1 Introduction

1.1 Simulated Annealing

The LAMMPS molecular dynamics code allows for massively parallel simulations with billions of atoms. However, as with all molecular dynamics (MD) simulations, the practical timescales of simulations are relatively short (10-100 ns). Of special interest in this work are MD simulations of systems with ‘rugged’ potential energy surfaces, which are characterized by a high number of local (meta-stable) minima separated by high energetic barriers. Due to the limited timescales of MD simulations, simulations of such systems can suffer from inadequate sampling because they are trapped in these local minima. One method to enhance the sampling of phase space is to simulate annealing. In simulated annealing simulations, a system is assigned a high initial temperature, allowing it to overcome high energy barriers, and then gradually cooled to the desired temperature. The simulated annealing technique is guaranteed to reach the global minimum of a system as the time taken to cool the system approaches infinity. However, actual MD simulations cannot be infinite in length. During simulated annealing simulations, the system can become trapped in local energy minima, escape from which is unlikely as the system is further cooled. The extent to which this occurs is specific to the system being simulated. Examples of simulated annealing simulations using linear and stepped cooling are shown in Fig. 2.3.

1.2 Parallel Tempering

The goal of parallel tempering (or replica exchange) MD simulations is to increase the efficiency of the sampling of the phase space of a system. In parallel tempering molecular dynamics simulations, several replicas of a system are simulated independently and simultaneously at different temperatures. At specified intervals, replicas with neighboring temperatures are exchanged with the Boltzmann weighted metropolis criterion

\[ P_{\text{accept}} = \min(1, e^{-\Delta E/kT}) \]

The random walk in temperature allows systems trapped in metastable states to escape by exchanging with a slab of a SiO\(_2\) surface at higher temperatures. Systems at high temperatures are able to efficiently overcome large potential barriers, while systems at low temperatures selectively gain access to low energy structures. An advantage of parallel tempering is that the BKS annealing can only take place if there is a significant difference between the potential energy of neighboring replicas over the course of a simulation. It has been shown that the number of replicas needed in a parallel tempering simulations scales approximately with the square root of the number of particles. Additionally, simulations with a large number of replicas require increased simulation times for replicas to ‘diffuse’ over the range of temperatures and effectively cross barriers. An example of a parallel tempering simulation is shown in Fig. 2.4.

1.3 Simulated Annealing combined with Parallel Tempering

By combining simulated annealing with parallel tempering, a method that shares the advantages of both techniques is created. A small set of replicas are given a common temperature and allowed to anneal at a high temperature, and simulated via parallel tempering. At specified times, each replica is cooled to a lower temperature, until the replicas are at the desired final temperature. This method keeps the efficient sampling of parallel tempering while relaxing the constraints on the large number of replicas needed. It has been shown to be more computationally efficient than simulated annealing for simulations of protein model structures, and requires fewer replicas than parallel tempering. However, to fully realize the benefit of parallel tempering, there must be a sufficient number of replica exchanges between temperature shifts, with an upper bound on the cooling rate of the simulated annealing. An example of a simulation using simulated annealing combined with parallel tempering is shown in Fig. 2.5.

1.4 Implementation in LAMMPS

The capability to run both simulated annealing and parallel tempering simulations already exists in LAMMPS. Simulated annealing combined with parallel tempering was implemented in LAMMPS, and can be executed with the anneal_temper command in a typical input script. To run simulations the following syntax is used:

```
annal_temp N X W f(x ID seed) seed T T' T''
```

- **N** = Total number of time steps to run
- **W** = Attempt tempering swap every this many steps
- **T, T', T''** = Shift temperature of T to T', T'' every this many steps
- **X** = Which entry on the temperature list (T1 T2 T3...) I am in simulations
- **ID of the fix that will control temperature during the run**
- **seed** = random number seed used to decide on adjacent temperature to partner with
- **seed2** = random number seed for Boltzmann factor in Metropolis swap

The number of temperature shifts between temperature shifts (Y) must be a multiple of the number of time steps between attempted swaps (X). If any individual world has a temperature of T, no more temperature shifts will occur. The method was validated by showing that it is reproduced typical parallel tempering simulations before shifting occurred, and that it reproduces typical simulated annealing simulations when no swaps were allowed.

2 Application

2.1 Amorphous Silica Surfaces

We will consider the application of simulated annealing and simulated annealing with parallel tempering to dry amorphous silica surfaces. Amorphous silica (a-SiO\(_2\)) surfaces can be created by simply cleaving bulk a-SiO\(_2\) along a desired plane. However, this creates an unreactive silica surface covered with highly reactive broken bonds that could only be produced experimentally with infinitely high strain rates. Simulated annealing has previously been applied to a-SiO\(_2\) surfaces to create realistic realistic a-SiO\(_2\) surfaces. Previous annealing simulations of a-SiO\(_2\) surfaces have shown that short annealing simulations tend to leave a surface covered with more defects, while longer simulations annealing simulations decrease number of defects on the surface. Experimental evidence suggests that real a-SiO\(_2\) surfaces are annealed over long timescales (hours) have very few defects and are permanently damaged with bridging oxygen atoms (Si-O-Si). Our goal is to approach realistic, defect free surfaces by accelerating annealing simulations with parallel tempering.

Realistic a-SiO\(_2\) surfaces are important for numerous applications, including simulations of the chemical reaction occurring on silica heat shields during reentry. Typical annealing simulations of a-SiO\(_2\) surfaces have a temperature range from 4000 K - 300 K. To run parallel tempering simulations, it is necessary to create a list of temperatures spanning this range. These temperatures must be chosen such that there is a reasonable swapping probability between replicas. It has been shown that for parallel tempering simulations of model proteins that a swapping probability of 20-40% is desirable.

For the purpose of our simulations, we will use a 20 A x 35 A x 35 Å supercell with the a-SiO\(_2\) slab at 4000 K. The number of replicas used must be large enough to span a temperature range that is increased simulation times for replicas to ‘diffuse’ over the range of temperatures and effectively cross barriers. An example of a parallel tempering simulation is shown in Fig. 2.4.

2.2 Results and Discussion

We will compare the results of simulated annealing to simulated annealing with parallel tempering. To perform a relevant comparison, simulated annealing simulations are run with a linear cooling schedule with the same temperature list as simulated annealing with parallel tempering simulations. Four pairs of simulations were run, each with different starting a-SiO\(_2\) surfaces cleaved from the bulk. We use two metrics to determine the efficacy of the simulations: surface defect structure and surface defect concentration. The surface energy is defined as the difference between the energy of the slab exposed to vacuum and the energy of the slab in the bulk, divided by the area of the slab. There are several types of defects predicted by the BKS potential on a-SiO\(_2\) surfaces under-coordinated silicon atoms (Si-... as shown in Fig. 2.5) non-bridging oxygen (Si=O) and Si-O=Si (shown in Fig. 2.6). These defects can be uniquely identified by their connectivity to other atoms in the slab. An annealed a-SiO\(_2\) surface with Si-... defects highlighted is shown in Fig. 2.6.

<table>
<thead>
<tr>
<th>Method</th>
<th>Total</th>
<th>Si-O=Si</th>
<th>Surface Energy (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulated Annealing</td>
<td>0.726</td>
<td>0.552</td>
<td>0.112</td>
</tr>
<tr>
<td>Simulated Annealing (2x)</td>
<td>0.748</td>
<td>0.482</td>
<td>0.165</td>
</tr>
<tr>
<td>Parallel Tempering with</td>
<td>0.771</td>
<td>0.482</td>
<td>0.152</td>
</tr>
<tr>
<td>Simulated Annealing</td>
<td>0.765</td>
<td>0.588</td>
<td>0.149</td>
</tr>
</tbody>
</table>

Table 1: Comparison of a-SiO\(_2\) Surfaces created with different methods

As shown in Table 1 the surfaces created by simulated annealing with parallel tempering have slightly fewer defects and slightly lower surface energies than those created with simulated annealing. An additional simulated annealing simulation run at high the cooling rates (and thus twice the CPU time) creates a surfaces with fewer defects but a higher surface energy than simulated annealing with parallel tempering. These results demonstrate that simulated annealing with parallel tempering is faster than simulated annealing alone for this system, and even has the potential to be more efficient in terms of total CPU time. It has been shown that this method, when finely tuned for certain systems, can be more efficient than simulated annealing alone. However, additional annealing simulations would need to be needed to confirm this.

3 Conclusions

The hybrid method of simulated annealing with parallel tempering was implemented in LAMMPS. This method shares the advantages of simulated annealing and parallel tempering, and uses fewer replicas than parallel tempering alone. We applied this method to a-SiO\(_2\) silica surfaces and found that it was more effective than simulated annealing at creating low-defect surfaces. However, to successfully apply this method to a general system, care must be taken in choosing the parameters to suit the specific needs of the system. The primary limitation of this method is that as the total number of atoms in a system increases, the maximum cooling rate decreases. This method would be most effective when applied to smaller systems of atoms, or simulations with computationally expensive interatomic potentials.

REFERENCES