longer amenable to standard AMD methods. However, the concept of QSD can be leveraged to generalize Parallel Replica Dynamics in order to handle this situation.

Consider the case where the solution has been in contact with the solid for a long time. The solute distribution will then correspond **to the QSD for the diffusion equation**. This simple observation implies that Parallel Replica Dynamics can be used to accelerate the dynamics through the use of a simple super-basin approach. The algorithm proceeds as follows:

1. Replicate the current state of the system, *excluding solute atoms*, onto every available processor
2. Draw random positions of the solute atoms according to the QSD (*independently on each replica*) and dephase as usual.
3. Let every replica do MD independently from one another, and monitor for any change in state. These now include reactions with solute atoms. Allow for solute to come in and out of the simulation cell.
4. As soon as one replica observes a transition, stop all other replicas
5. Let the replica that found the transition run until it has spent at least a correlation time within a state
6. Sum the total MD time spent on every replica, *excluding the dephasing time*, and add it to the MD clock
7. Go to 1

Step 2 can be efficiently carried out by constantly updating a free energy profile for solute atoms and by using it to numerically solve for the diffusion QSD. This same information can also be used to allow solute atoms to freely come in and out of the simulation cell (mimicking a coupling with a very large reservoir).

We are now developing a further extension to the method that would allow the solid sub-system to act as a source of solute (e.g., through dissolution of adsorbates or the crystal itself). Strictly speaking, these solute emission events could be handled with very long τ_{corr} , but we believe that more efficient alternatives are possible.



Acknowledgements and References

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