Applying Monte Carlo Simulated Annealing and Nudged Elastic Band Methods to find Minimum Energy Paths in Systems with Complex Potential Energy Surfaces

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Abstract

A method for finding the minimum energy path for complex surfaces with many potential paths is presented. In systems with a complex potential energy surface, many minimum energy paths can exist, adding difficulty in locating the true minimum energy path of the reaction. Implementing the nudged elastic band method on such a surface leads to erroneous computations of the activation energy as the minimum energy paths found can exhibit a proximity bias towards path initialization. Here the procedure for an algorithm is derived that, when combined with the nudged elastic band method, is able to locate the true minimum energy path for reactions over complex potential energy surfaces.

Contents

1 Introduction

Identifying the activation energy and thus reaction rates for processes such as catalysis, diffusion in solids or the dissociation of molecules on a surface is an active area of research for condensed matter physicists, chemists, materials science and is also increasingly important in biological systems such as enzyme catalysis [1]. Using molecular dynamics simulations to find the rare reaction event is impractical; for instance if the rare event happens 1000's of times per second, running an MD would take thousands of years of computational time to cover the average time between the rare events. Instead, a statistical approach known as transition state theory (TST) is used . Basic TST works through defining a transition state that separates the reactant and product sites. The transition state is a 3N-1 dimensional hyperplane that is normal to the unstable direction of a saddle point that divides the reactants and products. The reaction rate is then calculated as the probability of finding the reactant at that transition state. TST makes the following four assumptions. The first is the motions of the nucleus and electrons are decoupled through the Born-Oppenheimer approximation. The second is that classical dynamics can be used to describe the dynamics of the nuclei, ignoring quantum effects such as tunneling through the energy barrier. Third, the system is in a canonical ensemble, meaning that there is a Boltzmann distribution in the reactants. And last, it is assumed that the reactants do not recross the energy barrier [10]. A further, harmonic approximation can be made around the reactant site and saddle point, this is known as (hTST). This local harmonic approximation is a second order Taylor expansion of the potential around these sites and allows the configurational integrals of TST to be closed-form expressions. [10]. hTST is particularly useful in solid-state systems as the energy barriers are large compared to the kinetic energy of the system, allowing the system to reach thermal equilibrium after a reactive event. The rate equation derived through hTST is interpreted as

$$\kappa_{hTST} = [\texttt{Attempt Frequency}] * [\texttt{Probability of Success per Attempt}]$$

The most probable reaction coordinate is one that is a minimum in energy. That is, the reactants are most likely to follow a path through a potential energy surface (PES) where the potential energy is at a minimum perpendicular to the path. This is known as the minimum energy path (MEP) for the system. Since this path is a minimum in energy, it can be assumed that where the path traverses the transition state (hyperplane) of the system is the point of maximum energy of the path and is the bottle neck for the reaction. The issue of finding the MEP has been approached through several chain-of-state methods including the string method [2], the simplified string method [3], the nudged elastic band (NEB) [4][5][6], and the double nudged elastic band (DNEB) [7]. The method used to find the MEP in this paper is the NEB, as this has been found to be the most efficient and reliable method of the ones listed [8].

The NEB method, developed under hTST [9], finds the MEP of the system through minimizing a reaction path through the PES. The path is discretized into N+1 images. N is always even as the number of images must be odd in order to find the correct estimate for the saddle point energy. These images are connected through fictitious springs, which ensures their equal spacing throughout the minimization dynamics. The points are then

simultaneously relaxed under dampened conditions, allowing them to 'find' their minimum energy configuration. This minimum energy configuration traverses the hyperplane through some saddle point, which is the maximum energy of the path and thus the rate limiting activation energy.

It is fairly straight forward to implement the NEB on a simple PES, however on complex PES's with many possible MEP's initialized paths exhibit a proximity bias by converging to the nearest MEP. [4] In order to find the global minimum barrier energy, there must be sufficient sampling of the paths passing through the transition state barrier. One such sampling technique is the Monte Carlo simulated annealing process. The discussion of this paper will thus be centered around the implementation of the NEB to calculate MEP's, followed by a discussion of the theory of simulated annealing and finally a brief description of how Monte Carlo methods can be applied with simulated annealing to treat complex PES's.

2 Implementation of the NEB

The NEB is agnostic as to the definition for the PES. For example, NEB has been successfully used with PES's such as many-body potentials for silicon [12], point charge models for water molecules [13] and with plane wave based DFT calculations [12]. In this paper, the NEB was implemented on a LEPS potential with added harmonic potential energy (to simulate coupling to a surface) and an added gaussian potential to create two separate potential paths. The recipe to implement the NEB is the following. First the PES is defined so that the energy and gradient can be evaluated for each image. Next, the images are defined and given coordinates. Last, the dynamics of the system are defined and the potential energy of each image is minimized simultaneously according to the dynamics. How this is implemented is explained through the following procedure. Two images, R_0 and R_N are established at known boundary conditions of the system. That is, R_0, is in an initial potential energy well and R_N a final potential energy well. A linear interpolation is then projected between the two images and the line is populated with N+1 equally spaced images. This can be seen in Fig1.

The end images R_0 and R_N are fixed and the minimization dynamics of the curve takes place on the N-1 intermediate images. The force acting on each intermediate image, i, is defined as

$$F_i = -\nabla V(R_i)|_{\parallel} + F_i^s \cdot \hat{\tau}_{\parallel} \cdot \hat{\tau}_{\parallel} \tag{1}$$

Where, $\nabla V(R_i) = \nabla V(R_i) - \nabla V(R_i) \cdot \hat{\tau}_{\parallel} \cdot \hat{\tau}_{\parallel}$. is the true force minus the parallel component of the true force, $\hat{\tau}_{\parallel}$ is the bisected tangent between R_i and its two adjacent neighbors R_{i+1} and R_i, and F_i^s is the spring force defined through the following relation

$$F_i^s = k_{i+1}(R_{i+1} - R_i) - k_i(R_i - R_{i-1}) \tag{2}$$

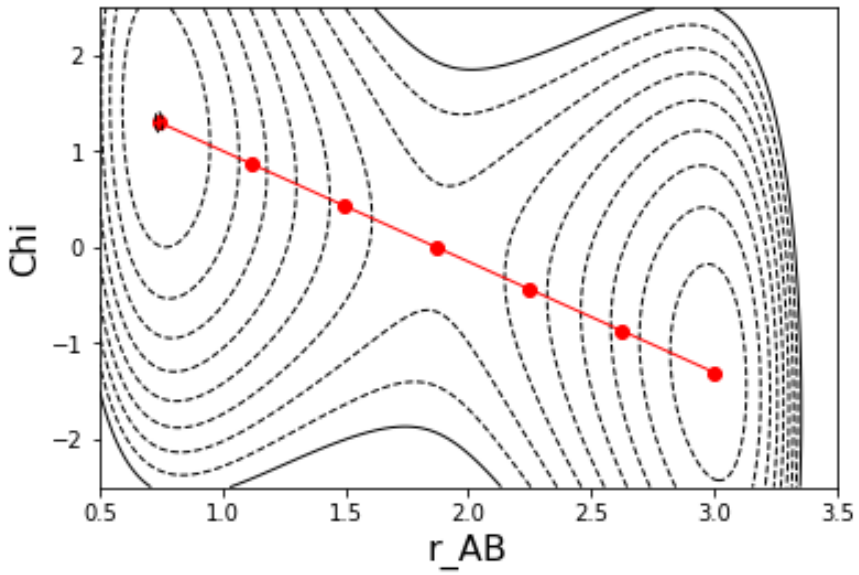

Figure 1: *Linear interpolation between initial and final configurations over a simple LEPs potential, N=8. The reaction is a simple supported proton exchange)*

Where k_i is the spring constant to the right and k_{i+1} to the left. The second term of equation (1) is the parallel component of the spring force only. By constraining the spring force to only its parallel component, the images are kept equally spaced throughout the minimization dynamics of the MEP. The minimization can be seen in Fig2.

Additionally, through constraining the true force from the PES to its perpendicular component, each image is constrained to finding its local minimum energy without reacting through the MEP. This 'reaction' can be seen through the limiting case of zeroing out the spring force. When this is done, the images tend to drag along the reaction path, conglomerating in the final potential well, as seen in Fig3. The process of projecting out the parallel component of the true force and the perpendicular component of the spring force in equation (1) is referred to as "nudging" and is where the NEB method acquires its name.

2.1 Tangent Definition

Central to the behavior of the NEB is how the tangent, in equation (1), is defined. The tangent controls the handling of kinks and extreme curvature in the MEP [9]. There are a few definitions of the tangent that can be used to varying success. A simple, normalized line segment between the two adjacent points,

$$\hat{\tau}_{\parallel} = \frac{R_{i+1} - R_{i-1}}{\|R_{i+1} - R_{i-1}\|} \tag{3}$$

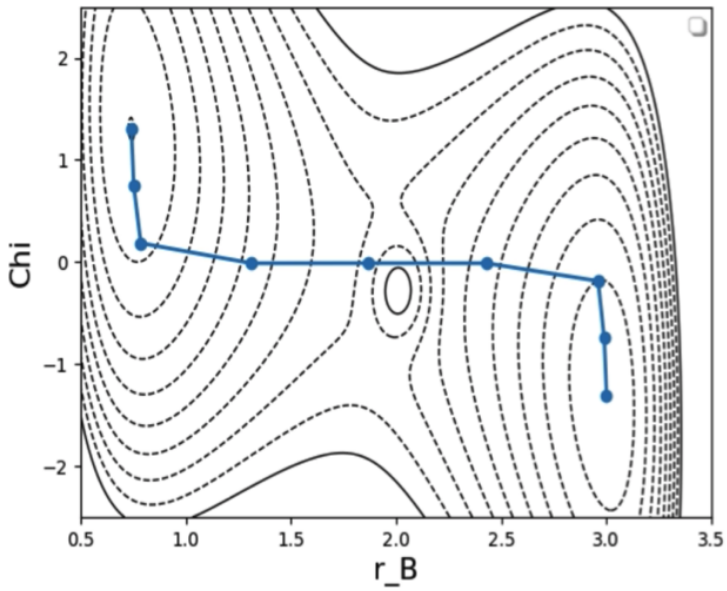

Figure 2: *An optimized MEP (with N=8) through a LEPS potential with an added Gaussian saddle point. The Gaussian is added for extra disorder. The initial state is on the right and the final state on the left.*

A slightly better definition of bisecting the vectors between the central image $R-i$ and its two adjacent neighbors R_{i+1} and R_{i-1}. This looks like the following

$$\hat{\tau_{\|}} = \frac{R_i - R_{i-1}}{\|R_i - R_{i-1}\|} + \frac{R_{i+1} - R_i}{\|R_{i+1} - R_i\|} \tag{4}$$

However, these definitions for the tangent tend to develop kinks along the path that do not dissipate with more time steps. The kinks prevent the MEP from converging to the true path as seen in Fig4 below.
A more sophisticated definition for the tangent incorporates a switching function that uses the potential energy of the image and its adjacent neighbors to pick a tangent definition. The definition for the tangent is picked using the following function

$$\hat{\tau_{\|}} = \begin{cases} \hat{\tau_{\|}}^{+} & \texttt{if } V_{i+1} > V_i > V_{i-1} \\ \hat{\tau_{\|}}^{-} & \texttt{if } V_{i+1} < V_i < V_{i-1} \end{cases}$$

Where, $\hat{\tau_{\|}}^{+} = R_{i+1} - R_i$, and $\hat{\tau_{\|}}^{-} = R_i - R_{i-1}$ And V_i is the potential energy of image i. If the potential energy of image i is a minimum or maximum relative to its adjacent neighbors,

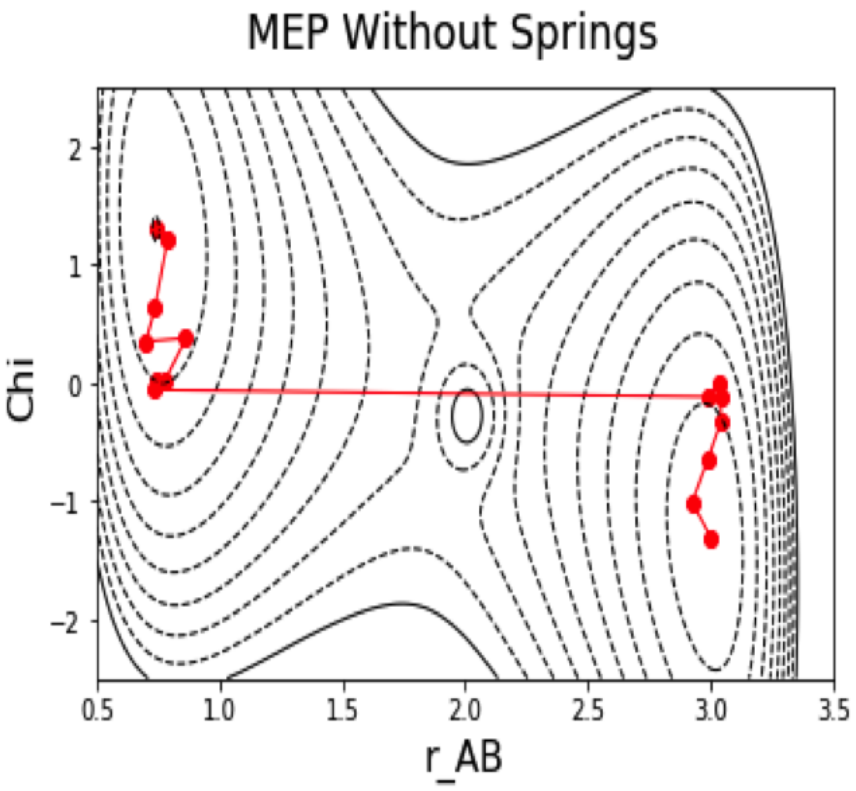

Figure 3: *An MEP traversing a LEPS potential with added disorder. Here the spring constant is zeroed and the MEP is minimized using a Verlet algorithm. The images tend to conglomerate in the potential wells and significant kinks develop along the path*

then a weighted average of the two vectors $\hat{\tau_{\|}}^{+}$ and $\hat{\tau_{\|}}^{-}$ is used.

$$\hat{\tau_{\|}} = \begin{cases} \hat{\tau_{\|}}^{+}\Delta V_i^{max} & \texttt{if } V_{i+1} > V_{i-1} \\ \hat{\tau_{\|}}^{-}\Delta V_i^{min} & \texttt{if } V_{i+1} < V_{i-1} \end{cases}$$

Where $\Delta V_i^{max} = max(|V_{i+1} - V_i|, |V_{i-1} - V_i|)$ and $\Delta V_i^{min} = min(|V_{i+1} - V_i|, |V_{i-1} - V_i|)$. This definition of the tangent handles areas of extreme curvature and avoids the development of kinks in the chain as seen in Fig5 below.
The NEB chain is minimized using modified molecular dynamics techniques. There are various methods that can be used for the minimization process; this paper used an efficient and simple technique called the velocity Verlet algorithm to integrate the equations of motion. At each time step, however, the velocities were updated with an added condition that either preserved or zeroed the updated velocity of each image. That is, if the velocity is perpendicular to the force it is zeroed, else the new velocity is updated with the projection of the velocity onto the force vector. This method works to dampen the velocity of each image as it overshoots its minimum.

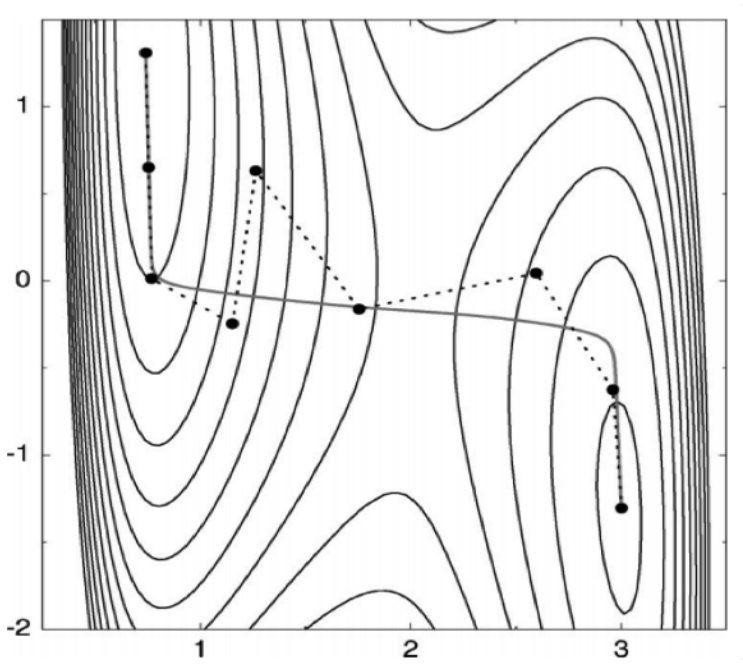

Figure 4: *Dotted line is the MEP as calculated using the tangent definition from equation (3). The solid line is the true MEP. (Image taken from [9])*

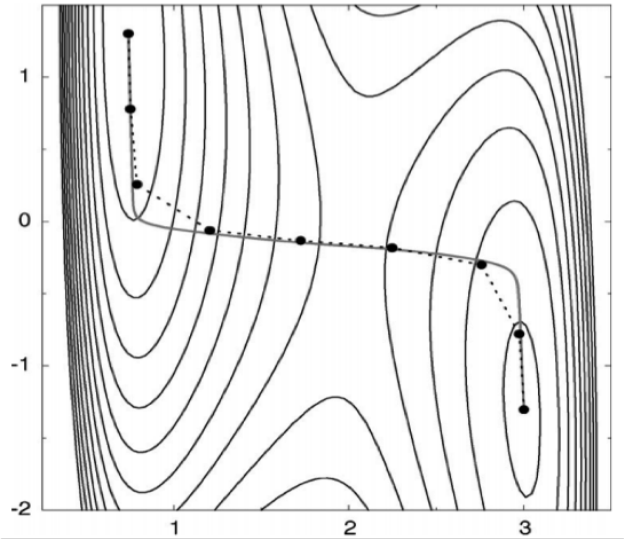

Figure 5: *Dotted line is the MEP as calculated using the tangent definition from equation (5) and (6). The solid line is the true MEP. (Image taken from [9])*

3 Simulated Annealing

The simulated annealing method is an optimization problem that takes its inspiration from the annealing of metals. A good analogy is the traveling salesman problem where the sales-

man is visiting many different cities and wants to find the shortest (minimized) route between them. Simulated annealing works through finding an initial path, finding an alternative path and then accepting either path with some probability, then finding new alternative paths and accepting them based on a probability function that is weighted against a randomly generated number. By weighting the probability function against a randomly generated number, the algorithm can accept paths that are not "as good", which keeps the optimization process from getting stuck in a local extreme.

The connection with annealing is that, a metal with many lattice site vacancies will seek equilibrium (minimization of the internal stress of the metal) through diffusion processes. The rate of equilibrium (recrystallization) is given by the Arrhenius rate equation which gives the rate of seeking equilibrium. Simulated annealing uses the annealing Arrhenius rate equation to sample many configurations at a temperature, picking out the best path, then lowering the 'temperature' and repeating the process. Through this random sampling of many different configurations as the temperature is cooled down, the global extreme configuration of the system is found and local extremes are avoided. The following is the procedure of how to implement simulated annealing (adapted from reference [14]).

Step 1: Choose the temperature of the system, $T \leq 1$, a reducing constant c , $0 < c < 1$; and the number of iterations N to be carried out.

Step 2: Define some generating function and generate a starting configuration, denoted E

Step 3: Generate a permutated configuration, denoted E'

Step 4: If $E' < E$ move to step 5; else generate a random number $R \in [0, 1]$, then if $R < e^{\frac{E-E'}{T}}$ go to step 5; otherwise go to step 6.

Step 5: Set $E = E'$

Step 6: Increase iterator i. If $i = N$ decrease temperature $T' = T * c$; else repeat Steps3-6; If T=0 terminate cycle

For the python pseudo code to these steps please see the appendix [16].

3.1 Monte Carlo Simulated Annealing

The NEB method works well on simple PES's with few paths to choose from. However, when implementing the NEB on a complex PES with many paths between the initial and final states (Fig6) care must be taken in initializing the path as the path will exhibit a proximity bias by converging to the MEP that is closest to the initialized guess. This presents an added degree of difficulty in finding the MEP for large and complex systems with many potential paths as an uninformed initialized path could converge to an MEP that does not pass through the global minimum saddle point energy, giving an erroneous activation energy. The proposed prescription for handling various MEP's is to run a Monte Carlo simulated annealing method.

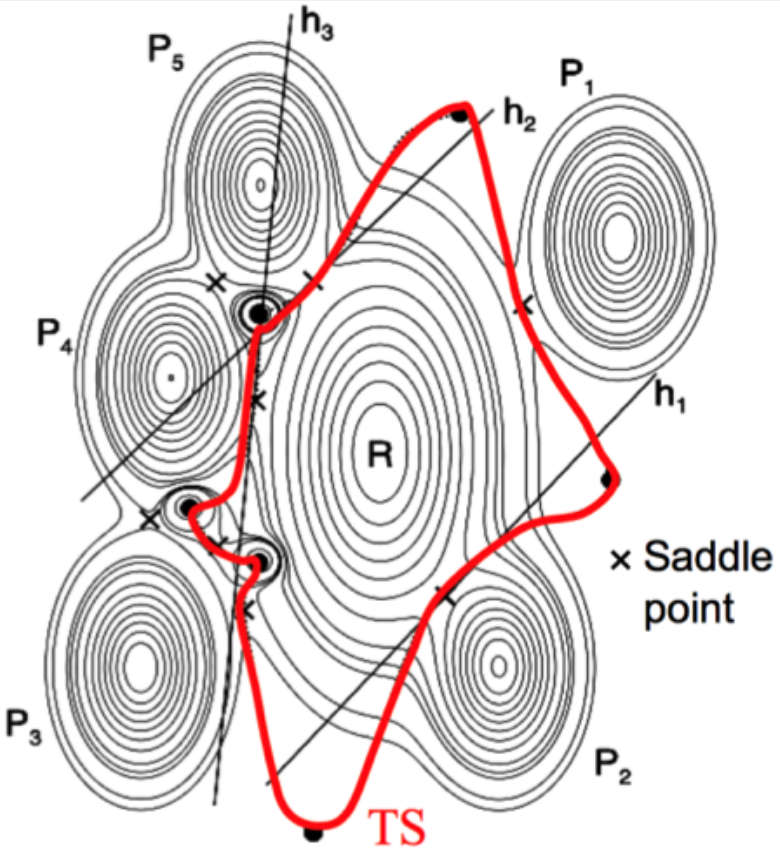

Figure 6: *[10] A potential energy surface with 5 unique product sites. The red line is a hyperplane dividing the transition states and is centered through the saddle points. The hyperplane is sampled and randomly generated paths cross from R to P_i through the sampled points.*

The Monte Carlo portion is implemented through a random uniform sampling of the hyperplane separating the reactant and product sites. The initialized interpolated line between the product and reactant site in this case is not necessarily linear but has some offset to ensure a smooth path is maintained while passing through the hyperplane at the sampled location. This is to ensure continuity in the path and to avoid kink formation from path initialization. The Monte Carlo step is added to Step 3 above. The path is then minimized and the algorithm continues on to Step 4 above. Thus each new path is compared to the previous path via the probability function in the simulated annealing cycle. As the algorithm samples the hyperplane, the true MEP is found.

4 Conclusion

The NEB method works extremely well in locating the MEP of a system and thus the activation energy. Other methods do exist, but find difficulty in handling areas of extreme

curvature in the PES and in locating the true activation energy either through over or under estimation. The NEB finds it's high resolution through the inclusion of the springs and the selective projection of the forces acting on each image; although the spring constant is an arbitrary choice. A further increase in accuracy of the NEB method brings resolution to the saddle point energy and is known as the Climbing Image NEB method (CI-NEB) [6]. CI-NEB is a further optimization of the image that is directly centered on the saddle point. When implementing the NEB, care must be taken in how the tangent is defined as this affects kink development and continuity in the path. Using a switching function to choose the tangent definition has been found to handle areas of extreme curvature nicely, avoiding the common problem of kink formation the MEP. Implementing the NEB on a complex PES with many MEP's is a fairly complicated process but is possible through using the optimization alogrithm defined above. That is, the hyperplane through the transition state of the system needs to be carefully defined in order to capture all the saddle points of the PES. The hyperplane then needs to be sufficiently sampled and the paths through it initialized as to capture the possible MEP's available. The possible MEP's then need to be compared while avoiding getting stuck in local a MEP. Through this process, handling of complex potential energy surfaces is possible.

Future work could explore extending the Monte Carlo simulated annealing assisted NEB method to explore time dependent potentials such as those found in nano catalytic systems with dynamic structural disorder [11]. This would require an investigation into the time evolution of the PES to ensure it does not violate TST.

5 Appendix

Python pseudo code for monte carlo simulated annealing

```
from random import random

def MC_sim_anneal(path):
    old_MEP = NEB(path) #generate initial MEP from
                        #linearly interpolated path
    T = 1.0 # Temperature
    T_min = 0.9 #cutoff temperature
    alpha = 0.9 #reducing constant for temperature
    while T > T_min:
        i=1
        while i <= 100: #arbitrarly large iterator
            new_path = MonteCarlo_path(path) #generate new path using Monte
                                             #carlo sampling of TS
            new_MEP = NEB(new_path) #generate new MEP from new sampled path
            ap = acceptance_probability(old_MEP,new_MEP,T)
            if ap > random():
                MEP = new_MEP
                old_MEP = new_MEP
            i += 1
        T = T*alpha
    return MEP
```

Figure 7:

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